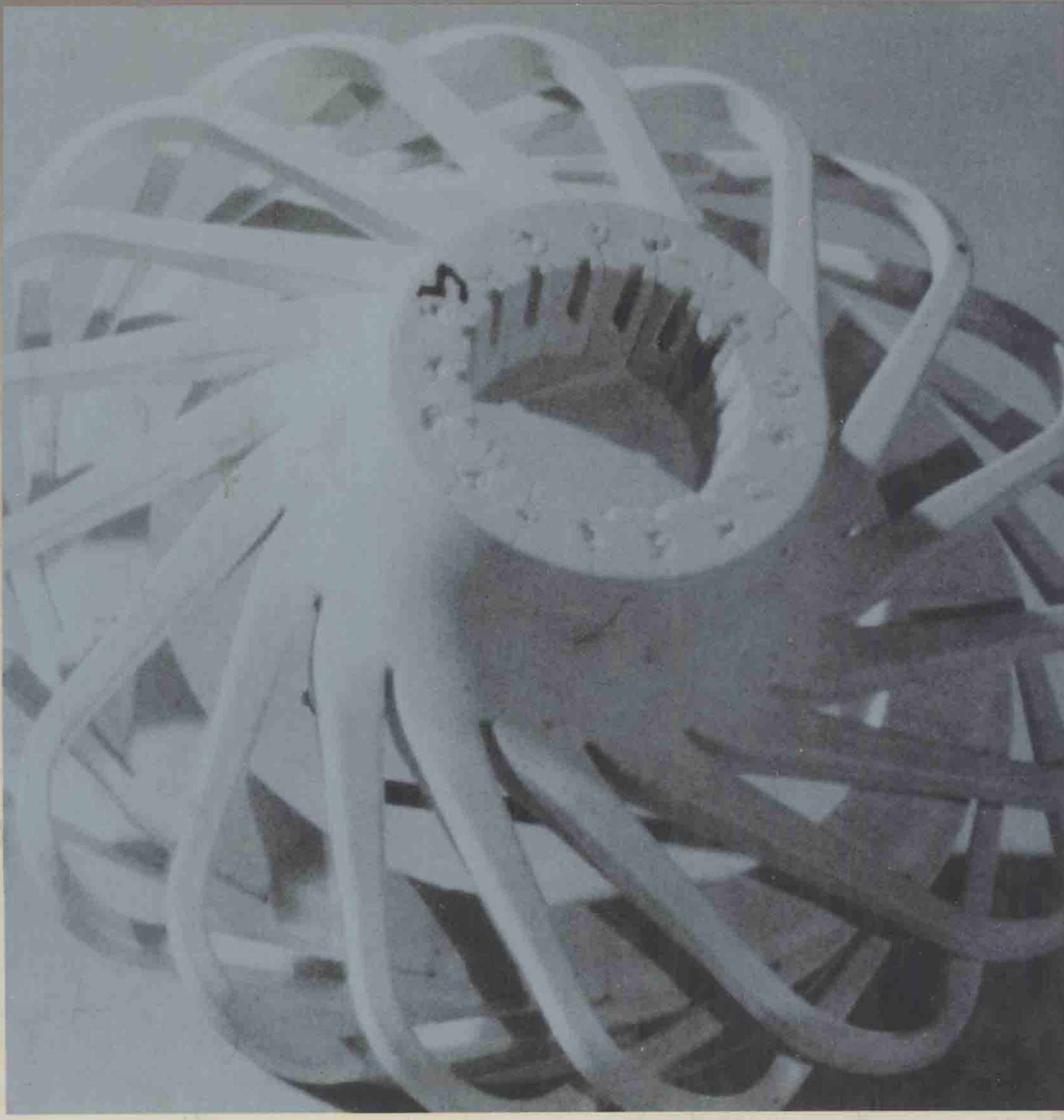
HANDBOOK OF STRUCTURAL CERAMICS

MEL SCHWARTZ



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Mel M. Schwartz Editor in Chief

Sikorsky Aircraft Division
United Technologies Corporation

McGraw-Hill, Inc.
New York St. Louis San Francisco Auckland Bogotá
Caracas Lisbon London Madrid Mexico Milan
Montreal New Delhi Paris San Juan São Paulo
Singapore Sydney Tokyo Toronto

To cara

Library of Congress Cataloging-in-Publication Data

Schwartz, Mel M.
Handbook of structural ceramics / Mel Schwartz.
p. cm.
Includes index.
ISBN 0-07-055719-5
1. Ceramics—Handbooks, manuals, etc. I. Title.
TP807.S343 1992
666—dc20 91-28316
CIP

1 2 3 4 5 6 7 8 9 0 DOC/DOC 9 7 6 5 4 3 2 1

ISBN 0-07-055719-5

The sponsoring editor for this book was Robert W. Hauserman, the editing supervisor was Ingeborg M. Stochmal, and the production supervisor was Donald Schmidt. This book was set in Times Roman. It was composed by McGraw-Hill's Professional Book Group composition unit.

