

Modern Ceramic Engineering

Properties, Processing, and Use in Design

Second Edition, Revised and Expanded

David W. Richerson

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and Use in Design
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Preface to the Second Edition

Since the first edition, ceramic technology has continued to evolve and expand. For example, ceramic matrix composites were just starting to be developed in the late 1970s and high-temperature ceramic superconductors had not yet been discovered. Thus, efforts were begun in 1985 to revise and gather information for a second edition. This effort was enhanced by the need to prepare short courses for the American Ceramic Society, the American Institute for Chemical Engineers, and NASA, and especially, to prepare an extensive home study course on ceramics, *Introduction to Modern Ceramics* (Course 56), for ASM International.

The second edition expands the discussion of some of the topics included in the first edition and adds important new topics. Topics that have been substantially expanded include ceramic structures and crystal chemistry, thermal behavior, electrical behavior, magnetic behavior, and all aspects of processing of ceramics. Complete new chapters have been added on phase equilibrium and toughening of ceramics. In addition, problems have been added to each chapter to increase this edition's suitability as a textbook.

Many individuals have been very helpful in the preparation of this second edition, and I gratefully acknowledge their support: Norman Hecht and Dale Wittmer, who offered many valuable revision suggestions; Paul Urban, Dominic Youngross, and Brooke Willis of ASM International, who coordinated much of the artwork preparation and text editing of materials used jointly in the ASM home study course and the second edition; the many individuals who provided technical reviews and expert suggestions (Vasantha R. W. Amarakoon, James F. Benzel, Alastair N. Cormack, Van Derck Frechette, Andrew Herczog, W. E. Lee, William G. Long, Anna E. McHale, Malcolm G. McLaren, James S. Reed, A. Safari, Daniel J. Shanefield, James R. Varner, and Thomas J. Whalen); and Rachel Goeckeritz, who helped with the manuscript typing and editing.

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Preface to the First Edition

Ceramic materials have become increasingly important in modern industrial and consumer technology, yet most engineers and technologists receive little or no training in ceramics and are unprepared to take advantage of their unique properties. This book was prepared to provide engineers, students, teachers, and technicians with an introduction to the structure, properties, processing, design concepts, and applications of advanced ceramics. Emphasis is on developing an understanding of why ceramics are different from metals and organics and then applying this understanding to optimum material selection. Many specific applications of advanced ceramics are discussed in this context. Some include heat engine components, armor, permanent magnets, phosphors, igniters, capacitor dielectrics, thermal barrier coatings, and oxygen sensors.

This book was initially begun to fill a gap as a textbook for engineering students in fields other than ceramics. However, the book evolved during preparation into a final form equally suitable as a textbook and a reference book for individuals in disciplines other than ceramics and in ceramics.

The book is divided into three parts, each of which augments the others, but which can also stand alone. The first part is entitled “Structures and Properties” and describes the source of physical, thermal, mechanical, electrical, magnetic, and optical properties in ceramics as compared to metals and organic materials. Specific ceramic materials with optimal properties for various types of applications are discussed together with potential limitations.

The second part is entitled “Processing of Ceramics” and reviews the fabrication processes used for manufacturing ceramic components. It discusses the specific steps in each process where property-limiting material flaws are likely to occur, and provides the reader with approaches for detecting these flaws and working with the ceramic fabricator to eliminate them.

The third part is entitled “Design with Ceramics” and applies the property, fabrication, and inspection principles learned in the first two sections to the selection and design of ceramic components for advanced engineering applications.

The need for a new text or reference book with a broad treatment of ceramic materials and technology was identified through preparation and teaching of a three-semester-hour ceramics course at Arizona State Uni-

photographs included within the book; Garrett Turbine Engine Company for providing technical data and photographs and for aiding in manuscript preparation; Greg Brigham for preparing most of the line illustrations; Floyd Brown for his encouragement and help in manuscript preparation; Dr. Nelson W. Hope and Denise B. Birnbaum for help in obtaining references and data sources; Dr. Robert Shane for his patience, encouragement, and technical and editorial suggestions; and particularly, Christy F. Johnson, Judith A. Martindale, Angie F. Peters, and Michael Anne Richerson for the extensive task of word processing in preparing initial drafts and the final manuscript.

