CONCISE ENCYCLOPEDIA OF ADVANCED CERAMIC MATERIALS

Editor

R J BROOK

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ADVANCED CERAMIC MATERIALS

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HONORARY EDITORIAL ADVISORY BOARD

FOREWORD

In the short time since its publication, the *Encyclopedia of Materials Science and Engineering* has been accepted throughout the world as the standard reference about all aspects of materials. This is a well-deserved tribute to the scholarship and dedication of the Editor-in-Chief, Professor Michael Bever, the Subject Editors and the numerous contributors.

During its preparation, it soon became clear that change in some areas is so rapid that publication would have to be a continuing activity if the Encyclopedia were to retain its position as an authoritative and up-to-date systematic compilation of our knowledge and understanding of materials in all their diversity and complexity. Thus, the need for some form of supplementary publication was recognized at the outset. The Publisher has met this challenge most handsomely: both a continuing series of Supplementary Volumes to the main work and a number of smaller encyclopedias, each covering a selected area of materials science and engineering, will be published in the next few years.

Professor Robert Cahn, the Executive Editor, was previously the editor of an important subject area of the main work and many other people associated with the Encyclopedia will contribute to its Supplementary Volumes and derived Concise Encyclopedias. Thus, continuity of style and respect for the high standards set by the *Encyclopedia of Materials Science and Engineering* are assured. They have been joined by some new editors and contributors with knowledge and experience of important subject areas of particular interest at the present time. Thus, the Advisory Board is confident that the new publications will significantly add to the understanding of emerging topics wherever they may appear in the vast tapestry of knowledge about materials.

The appearance of Supplementary Volumes and the new series *Advances in Materials Science and Engineering* is an event which will be welcomed by scientists and engineers throughout the world. We are sure that it will add still more luster to a most important enterprise.

Walter S Owen
Chairman
Honorary Editorial Advisory Board

EXECUTIVE EDITOR'S PREFACE

As the publication of the *Encyclopedia of Materials Science and Engineering* approached, Robert Maxwell resolved to build upon the immense volume of work which had gone into its creation by embarking on a follow-up project. This project had two components. The first was the creation of a series of Supplementary Volumes to the Encyclopedia itself. The second component of the new project was the creation of a series of Concise Encyclopedias on individual subject areas included in the Main Encyclopedia to be called *Advances in Materials Science and Engineering*.

These Concise Encyclopedias are intended, as their name implies, to be compact and relatively inexpensive volumes (typically 300–600 pages in length) based on the relevant articles in the Encyclopedia (revised where need be) together with some newly commissioned articles, including appropriate ones from the Supplementary Volumes. Some Concise Encyclopedias will offer combined treatments of two subject fields which were the responsibility of separate Subject Editors during the preparation of the parent Encyclopedia (e.g., dental and medical materials).

At the time of writing, 11 Concise Encyclopedias have been contracted and others are being planned. These and their editors are listed below.

Concise Encyclopedia of Advanced Ceramic Materials	Prof. Richard J Brook
Concise Encyclopedia of Building & Construction Materials	Prof. Fred Moavenzadeh
Concise Encyclopedia of Composite Materials	Prof. Anthony Kelly CBE, FRS
Concise Encyclopedia of Magnetic & Superconducting Materials	Dr Jan E Evetts
Concise Encyclopedia of Materials Characterization	Prof. Robert W Cahn & Prof. Eric Lifshin
Concise Encyclopedia of Materials Economics, Policy & Management	Prof. Michael B Bever
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Concise Encyclopedia of Polymer Processing & Applications	Mr Patrick J Corish
Concise Encyclopedia of Semiconducting Materials & Related Technologies	Prof. Subhash Mahajan & Dr Lionel C Kimerling
Concise Encyclopedia of Wood & Wood-Based Materials	Prof. Arno P Schniewind

All new or substantially revised articles in the Concise Encyclopedias will be published in one or other of the Supplementary Volumes, which are designed to be used in conjunction with the Main Encyclopedia. The Concise Encyclopedias, however, are "free-standing" and are designed to be used without necessary reference to the parent Encyclopedia.