Printed and bound by R. R. Donnelley & Sons Company.

PREFACE

The hot tip of materials in the mid-1960s was "composites." This whispered word has changed, and the word for the decade is "ceramics." The industrial engineer understands the term as shorthand for a class of materials and a set of processes that may transform the next generation of industrial products just as surely as composites and thermoplastic plastics changed the present generation.

The gestation period for advanced structural ceramics is over; they are a reality and primed to explode. Some of the applications were never thought of previously. Ceramics are finding increased usage in many load-bearing applications, such as cutting tools, automotive-engine components, heat exchangers, wear parts, and aerospace. Other uses include gene-splicing equipment, office machinery, and replacement parts for the human body.

Unfortunately, the customer for ceramic components has had nowhere to turn for unbiased advice and guidance on the use of structural ceramics in engineering. The most experience is generally with the manufacturers, while specialists, who may know much about principles and the science, know little about the ins and outs of commercial products. The scientific literature is rather unstructured and unbalanced, weighted primarily in favor of the exotic or the unobtainable. The result has been trial and error and test.

This Handbook has been written with the aim to clear a straightforward path through the jungle of scientific and commercial literature, to provide processing techniques and procedures, classes of ceramics, current mechanical property data for design purposes, materials and their methods of manufacture, and subsequent fabrication and assembly methods, leading to the broad base of structural ceramic applications, including composites. This will answer most questions for the newly exposed and inexperienced user of ceramics as well as for the designer, ceramist, and materials and process engineer, who can then approach the use of ceramics in an appropriate way and will be in a better position to negotiate from a basis of some understanding and background knowledge.

In order for the forecasts expected of these twenty-first-century materials to be realized, ceramics must be refined to meet their statistical characterization, including: (1) designing for reliability; (2) improving the forming techniques to minimize the size and number of flaws in the finished piece; (3) improving or replacing the sintering process during which thermal conditions may create flaws; (4) reducing cost; (5) improving thermodynamic and mechanical stability in existing materials or with development of new materials; and (6) seeking nondestructive techniques that allow manufacturers to evaluate the finished part for flaw size and frequency.

Another development that remains is the emergence of effective new ways to toughen up ceramics in order to make them more competitive. One way is to work with ceramic-matrix composites. Ceramic–ceramic-reinforced composites are remarkable for their great hardness and heat resistance combined with thermal-shock resistance. Most important, their creep resistance, or ability to withstand high stress at elevated temperatures, is the best of any material yet produced. Since high-temperature creep of these materials occurs mainly by atomic diffusion at grain boundaries, their creep resistance is dependent on their grain size. The role of fiber reinforcements is thus to stiffen up the composite and prevent shape changes in components subject to high stress at elevated temperatures. Another approach is through transformation toughening; a third is by grain refinement.

All of these approaches are covered in this Handbook in order to show that the yet inadequate fracture toughness and the low damage tolerance of these brittle ceramic materials, which are both considered substantial obstacles to the use of these "perfectly ordered" ceramics in critical structural applications, are slowly being overcome.

Ceramists have long felt that other technical specialists, designers in particular, do not understand ceramics and often appear reluctant to learn about them. However, today ceramists both educate and interact with other technical disciplines and communities.

Second, finding ceramists with a high degree of mathematical cunning is difficult. Yet the real challenge facing today's ceramist is the need to learn about other related technologies and their economic factors, and then to take this information and, in collaboration with people from other disciplines, combine ceramics and other materials into components having an optimum balance between performance and total cost.

The key is to stiffen up materials, but the engineering is difficult because altering the composition of ceramics may also alter the directional properties of the material. Today we are moving toward engineering the right material for a job from the molecular level.

In the future the engineer and the ceramist may be able to participate in developing intelligent processing of materials (IPM). The IPM approach uses computerized "expert systems" to help make ceramic materials that have properties far surpassing those commonly used. IPM allows exceptional and reliable qualities to be built into materials during processing rather than by inspection. IPM technology differs from conventional automated processing that controls parameters such as temperature and pressure with preselected values. IPM allows for diversities in the incoming materials. It uses on-line measurements in real time to adjust a wide range of processing variables.