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versity and a series of half-day and three-day ceramics courses for the American Society for Metals (ASM).

The course at Arizona State University was begun in 1975 with the objective of providing students of engineering and technology and experienced engineers of nonceramic disciplines with a better understanding of ceramic materials and their unique properties and processing and design requirements. Different textbooks were tried for this course each time it was taught, including *Introduction to Ceramics* by Kingery, Bowen, and Uhlmann; *Physical Ceramics for Engineers* by Van Vlack; and *Ceramics for High Performance Applications* edited by Burke, Lenoe, and Katz. All three were excellent books, but none turned out to be appropriate for the objectives of the course. *Introduction to Ceramics* was too detailed and analytical and did not cover processing, the effects of processing on properties, machining, nondestructive inspection, failure analysis, and ceramic design approaches. *Physical Ceramics for Engineers* was more engineering oriented, but also did not cover the scope required by the course. *Ceramics for High Performance Applications* was directed largely toward gas turbine and advanced heat engine applications and was therefore also too narrow in scope. As a result, the bulk of the course at ASU was presented from notes derived from numerous sources and personal experience.

The two three-day courses taught for ASM were entitled "High-Strength Ceramics for Engineering Applications" and "Impact of Ceramics on Modern Engineering." The half-day sessions were part of a three-day course entitled "High-Temperature Structural Materials." These courses were presented to engineers and technicians from a variety of disciplines. As was the case with the ASU course, no suitable text or reference book was available. The notes were further expanded to prepare for these courses, especially in the areas of the relationships of structure and processing to properties, design approaches, failure analysis, and discussion of specific applications.

The ASU and ASM courses clearly identified the need for a new text or reference book that would provide a broad treatment of ceramic materials and technology that could be understood and implemented by engineers, technicians, students, and teachers. The resulting book was two years in writing and is based on the course notes plus considerable additional literature research.

Many organizations and individuals have supported this effort, and I would like to take this opportunity to thank as many as possible: the Arizona State University Division of Technology and the American Society for Metals (especially Nick Jessen) for sponsoring and supporting the ceramic courses; the Defense Advanced Research Projects Agency, the Air Force Materials Laboratory and the Air Force Aero-Propulsion Laboratory for sponsoring the programs that produced many of the examples and

Introduction

The objective of this book is to provide an increased understanding of ceramic technology and its practical application. The approach is non-mathematical and concentrates on the basic material and property concepts needed to provide the reader with a working knowledge of the more important ceramic materials and design considerations.

The book is divided into three parts:

Part I: Structures and Properties

Part II: Processing of Ceramics

Part III: Design with Ceramics

Part I explores the physical, thermal, mechanical, electrical, magnetic, and optical properties of ceramics and their relationship to atomic bonding, crystal structure, and microstructure. Comparison with metals and organic materials is emphasized and concepts of ceramic design begin to evolve.

Part II studies the ceramic fabrication processes, describing in detail each step from raw material selection to shape-forming to quality control. Each process step is discussed in terms of its relationship to the properties and acceptability of the final ceramic component. Understanding of the way a component is fabricated can often help an engineer resolve an application problem.

Part III applies the information covered in the first two parts to the design of ceramics. Emphasis is on the differences in design approach required for ceramics as compared to metals and plastics. The importance and techniques of fracture analysis are also described in Part III, as well as techniques to increase toughness to resist fracture. The final chapter discusses material selection for specific applications.

Ceramics are encountered in virtually every facet of industry and everyday life. An understanding of what a ceramic is and what it can do significantly broadens the scope and effectiveness of an engineer, technician, or instructor.