The Executive Editor is personally responsible for the selection of topics and authors of articles for the Supplementary Volumes. In this task, he has the benefit of the advice of the Senior Advisory Editor and of other members of the Honorary Editorial Advisory Board, who also exercise general supervision of the entire project. The Executive Editor is responsible for appointing the Editors of the various Concise Encyclopedias and for supervising the progress of these volumes.

Robert W Cahn
Executive Editor

EDITOR'S PREFACE

The present volume takes as its foundation the set of articles in the *Encyclopedia of Materials Science and Engineering* and its Supplementary Volumes which relate to the subject of ceramics. Opportunity has additionally been taken to complement the initial group of articles either to recognize developments which have occurred in the intervening period or to repair omissions which may have occurred in the original collection. The purpose of the volume is to provide accessible accounts of the different topics which go to make up the subject of advanced ceramics; the accounts are intended to be above all clear, correct and current in their thinking so that the reader can find an authoritative and reliable guide both to the subject and to key papers in the related literature.

The attractions of the encyclopedia format are several. The most value arises perhaps for readers who are not immediately familiar with a given subject: they can be helped to form a rapid opinion where they may themselves not be expert but where they can rely upon the friendly counsel of a sympathetic specialist who has taken care to make the subject approachable. An attraction for those more familiar with the theme arises from the accidental juxtapositions which can arise from the alphabetic format. Articles of notably different character are brought together in the collection and the contrasts can in themselves be a stimulus to further reflection. These advantages are perhaps most obvious when the range of subjects within the encyclopedia is broad. If the volume becomes too sharply focused in theme then the opportunities for radically different approaches become less apparent. In the present instance it is hoped that the very breadth of the subject of ceramics will allow the volume to retain some of the special character which arises from the encyclopedia style.

The term "advanced ceramics" is one which has often been recognized as unfortunate. The term attempts to describe those products which are ceramics by nature—namely inorganic, nonmetallic solids—but which have been developed in response to highly specialized requirements in the last half century or so. There is no wish in the use of the term "advanced" to suggest that products within the traditional ceramics sector are of a less elegant or developed nature; the difference lies more in the relative weight that is placed upon the role of natural raw materials during fabrication.

In selecting the subject span for advanced ceramics, the European convention has been followed. According to this viewpoint, ceramics are substantially formed from polycrystalline materials. In the attempt to keep the encyclopedia within a reasonable length, the decision has therefore been made to omit references to single-crystal materials and to glass; survey articles for the latter have, however, been included. It is recognized that many users of the encyclopedia will be wanting prompt and focused comment relating to practical matters and this has influenced the framework on which the volume has been constructed. Many articles are concerned with specific chemical systems where a summary of the origins, processing, and application of the system in question can be given. There is also a series of articles concerned with the specific steps in the processing of ceramics since these are common to many systems. These two broad categories are then interlaced with articles relating to particular applications sectors or to particular phenomena. The hope is that this third group can act as a network between the other articles. The different groupings should in sum provide an interlinked and coherent treatment of the subject.

It is important to acknowledge the contribution made by the many authors in responding to the special requirements set by an encyclopedia. A variety of styles will be recognized but a common intent to provide an accurate and accessible summary of the theme can in all cases be recognized. I am also grateful to Dr Perduijn of the Philips Laboratories who was responsible for the section on ceramics processing in the original encyclopedia; as already noted, many of the articles in the present volume are selected from this section and the logical planning that went into its design has greatly simplified the organization of this Concise Encyclopedia. I would like to thank Sabine Paulsen who has been responsible for many of the organizational aspects of the encyclopedia at the Max Planck Institute and to Dr Colin Drayton, Mr Michael Mabe and Mr Peter Frank who have in turn proved such sympathetic colleagues at Pergamon Press. A final word of thanks is also owed to Professor Cahn; his enthusiasm for materials as a subject and for encyclopedias as a mechanism by which such a subject can be made both stimulating and palatable has proved itself unrelentingly charming and charmingly unrelenting.

Richard Brook
Editor

GUIDE TO USE OF THE ENCYCLOPEDIA

This Concise Encyclopedia is a comprehensive reference work covering all aspects of advanced ceramic materials. Information is presented in a series of alphabetically arranged articles which deal concisely with individual topics in a self-contained manner. This guide outlines the main features and organization of the Encyclopedia, and is intended to help the reader to locate the maximum amount of information on a given topic.