Many studies are indicating that U.S. manufacturers of advanced ceramics are facing a type of international competition today as never before. Every individual U.S. company is competing against foreign consortia organized on a country basis or even on a regional basis. In fact, the Japanese describe as "first" generation the traditional ceramics—brick, pottery, and so on—which are made from natural materials. Fine or high-tech ceramics are the "second" generation. They are trying to establish a "third" generation of ceramics with high reliability and toughness, with the aim of instituting an integrated technology system for these ceramics supported by performance estimation, testing, and simulation, and of designing technology for many applications. The United States must be able to compete in this billion dollar industry now and in the next decades.

Many of the obstacles can be surmounted by technologies now in the laboratories. Studies of synthetic raw materials for advanced ceramic composites are ongoing, with research to improve the performance of or to find substitutes for refractories requiring imported raw materials and to enable the development of advanced ceramic composites with high fracture toughness and temperature properties, which could replace metals requiring critical chrome, cobalt, manganese, or tantalum.

Other research efforts include studies of green-body and sintered microstructures, intergranular bond phases, and processing of high-purity raw materials, all directed at producing wear- and corrosion-resistant advanced ceramic materials.

I wish to acknowledge the able support and contributions of Drs. John B. Wachtman, Jr., and Dale Neisz, Center for Ceramics Research, Rutgers University, for Chapter 3, and Dr. Makuteswara Scrinivasan, consultant and formerly with the Carborundum Company and Union Carbide Corporation, for Chapters 2 and 6.

Mel M. Schwartz

ABOUT THE EDITOR

Mel M. Schwartz is an engineer with the Sikorsky Aircraft Division of United Technologies. Previously he was in charge of manufacturing research and development for the Aircraft Division of Rohr Industries and a manufacturing manager at Martin Marietta Corporation. He has taught welding metallurgy at San Diego City College and manufacturing processes and matrials at San Diego State University, and he has lectured at Yale University. Mr. Schwartz is a Fellow of SAMPE International and ASM International. He is a recipient of the SAMPE Lubin Award. He is the author or editor of several other books, including ASM International's *Ceramic Joining* and the second edition of McGraw-Hill's *Composite Materials Handbook*.

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CHAPTER 1
GENERAL INTRODUCTION TO CERAMIC MATERIALS

1.1 INTRODUCTION

Ceramic materials technology and research and development in the United States are in a reasonably healthy state. However, several factors must be overcome for them to remain competitive into the future. Materials science and engineering are an enabling technology, highly leveraged in, and critical to, many areas of advanced technology. Our major trading partners in Asia and Europe are gaining on or exceeding our capabilities in the production of many materials and materials systems, ceramics being one of them.

This has come about through stepped-up investments in advanced ceramics materials technologies by other countries. As a result, the U.S. industry stands a greater risk of becoming "blindsided" by materials developments occurring elsewhere in the world. Other concerns include the substantial cutbacks in basic research by some materials industries, weaknesses throughout the U.S. materials R&D infrastructure in synthesis and processing research, our growing dependence on Europe and Asia for new developments in advanced-characterization instrumentation, and the low numbers of universities maintaining medium-sized facilities for ceramics engineering research.

"The opportunities are out there," said Dr. H. Kent Bowen of M.I.T. "Laboratory specimens have already been made that can fulfill the needs of the high-technology ceramics industry."

However, a lack of comprehensive government programs has hurt the U.S. effort, as well as a slow start by U.S. industry. Basic research has been satisfactory, but industry is too fragmented to take full advantage of it. There has not been enough cooperation and information exchange between powder producers, processors, manufacturers, machining companies, designers, and researchers.[1–3]

"Companies are so concerned about keeping information proprietary that one can't even buy ceramic powder to try and improve the processing of the material," according to Dr. D. Readey, Chairman of the Ceramic Engineering Department at Ohio State University.

Compounding the problem of lack of researchers is the unfamiliarity of product design engineers with the special properties of ceramics. "There are techniques today which permit design with brittle materials," says Dr. Readey. "If you have reasonably reliable data, you can design for a given stress. However, most materials engineers are completely ignorant of the ways to design with ceramics."