The following exercise will help illustrate the variety of engineering applications of ceramic materials. Prior to reading the rest of the book the reader is requested to write down his or her best estimate (based on previous experience) of which ceramic material or materials would be optimal for each of the following categories and which special properties of each ceramic make it the best choice.

1. Sandblast nozzle
2. Insulating refractory for furnace lining
3. Seal
4. Pottery
5. High-temperature heat exchanger
6. Armor
7. Permanent magnet
8. Ceramic quench block to draw heat away from a heat source as fast as possible
9. Thermal protection material such as that required for a reentry vehicle like the Space Shuttle
10. Transparent material requiring uniform properties in all directions (isotropic)
11. Material having high thermal expansion in one direction and low thermal expansion in the other direction
12. Material that can be formed to shape in the green state and does not change dimension during the densification or firing operation
13. Grinding media for a ball mill
14. Low-cost fibers to be mixed with organics into a composite for structural applications
15. Coating that can be applied by molten-particle-spray techniques that significantly reduces the temperature of the substrate during subsequent high-temperature exposure
16. Low-cost mold material for slip casting
17. Material to separate and protect thermocouple wires
18. Material capable of surviving extreme thermal shock
19. Substrate for electrical devices
20. Kiln furniture for a high-purity diffusion furnace for doping diodes and other electrical devices
21. Ceramic material that increases the charge storage capability of a capacitor by a factor of 1600
22. Very-low-density material used for insulation in high-temperature furnace construction
23. Radome
24. Gas-turbine stator
25. High-temperature cement that can be applied on-site
26. Material used in cutoff and grinding wheels
27. Cutting tool insert for turning or milling metal
28. High-temperature heating element or igniter
29. Bearings

Although this list represents only a small sampling of the many types of ceramics and their diverse applications, it illustrates how widely used

ceramics are and how important it is that engineers be familiar with the terminology and with the types and properties of ceramic materials. To illustrate this point further, the reader is requested to answer in writing another question: What are the applications of ceramic materials within a typical home? A list of 10 should be easy; a list of 20 is more challenging, but achievable.

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I

STRUCTURES AND PROPERTIES

Individuals who have not previously studied ceramics typically ask: “What is a ceramic?” or “What is the difference between a ceramic and metal?” Most people have the concept that a ceramic is brittle, has a high melting temperature, is a poor conductor of heat and electricity, and is nonmagnetic, and that a metal is ductile, is a good conductor of heat and electricity, and can be magnetic. These stereotyped viewpoints are not necessarily true for either ceramics or metals. In fact, there is no clear-cut boundary that separates ceramics into one class and metals into another. Rather, there are intermediate compounds that have some aspects typical of ceramics and some typical of metals.

The nature of a material is largely controlled by the atoms present and their bond mechanism. Chapter 1 discusses the types of atomic bonding and the atomic elements that are most likely to combine to form ceramic, metallic, and organic materials. Chapter 2 discusses crystal structures and the crystal chemistry relationships that govern which atoms are most likely to form which structures. Chapter 3 reviews the concepts of phase equilibria and phase equilibrium diagrams. Chapter 4 discusses physical and thermal behavior in terms of the atomic elements present, the bond mechanism, and the crystal structure. Chapters 5 to 7 do the same for mechanical, electrical, dielectric, magnetic, and optical behavior. Chapter 8 discusses time-dependent and environment-dependent behavior. Chapters 4 to 8 all identify specific ceramic materials that exhibit the behavior being discussed.

1

Atomic Bonding and Crystal Structure

Chapter 1 reviews the configuration of electrons in atoms of different elements and discusses how these configurations control the nature of bonding between different atoms. Metallic, ionic, covalent, and van der Waals bonding are described. Some concepts of crystal structure, polymorphism, and noncrystalline structures are introduced. The chapter concludes with a brief review of organic structures.