Accessibility of material is of vital importance in a reference work of this kind and article titles have therefore been selected, not only on the basis of article content, but also with the most probable needs of the reader in mind. An alphabetical list of all the articles contained in this Encyclopedia is to be found on pp. xv and xvi.

Articles are linked by an extensive cross-referencing system. Cross-references to other articles in the Encyclopedia are of two types: in text and end of text. Those in the body of the text are designed to refer the reader to articles that present in greater detail material on the specific topic under discussion. They generally take one of the following forms:

> ...which is fully described in the article *Ceramics Process Engineering.*
>
> ...other applications of ceramic materials (see *Nuclear Waste Storage Materials*).

The cross-references listed at the end of an article serve to identify broad background reading and to direct the reader to articles that cover different aspects of the same topic.

The nature of an encyclopedia demands a higher degree of uniformity in terminology and notation than many other scientific works. The widespread use of the International System of Units has determined that such units be used in this Encyclopedia. It has been recognized, however, that in some fields Imperial units are more generally used. Where this is the case, Imperial units are given with their SI equivalent quantity and unit following in parentheses. Where possible the symbols defined in *Quantities, Units, and Symbols*, published by the Royal Society of London, have been used.

All articles in the Encyclopedia include a bibliography giving sources of further information. Each bibliography consists of general items for further reading and/or references which cover specific aspects of the text. Where appropriate, authors are cited in the text using a name/date system as follows:

> ...as was recently reported (Smith 1988).
>
> Jones (1984) describes...

The contributor's name and the organization to which they are affiliated appear at the end of each article. All contributors can be found in the alphabetical List of Contributors, along with their full postal address and the titles of the articles of which they are authors or co-authors.

The article *Advanced Ceramic Materials: An Overview* provides an overview of the field of ceramic materials and discusses in brief the issues covered by the articles in the body of the work.

The most important information source for locating a particular topic in the Encyclopedia is the multilevel Subject Index, which has been made as complete and fully self-consistent as possible.

ALPHABETICAL LIST OF ARTICLES

CONCISE ENCYCLOPEDIA OF

ADVANCED CERAMIC MATERIALS

ADVANCES IN MATERIALS SCIENCE AND ENGINEERING

This is a new series of Pergamon scientific reference works, each volume providing comprehensive, self-contained and up-to-date coverage of a selected area in the field of materials science and engineering. The series is being developed primarily from the highly acclaimed *Encyclopedia of Materials Science and Engineering*, published in 1986. Other titles in the series are listed below.

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NOTICE TO READERS

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If your library is not already a standing order/continuation order customer to the series **Advances in Materials Science and Engineering**, may we recommend that you place a standing/continuation order to receive immediately upon publication all new volumes. Should you find that these volumes no longer serve your needs, your order can be cancelled at any time without notice.

ROBERT MAXWELL
Publisher at Pergamon Press

CONTENTS

A

Advanced Ceramic Materials: An Overview

Ceramics make up one part of the portfolio of materials available for use and development in civilization and are in this respect complementary to the metals and polymers. The fabrication and application of ceramics are among the oldest technological skills, and modern products which bear a close and direct relationship to these ceramics include pottery, structural clay products and clay-based, heat-resistant (refractory) materials, all of which exploit the availability and properties of a particular group of nonmetallic, inorganic raw materials, the clays. These products constitute the traditional ceramics.