Some of the other negative perceptions of ceramic material usage include:

Very high raw-material purity requirements
Expensive, highly sophisticated processing
Inconsistent reliability or reproducibility
Insufficient standard reference materials
Lack of standard testing procedures
Poorly developed NDE procedures

Developments and plans for standard measurement methods and data gathering of fundamental material properties are ongoing programs. Therefore the high-performance ceramics based on carbides, nitrides, oxides, beryllides, and possibly aluminides are the future.[4–6]

1.2 CERAMICS AND METALS

The so-called advanced, or high-performance, or fine, or technical, or structural ceramics are materials such as silicon nitride (Si_3N_4), silicon carbide (SiC), zirconia (ZrO_2), boron carbide (B_4C), alumina (Al_2O_3), sialon (Si–Al–O–N), and beryllia (BeO). These materials have been developed to provide predictable and repeatable physical properties, allowing their use in applications such as seals in automobiles, electronic substrates, wear components, and high-temperature bearings.

Yet in the minds of many engineers, technical ceramics are perceived as still being in the laboratory. The fact is that not only did these materials enter the marketplace as replacements for other ceramics, they have displaced metals in several traditional areas.

The present definition of ceramics includes not only the traditional materials made by heating naturally occurring substances, but also the highly refined and synthesized materials engineered for modern chemical, mechanical, electrical, optical, and magnetic properties.

Most people think that a ceramic is brittle, high-melting, nonconducting (of both heat and electricity), and nonmagnetic. They also think that metals have opposite properties. These stereotyped viewpoints are not necessarily true for ceramics or metals. In fact, there is no clear-cut boundary between the two. Rather, there are intermediate compounds that have some aspects typical of ceramics and others typical of metals.

Ceramics and metals are two groups of materials whose main difference is that they each represent a different combination of physical properties. Because of their availability and predictability, most people are accustomed to working with, thinking in terms of, and designing with metals. This represents an almost subconscious acceptance of a typical metal's ductility and strength combined with electrical and thermal conductivity.

In addition, there are misconceptions about the properties of advanced ceramics based on experiences with traditional ceramics: "like a coffee cup, drop it, it breaks." Educating and making engineers aware of the increasing body of knowledge about these materials is the first step in viewing ceramics as legitimate materials for use in demanding applications.[7–9]

Perhaps the most significant difference between traditional metals and ceramics lies in their ductility. Owing to the highly localized covalent-ionic bonding typical of ceramics, their macroscopic properties are brittle in nature. Brittle materials behave elastically until they fail catastrophically, as opposed to ductile materials, which deform plastically after the elastic limit has been reached, but prior to failure.

The nature of a material is largely controlled by the type of bonding between its constituent atoms, which in turn is controlled by the electron configuration of the atoms. Elements with unfilled outermost electron shells interact with other atoms, such that electrons are shared or exchanged between these atoms to achieve full shells.

Pure metals consist of atoms of a single size and an electron configuration in a close-packed arrangement. The outer electrons are shared freely by all the atoms in the structure. This mutual sharing of electrons provides the bond force that holds the atoms together into a metal crystal. It also provides the basis for most of the properties that we associate with a metal: ductility, high electrical conductivity, thermal conductivity, and thermal expansion.

Atoms in a ceramic material are primarily held together by covalent or ionic bonding, or a combination of the two. In covalent bonding, electrons are shared, but only by two adjacent atoms. This results in a directional bond. Such bonds can produce strong, rigid three-dimensional structures (such as diamond, SiC, or Si_3N_4), fibrous chain structures (such as asbestos), and laminar structures (such as graphite, mica, and clays). Characteristics of covalent ceramics include high hardness, superior chemical inertness, no ductility, low thermal expansion, and low electrical conductivity.

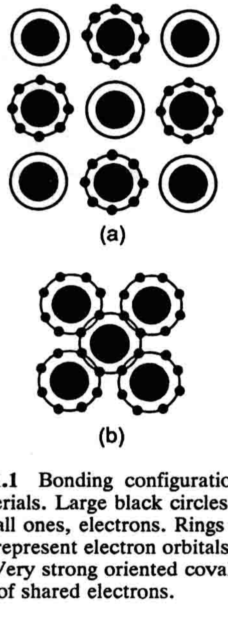

FIGURE 1.1 Bonding configurations in ceramic materials. Large black circles represent atoms, small ones, electrons. Rings surrounding atoms represent electron orbitals. (*a*) Ionic bond. (*b*) Very strong oriented covalent bond, consisting of shared electrons.