1.1 ELECTRONIC CONFIGURATION OF ATOMS

An atom can be visualized in a simplified manner as a positively charged nucleus surrounded by negatively charged electrons. The energy of the electrons varies such that specific electrons are located in specific shells around the nucleus. These are called *quantum shells*. Each shell is referred to by a *principal quantum number* n , where $n = 1, 2, 3 \dots$. The total number of electrons in a shell is $2n^2$. Thus the lowest-energy quantum shell ($n = 1$) has only 2 electrons and successively higher energy shells have 8 ($n = 2$), 18 ($n = 3$), 32 ($n = 4$), and so on, electrons, respectively.

Although electrons within a quantum shell have similar energy, no two are identical. To distinguish among these electrons, shells are divided into subshells called *orbitals*, which describe the probability of where pairs of electrons will be within the shell with respect to the nucleus. The first quantum shell has only two electrons, both in the s orbital, with a spherical probability distribution around the nucleus at a radius of approximately 0.5 Å. These two electrons have identical energy, but opposite magnetic behavior or spin.

The second shell has eight electrons, two in s orbitals and six in p orbitals. All have higher energy than the two electrons in the first shell and are in orbitals farther from the nucleus. (For instance, the s orbitals of the second shell of lithium have a spherical probability distribution at about 3 \AA radius.) The p orbitals are not spherical, but have dumbbell-shaped probability distributions along the orthogonal axes, as shown in Fig. 1.1. These p electrons have slightly higher energy than s electrons of the same shell and are in pairs with opposite spins along each axis when the shell is full.

The third quantum shell has d orbitals in addition to s and p orbitals. A full d orbital contains 10 electrons. The fourth and fifth shells contain f orbitals in addition to s , p , and d orbitals. A full f orbital contains 14 electrons.

A simple notation is used to show the electron configurations within shells, to show the relative energy of the electrons, and thus to show the order in which the electrons can be added to or removed from an atom during bonding. This notation can best be illustrated by a few examples.

Example 1.1 Oxygen has eight electrons and has the electron notation $1s^2 2s^2 2p^4$. The 1 and 2 preceding the s and p designate the quantum shell, the s and p designate the subshell within each quantum shell, and the superscripts designate the total number of electrons in each subshell. For oxygen the $1s$ and $2s$ subshells are both full, but the $2p$ subshell is two electrons short of being full.

Example 1.2 As the atomic number and the number of electrons increase, the energy difference between electrons and between shells decreases and overlap between quantum groups occurs. For example, the $4s$ subshell of iron fills before the $3d$ subshell is full. This is shown in the electron notation by

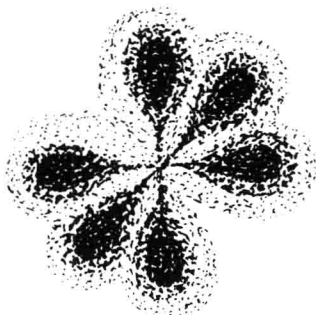
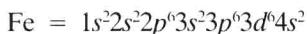


Figure 1.1 Electron probability distributions for p orbitals. The highest probability electron positions are along the orthogonal axes. Two electrons, each with opposite spin, are associated with each axis, resulting in a total of six p electrons if all the p orbitals in the shell are filled.

listing the order of fill of energy levels in sequence from the left of the notation to the right:



Example 1.3 Electronic notation helps a person visualize which electrons are available for bonding and to estimate the type of bond that is likely to result. Unfilled shells contribute to bonding. Electron notation is often abbreviated to include only the unfilled and outer shells. The iron electron notation is thus abbreviated to $3d^6 4s^2$, which tells the reader that all the subshells up to and including $3s$ are filled. Yttrium is abbreviated from $1s^2 2s^2 2p^6 3d^{10} 4s^2 4p^6 4d^1 5s^2$ to $4d^1 5s^2$ or even more simply, $4d 5s^2$. Figure 1.2 lists the abbreviated electron configurations of the elements arranged according to the periodic table. Another form of abbreviation lists the nearest inert gas of lower atomic number and also identifies the electrons in outer shells. For example, Mg consists of the neon inner structure $1s^2 2s^2 2p^6$ plus $3s^2$ and is abbreviated $[\text{Ne}]3s^2$. Similarly, Ti can be abbreviated $[\text{Ar}]3d^2 4s^2$ and I abbreviated $[\text{Kr}]4d^{10} 5s^2 5p^5$.