At a much later stage in historical development, there appeared a range of products which were similarly formed from nonmetallic, inorganic solids but which relied on very considerable raw material modification and refinement or even on the synthesis of entirely new compositional systems in order to provide properties matched to more specific and exacting requirements. Examples of these materials are the simple binary oxides such as alumina (Al_2O_3), magnesia (MgO) and zirconia (ZrO_2), or the ternary oxides such as the spinels (compounds based on $MgAl_2O_4$) and the perovskites (those based on $CaTiO_3$) (see *Aluminum Oxide*; *Magnesium and Alkaline-Earth Oxides*; *Perovskites*; *Spinel and Spinels*; *Zirconia and Hafnia*). There are also more complex oxide systems synthesized to satisfy an exact property requirement, as for example the ionically conducting material $Na_{3.1}Zr_{1.55}Si_{2.3}P_{0.7}O_{11}$. In addition, there are groups of nonoxide ceramics such as the carbides (SiC, silicon carbide or carborundum, is an important example), the nitrides (Si_3N_4, silicon nitride), the borides, the silicides, the halides and other such categories of solid compound (see *Borides*; *Halides*; *Nitrides*; *Silicides*; *Silicon Carbide*). With the possibility of mixtures between these types (the sialons, a set of materials based on combinations of Si_3N_4 with Al_2O_3 and other oxides, are the prime example (see *Sialons*)), it is apparent that the variety of such ceramic systems becomes very wide. As recognition of the differences that lie between these systems and the classical or traditional clay-based systems, a number of attempts have been made to establish a distinctive term to describe them. No usage has won general acceptance and the forms "technical," "special," "engineering," "fine" and, as here, "advanced" will all be encountered. The distinction, despite its occasional convenience, should not be overemphasized; there is much to be gained from transfer of technology and experience from the "traditional" to the "advanced" sectors and vice versa.

1. Applications

The applications for which advanced ceramics have been developed and proposed are many. A first division can, however, be made into categories of materials with electrical and electronic functions, those with mechanical function at ambient temperatures and those with mechanical function at elevated temperatures.

The first application of ceramics in the electrical context was as an insulator, and electrical porcelains and aluminas sustain an important role in this connection. In the period since 1940, however, a great diversification in function has occurred with innovations in materials development and in the associated solid-state theory taking place in concert. Thus, the range of magnetic materials based on the ferrimagnetism of the spinel ferrites and the range of dielectric phenomena (notably ferroelectricity and piezoelectricity) encountered in the perovskite titanates have sprung from a close linking of solid-state scientists and engineers with the materials design of ceramics. The products stemming from this dramatic development now form an established industry characterized by rapid innovation and an increasing sophistication of materials specification.

Mechanical applications at ambient temperature are largely based on the combination of wear resistance, hardness and corrosion resistance which many ceramics (notably alumina and silicon carbide) provide. Such applications include wear parts in medical engineering (total prostheses for hip joints), in process plant (pump components and valve faces, lining for pipework) and in mechanical engineering (bearings and valves). Alongside the many advantages which ceramics bring to these uses, the principal disadvantage and impediment to more rapid exploitation has been that, while the materials can display great strength (the attainment of 1 GPa associated with high-strength steels is no longer seen as exceptional), the mode of fracture is most commonly brittle, resulting in sudden and complete failure of the component. The reluctance of engineers to welcome ceramics more enthusiastically is mainly caused by the severity of the design problems posed by this attribute.

Despite the great advances being made elsewhere, mechanical applications at elevated temperatures are seen as perhaps the key target for the realization of the promise of advanced ceramics. The properties that lie behind this promise include wear resistance, hardness, stiffness, corrosion resistance and relatively low density. The main attraction, however, is the refractoriness of ceramics; that is, the high melting point and the retention of mechanical strength to high temperature.

Some materials of interest for engineering applications are listed, together with their melting (or sublimation) temperatures, in Table 1.

The significance of these properties can already be seen in one successful application, namely in the use of ceramic tool tips (aluminas and sialons) for the high-speed machining of metals. The conditions of operation of the tip are arduous (high tip temperature, high mechanical loads, severe impact conditions in intermittent machining) and the success of ceramics in this sector is one of the most convincing demonstrations of their eventual suitability for a wider range of applications in high-temperature engineering. Of these, undoubtedly the most significant in terms of eventual scale is that of components for heat engines (diesels and turbines), the objective being to allow a raising of the operating temperature and, with it, engine efficiency and fuel economy.