Ionic bonding involves transfer of one or more electrons between adjacent atoms, producing oppositely charged ions, bonded by coulombic attraction. Examples of ceramics with a highly ionic bond include sodium chloride, calcium fluoride, and magnesium oxide. Al_2O_3, SiO_2, and ZrO_2 show both ionic and covalent characteristics. (See Fig. 1.1 and Table 1.1.)

Ionic ceramics tend to form close-packed structures similar to those of pure metals, except that no free electrons are present and alternate atoms are of substantially different size. As a result, ionic ceramics have low ductility, high thermal expansion, and low electrical conductivity. Some have ionic conductivity at high temperatures because of diffusion of the charged ions through the structure. A good example is ZrO_2. At high temperatures, the negatively charged ions can move through the structure and carry an electric current. This material has been used in oxygen sensors to monitor the level of combustion in industrial processes.

TABLE 1.1 Properties of Some Advanced Ceramics

Type	Atomic bonding	Examples	Properties
Oxides	Ionic	Al_2O_3 (sapphire)	Hard-wearing, good creep properties
		Cr_2O_3	
		Fe_2O_3 (hematite)	
		MgO	
		ZrO_2 (PSZ)	
		$LiAl_2SiO_6$ (glass ceramic)	
Carbides	Less ionic interstitial compounds	ZrC	Very hard
		TiC	Very hard
		VC	Very hard
		NbC	High *E* moduli
		B_4C	High-temperature stability
	Covalent	SiC*	Poor creep properties
		WC	Used for cutting tools, abrasives, and dies
Nitrides	Covalent	BN (ambourite)	Low density
		Si_3N_4	High-temperature stability
		AlN	Very hard
		Sialon†	Good creep properties
		TiN	Used for cutting tools, gas turbine wheels, nozzles, and crucibles
Borides	Covalent	LaB_6	Excellent conductor
		ZrB_2	Used for electron microscope filaments, good creep properties

*SiC has properties more typical of nitrides.
†An alloy of Si, Al, O, and N.
Source: From Richardson.[3]

Ceramics Processing

In order to continue the enthusiastic swell that has been building for the potential of advanced ceramics as a unique class of engineering materials for certain high-performance applications, ongoing research is aimed at characterizing this independent class of materials, increasing the basic knowledge base, and developing the technology required to ensure the production of reliable, reproducible, and cost-competitive ceramic products.

Two specific areas receiving attention are inadequate fabrication techniques and the high sensitivity of ceramics to thermal and mechanical shock (inherent brittleness). Intense research worldwide is the focus of scientists, engineers, chemists, designers, and material specialists to solve these problems. While inadequate fabrication techniques can be solved in time as the technology matures, the problem of inherent brittleness cannot be avoided and ways must be found to manage it. (See Table 1.2.)

Ceramic materials are very sensitive to small flaws introduced during process-

TABLE 1.2 Characteristics of Advanced Ceramics

Advantages	
High melting point	Good dielectric properties
High stiffness	Thermal/electrical insulators
High hot strength	Semiconductor properties
High compressive strength	Ion-conductor properties
High hardness	Magnetic properties
Wear and corrosion resistance	Biocompatibility
Low density (lightweight)	Abundant raw materials
Limitations	
Susceptible to thermal and mechanical shock (brittle)	
Gaps in understanding and experience	
Difficult to fabricate	
Poor reproducibility	
High cost	

ing and in service. The multistage fabrication process for ceramics includes powder production, powder conditioning, shaping, and densification. Flaws, either physical (foreign inclusions or porosity) or chemical (impurities leading to second-phases, particularly liquids) can occur in each of these stages and cannot be corrected in subsequent processing stages.

The goal in powder processing is to achieve the highest degree of intimate mixing; in powder conditioning, to avoid the formation of hard agglomerates; in shaping, to avoid porosity; and in densification, to avoid the formation of glassy phases in grain boundaries. (See Table 1.3.)

Because the starting powder determines the ultimate quality of the ceramic part, there is a need to develop improved starting powders with high chemical purity and controlled particle sizes. Also needed are the tools necessary to characterize the physical and chemical properties of fine powders, as well as standard reference materials.