1.2 BONDING

The unfilled outermost electron shells are involved in bonding. The elements He, Ne, Ar, Kr, Xe, and Rn have full outer electron shells and thus are very stable and do not easily form bonds with other elements. Elements with unfilled electron shells are not as stable and interact with other atoms in a controlled fashion such that electrons are shared or exchanged between these atoms to achieve stable full outer shells.

The three primary interatomic bonds are referred to as metallic, ionic, and covalent. These provide the bond mechanism for nearly all the solid ceramic and metallic materials discussed in later chapters. Other secondary mechanisms referred to as van der Waals bonds also occur, but are discussed only briefly.

Metallic Bonding

As the name implies, *metallic bonding* is the predominant bond mechanism for metals. It is also referred to as *electronic bonding*, from the fact that the valence electrons (electrons from unfilled shells) are freely shared by all the atoms in the structure. Mutual electrostatic repulsion of the negative charges of the electrons keeps their distribution statistically uniform throughout the structure. At any given time, each atom has enough electrons grouped around it to satisfy its need for a full outer shell. It is the mutual attraction of all the nuclei in the structure to this same cloud of shared electrons that results in the metallic bond.

Because the valence electrons in a metal distribute themselves uniformly and because all the atoms in a pure metal are of the same size, close-packed structures result. Such close-packed structures contain many slip planes along which movement can occur during mechanical loading, producing the ductility that we are so accustomed to for metals. Pure metals typically have very high ductility and can undergo 40 to 60% elongation prior to rupturing. Highly alloyed metals such as the superalloys also have close-packed structures, but the different-size alloying atoms disrupt movement along slip planes and decrease the ductility. Superalloys typically have 5 to 20% elongation.

The free movement of electrons through the structure of a metal results in high electrical conductivity under the influence of an electrical field and high thermal conductivity when exposed to a heat source. These properties are discussed in more detail in Chaps. 4 and 6.

Metallic bonding occurs for elements to the left and in the interior of the periodic table (see Fig. 1.2 and the complete periodic table on p. 850). Alkali metals such as sodium (Na) and potassium (K) are bonded by outer s electrons and have low bond energy. These metals have low strength and low melting temperatures and are not overly stable. Transition metals such as chromium (Cr), iron (Fe), and tungsten (W) are bonded by inner electrons and have much higher bond strengths. Transition metals thus have higher strength and higher melting temperatures and are more stable.

Ionic Bonding

Ionic bonding occurs when one atom gives up one or more electrons and another atom or atoms accept these electrons such that electrical neutrality is maintained and each atom achieves a stable, filled electron shell. This is best illustrated by a few examples.

Example 1.4 Sodium chloride (NaCl) is largely ionically bonded. The Na atom has the electronic structure $1s^2 2s^2 2p^6 3s$. If the Na atom could get rid of the $3s$ electron, it would have the stable neon (Ne) structure. The chlorine atom has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^5$. If the Cl atom could obtain one more electron, it would have the stable argon (Ar) structure. During bonding, one electron from the Na is transferred to the Cl, producing a sodium ion (Na^+) with a net positive charge and a chlorine ion (Cl^-) with an equal negative charge, resulting in a more stable electronic structure for each. This is illustrated in Figure 1.3. The opposite charges provide a Coulombic attraction that is the source of ionic bonding. To maintain overall electrical neutrality, one Na atom is required for each Cl atom and the formula becomes NaCl.

Example 1.5 The aluminum (Al) atom has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^1$. To achieve a stable Ne structure three electrons would have