The great attraction of this development has long been recognized, and from earlier experience it is known that ceramics pose severe problems in such applications, the main ones being susceptibility to thermal shock (the tendency to sudden fracture on the part of ceramics exposed to sudden cooling is familiar even in the domestic environment) (see *Thermal Shock*) and to sudden brittle fracture when subjected to impact. The reasons for thinking that successful development of engine components will eventually result are the large levels of current financial support, the pressing requirement for the resulting economies, the dramatic advances in materials quality and, particularly, the fact that the origins of the associated problems are now better recognized. A key feature will be the quality and refinement that it is possible to bring to the processing involved in the fabrication of the ceramics.

In summary, therefore, the advanced ceramics have won a place in everyday use through their successful exploitation in a wide variety of electrical and magnetic applications and in growing range of mechanical applications of which tool tips are perhaps the most established. A large question remains, however, in estimating the extent to which they will be capable of entering mainstream mechanical engineering as highly stressed components in high-temperature engineering systems.

Table 1
Melting or sublimation temperatures of some materials used in engineering applications

Material		Melting point (°C)
Aluminum oxide (alumina)	Al_2O_3	2054
Zirconium oxide (zirconia)	ZrO_2	2770
Silicon carbide	SiC	2650
Silicon nitride	Si_3N_4	1900[a]
Nickel	Ni	1453
Aluminum	Al	660

a Sublimation temperature

2. Fabrication

One consequence of the high melting point of ceramics is that they are generally fabricated from powders. The shortest flow chart then follows the pattern shown in Fig. 1. In considering this pattern, it is convenient to split the processing into two parts, namely those processes that come before the shaped powder form (processing before firing) and those that come after (firing) (see *Ceramics Process Engineering*). In this section, some of the considerations of special concern to ceramics for mechanical engineering applications are reviewed.

Until recently, the changes that happen during firing have received the bulk of the attention given to ceramics processing, and the understanding of these changes is now considerable. In the most idealized form, solid-state sintering, the powder consists of individual crystal grains which remain solid throughout the heat treatment (see *Solid-State Sintering*). The system is heated to temperatures where diffusion of the atoms in the solid state can occur. Atom movements (see Fig. 2) can then bring about a reduction in the surface energy of the system either by densification

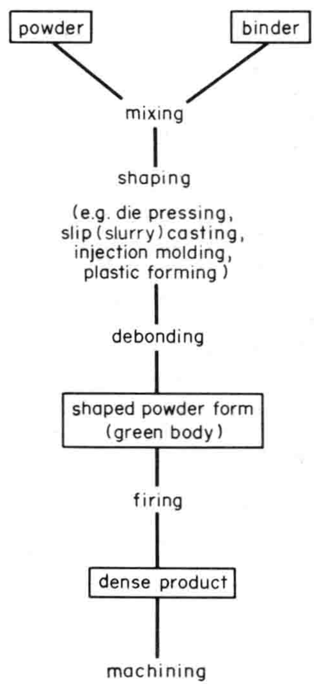

Figure 1
Basic flow chart for the fabrication of ceramics

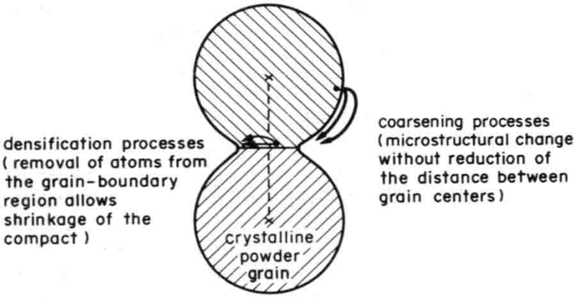

Figure 2
Schematic indication of the distinction between densifying and nondensifying microstructural changes resulting from atom movement during the firing of ceramic powders

(movement of atoms from the grain-boundary region to the solid–gas interface) or by coarsening (movement of atoms between different regions on the solid–gas interface). Since the former process results in a reduction in the particle–particle distance, shrinkage of up to 20% occurs and porosity is removed as required for component fabrication (see Fig. 3). The coarsening process consumes the surface energy, which provides the driving force for densification, without at the same time reducing the level of porosity (see Fig. 4).