Wachtman[10] recently said: "Ceramics constitute an enabling technology, and under the right circumstances a ceramic material gives a performance enhancement which makes it a required component in achieving competitive performance. At the same time ceramics can have a high performance leverage. The amount of ceramic needed for a performance improvement is often only a small portion of an overall device or system." Therefore, to take advantage of these ceramic properties, the processing and design variables are critical. Three particular areas are receiving considerable attention:

1. Improved ceramic processing, to increase reliability by reducing structural defects and reducing costs
2. Improved design practice, to exploit their good properties while minimizing their limitations
3. Basic materials engineering principles, to design optimized compositions and microstructures for improved properties

Research and development activities to realize improvements in these areas include, according to Wachtman:[10]

TABLE 1.3 Potential Flaws during Manufacturing

Powder production
Unfavorable particle size, shape, and distribution
Off composition
Foreign inclusions
Hard agglomerates
Powder conditioning
Unfavorable agglomerate size distribution
Hard agglomerates
Varying agglomerate density distribution
Varying additive distribution
Insufficient binder
Organic fiber inclusions
Powder shaping (green compacts)
Porosity, voids, and cracks
Varying density
Nonuniform binder and additive distribution
Segregation
Residual binder
Organic inclusions
Densification
Porosity, micropore clusters, voids, and cracks
Nonuniform grain size and growth
Harmful grain-boundary phases (glassy phases)
Inclusions
Rough surface

Production of ceramics with finer grain sizes, extending even to sizes below one micron.

Fine grain size is important because the strength of ceramics is dependent on flaw size, which usually correlates with the size of the grains. Fine grain size material can give higher strength if the processing is carefully controlled. The lower the sintering temperature, the finer the grain size, and this leads to advantages in processing.

Ceramics are being systematically designed as multiphase composites. For example, a new family of ceramic composites composed of cordierite (magnesium aluminum silicate) and mullite (magnesium aluminate) is being developed for electronic substrate applications. The composite offers an advantage over the conventional alumina substrate in having a better thermal expansion match to silicon and a lower dielectric constant. The composite offers new processing challenges because a multicomponent suspension must be used and because sintering in two-phase systems presents problems of compatibility of deformation.

New chemical routes and better control of the chemistry of conventional processing routes is leading to better properties and better quality control.

The sol-gel process as well as other processes with distinct differences in detail, including the synthesis of very fine powders of uniform size by careful control of nucleation and growth, are discussed in Chaps. 4 through 6.

Another area receiving considerable attention is the use of computer modeling, which can permit the optimization of a set of properties rather than a single property. Other fields akin to processing as well as manufacturing technology (surface phenomena, joining, and tribological behavior) are being studied on a more scientific basis and are covered in Chaps. 7 and 8.

Material Processing

Advanced ceramic materials have attracted considerable attention because they present important new business opportunities and could improve national competitiveness significantly. Success in meeting these expectations, however, will depend on many conditions influencing the development and marketing of these advanced materials.

The displacement of outmoded materials by superior substitutes is a recurring theme in the history of materials development. Just as wood was displaced by bronze, which in turn was replaced by steel, so, too, are conventional steels (as well as other metals and glass) now being superseded by modern engineering polymers and structural ceramics. From this viewpoint, the introduction of advanced ceramic materials is evolutionary rather than revolutionary.

Nevertheless, distinct differences do exist between contemporary advanced ceramic materials and their forerunners. The most notable changes from past materials development were from new economic conditions and related information requirements. These changes include the rapid proliferation of new materials, the ability to serve small specialty markets, effects on manufacturing processes, and a much wider spectrum of scientific and industrial input.

Perhaps the most important feature of modern ceramic material development has been the accelerating rate at which new materials have been created and marketed.

A major cause of the dramatic growth in the number and variety of new ceramic materials has been the increasing ability of scientists to restructure materials at the molecular level. A seemingly infinite assortment of materials with different properties can be generated by reassembling their atomic structures. This capability is related to other factors that also have been instrumental in promoting a multiplicity of new and advanced structural ceramic materials, such as the birth of powerful computers and other sophisticated research tools and experimental techniques, the pressure of global competition, and the rise of worldwide information and communication systems for disseminating and exchanging scientific knowledge.

The rapid development of advanced materials has important implications. First, the large number and the diversity of new materials coming on stream will raise many questions about their effects on numerous issues. As the demand for data on materials increases, the ceramic industry is beginning to tax the capabilities of traditional materials information sources.

Another implication of rapid ceramic materials innovation is that the time-demand profile of future materials may be very brief, that is, the sequence of demand growth, maturation, and decline for new materials will be shorter than in the past since rapid technological improvements introduce so many superior competitors that substitution occurs earlier and more frequently. The shorter life span and greater turnover rate of future ceramic materials mean that the dynamics of materials development and marketing will be increasingly challenging.

The foregoing implications are significant to the government agencies and trade organizations that are expected to provide information on developments in