The rates of these processes are enhanced by higher fabrication temperatures and by fine particle size, and densification is further enhanced if pressure can be applied to the system during heating, thus increasing the driving force for shrinkage and pore elimination. Coarsening is reduced if the powder particles in the initial compact are all of similar size. The consequence is that the firing process commonly requires high temperatures (e.g., 1400–1650 °C for Al_2O_3, 1400–1700 °C for ZrO_2 and 1800 °C for sinterable Si_3N_4 are typical), fine particles (from 1 μm down to 30 nm is the commonly explored range) and uniform particles.

A common difficulty that can occur in the heat treatment of powder preforms, for example, with silicon nitride and silicon carbide, is that coarsening processes are relatively favored with the result that the heating of the pure powders is in itself an ineffective means of producing dense components. One solution here is to use an additive which produces a liquid phase between the grains at the firing temperature; this then acts as a rapid diffusion path for material from the grain boundary and densification can occur, particularly if assisted by pressure (see *Liquid-Phase Sintering*). Magnesium oxide (5 wt%) acts this way to permit sintering of silicon nitride powders (see Fig. 5).

A second problem arises from the use of fine powders in the search for the enhanced activity capable of yielding high-density components. As powder sizes go

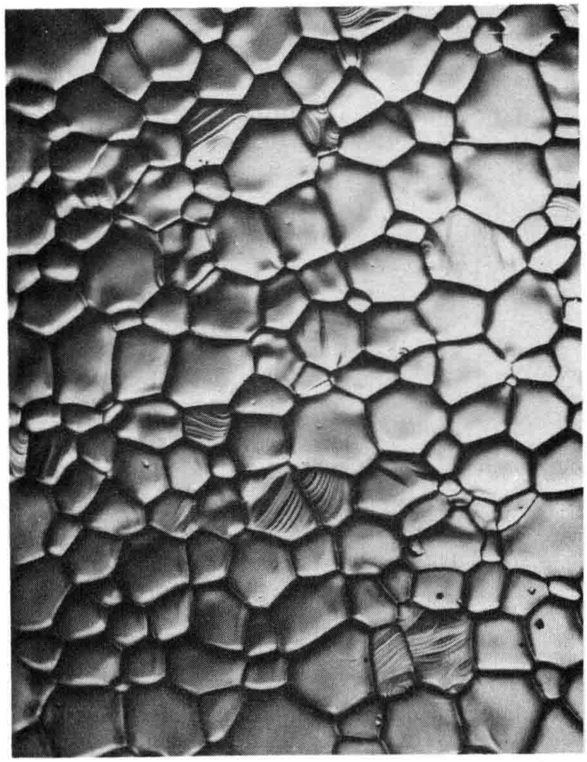

Figure 3
The surface of an alumina ceramic from which all porosity has been removed during the firing of the powder; the microstructure consists of the crystalline grains and the boundaries (interfaces) between them (courtesy of E. W. Roberts)

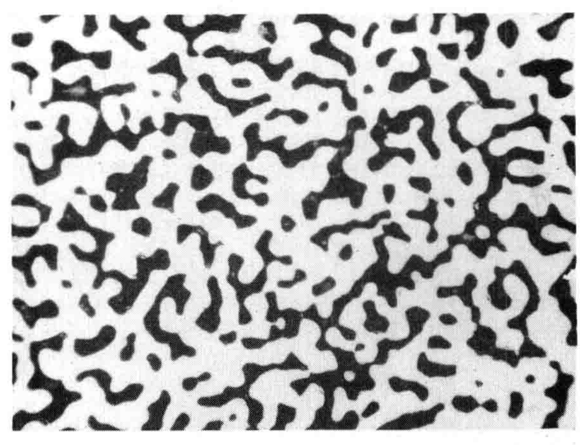

Figure 4
The sintering of silicon results in the formation of a continuous network of solid material (white) and porosity (black); this microstructural change is not accompanied by any shrinkage (courtesy of C. F. Paine)

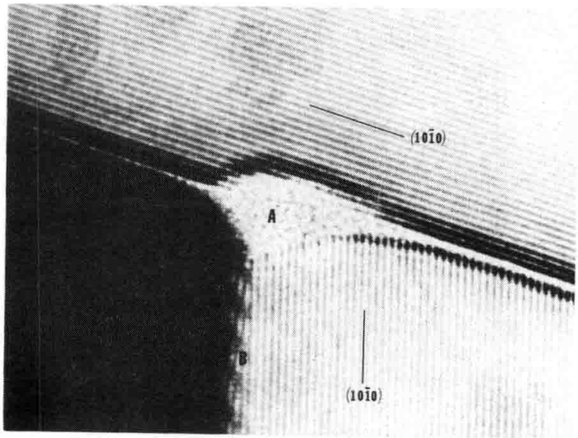

Figure 5
The existence of a continuous grain-boundary phase between the crystalline grains of Si_3N_4 hot pressed with MgO additive can be seen in high-resolution electron microscopy; the film is some 0.8 nm thick (courtesy of D. R. Clarke)

below 1 μm, there is increased difficulty in powder handling and increased tendency for particles to interact with one another giving rise to the formation of agglomerates which then act to all intents and purposes in the same way as a coarse powder with a size corresponding to that of the agglomerate. The benefits of fine powders have been confirmed (zirconium dioxide can be sintered to full density at 1100 °C in place of the more normal 1700 °C if a genuine particle size of 30 nm can be achieved), but the precautions needed to avoid agglomerate formation in powders of such size are demanding.

A final problem is that conventional firing can only yield results as good in terms of uniformity as the quality of powder compact produced by the earlier processing. If severe variations in packing density occurs in the compact, then corresponding inhomogeneities and faults will occur in the finished product. Two general approaches can be adopted. In the first, removal of suspected flaws is attempted in a final processing step; thus, in hot isostatic pressing (hipping), partly sintered components of reasonable density are heated under an imposed gas pressure to remove the last trace of porosity (see *Hot Isostatic Pressing*). The development of sophisticated nondestructive-evaluation methods, capable of confirming that all porosity has been removed, is an important element in this approach and is currently an area receiving much research attention (see *Nondestructive Evaluation*). A second approach sets out with the objective of making the ideal powder compact during the processing before firing. This approach requires meticulous powder preparation by controlled nucleation and growth from solution followed by structural assembly achieved by careful balance of interparticle forces within the solution; the resulting fault-free arrangement of powder particles in the system prior to firing offers a promising basis for the fabrication of optimal microstructures in the final product (see Fig. 6).

The present position with respect to processing can be summarized by noting that the target of development programs is that of achieving convenient, practical and reproducible fabrication procedures. The center of activity has if anything now moved into the prefiring stage where powder preparation and handling methods are being developed with a view to reducing the maximum fault size within the material. At present, it appears that piror to the eventual sophistication illustrated in Fig. 6, very substantial improvements can be made by applying to the fabrication of ceramics the clean room conditions and other refined production engineering methods long familiar in semiconductor-grade work.

3. *Microstructures*

The processing methods that are adopted determine, as noted earlier, the eventual microstructure of the resulting ceramic; that is, the nature, quantity and distribution of the structural elements or phases making up the material (see *Microstructure and Processing History*). Thus, if entirely solid-state sintering processes are used and are fully successful, simple single-phase structures (Fig. 3) consisting of crystalline grains and the interfaces between them can be produced. Less complete densification can result in the persistence of a residual pore phase between the grains

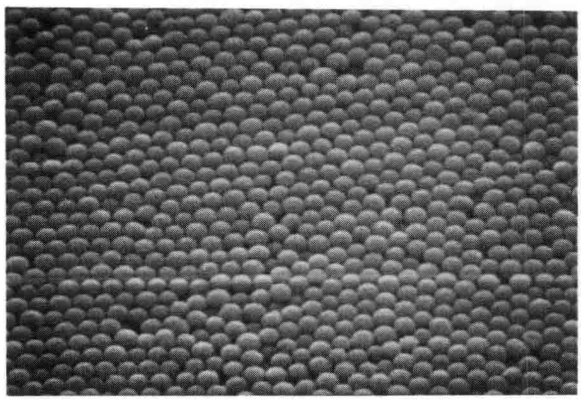

Figure 6
The extent of sphere ordering that can be achieved with uniform submicrometer TiO_2 spheres offers a basis for the preparation of unfaulted structures prior to the firing stage (courtesy of E. A. Barringer and H. K. Bowen)