Series in Materials Science and Engineering

FUNDAMENTALS OF CERAMICS

M W Barsoum

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Dedicated to classy Kate and inquisitive Michael,
the future scientist.

About the Author

Dr. Barsoum is currently a Distinguished Professor at Drexel University. He and his research group were the first to fabricate and fully characterize an important new class of machinable ternary carbides and nitrides, the $M_{N+1}AX_N$ (so-called MAX) phases. Since 1996, Dr. Barsoum and his collaborators have published over 60 refereed papers on these ternary carbides and nitrides, including ones in *Nature* and *Science*. Dr. Barsoum has authored or co-authored over 100 refereed publications, 6 US patents awarded and 4 pending. In 2000 he was awarded a Humboldt-Max Planck Research award for Senior US Research Scientists. He spent his 2000–2001 sabbatical year at the Max Planck Research Institute in Stuttgart, Germany.

Preface to Second Printing

The major difference between this printing and the first is in the number of typos and other errors. The first printing, like most first printings, had its fair share of mistakes; some more serious than others. Needless to say these mistakes detracted from the mission at hand. I am certain that the vast majority of typos and other errors have been taken care of. In addition to correcting the mistakes, some of the figures have been redrawn to render them clearer.

Michel W. Barsoum

Preface to First Printing

It is a mystery to me why, in a field as interesting, rich, and important as ceramics, a basic fundamental text does not exist. My decision to write this text was made almost simultaneously with my having to teach my first introductory graduate class in ceramics at Drexel a decade ago. Naturally, I assigned Kingery, Bowen, and Uhlmann's *Introduction to Ceramics* as the textbook for the course. A few weeks into the quarter, however, it became apparent that KBU's book was difficult to teach from and more importantly to learn from. Looking at it from the student's point of view it was easy to appreciate why — few equations are derived from first principles. Simply writing down a relationship, in my opinion, does not constitute learning; true understanding only comes when the trail that goes back to first principles is made clear. However, to say that this book was influenced by KBU's book would be an understatement — the better word would be inspired by it, and for good reason — it remains an authoritative, albeit slightly dated, text in the field.

In writing this book I had a few guiding principles. First, nearly all equations are derived, usually from first principles, with the emphasis being on the physics of the problem, sometimes at the expense of mathematical rigor. However, whenever that trade-off is made, which is not often, it is clearly noted in the text. I have kept the math quite simple, nothing more complicated than differentiation and integration. The aim in every case was to cover enough of the fundamentals, up to a level deep enough to allow the reader to continue his or her education by delving, without too much difficulty, into the most recent literature. In today's fast-paced world, it is more important than ever to understand the fundamentals.

Second, I wanted to write a book that more or less "stood alone" in the sense that it did not assume much prior knowledge of the subject from the reader. Basic chemistry, physics, mathematics, and an introductory course in materials science or engineering are the only prerequisites. In that respect, I believe this book will appeal to, and could be used as a textbook in, other than material science and engineering departments, such as chemistry or physics.

Pedagogically I have found that students in general understand concepts and ideas best if they are given concrete examples rather than generalized treatments. Thus maybe, at the expense of elegance and brevity, I have opted for that approach. It is hoped that once the concepts are well understood, for at least one system, the reader will be able to follow more advanced and generalized treatments that can be found in many of the references that I have included at the end of every chapter.

Successive drafts of this book have been described by some reviewers as being arid, a criticism that I believe has some validity and that I have tried to address. Unfortunately, it was simply impossible to cover the range of topics, at the depth I wanted to, and be flowery and descriptive at the same time (the book is already over 650 pages long).

Another area where I think this book falls short is in its lack of what I would term a healthy skepticism (à la Feynman lectures, for instance). Nature is too complicated, and ceramics in particular, to be neatly packaged into monosize dispersed spheres and their corresponding models, for example.

I thus sincerely hope that these two gaps will be filled in by the reader and especially the instructor. First, a little bit of "fat" should make the book much more appetizing — examples from the literature or the instructor's own experience would be just what is required. Second, a dose of skepticism concerning some of the models and their limitation is required. Being an experimentalist, I facetiously tell my students that when theory and experiment converge one of them is probably wrong.

This book is aimed at junior, senior, and first-year graduate students in any materials science and engineering program. The sequence of chapters makes it easy to select material for a one-semester course. This might include much of the material in Chapters 1 to 8, with additional topics from the later chapters. The book is also ideally suited to a two-quarter sequence, and I believe there may even be enough material for a two-semester sequence.

The book can be roughly divided into two parts. The first nine chapters deal with bonding, structure, and the physical and chemical properties that are influenced mostly by the type of bonding rather than the microstructure, such as defect structure and the atomic and electronic transport in ceramics. The coverage of the second part, Chaps. 11 to 16, deals with properties that are more microstructure dependent, such as fracture toughness, optical, magnetic, and dielectric properties. In between the two parts lies Chap. 10, which deals with the science of sintering and microstructural development. The technological aspects of processing have been deliberately omitted for two reasons. The first is that there are a number of good undergraduate texts that deal with the topic. Second, it is simply not possible to discuss that topic and do it justice in a section of a chapter.

Chapter 8 on phase diagrams was deliberately pushed back until the notions of defects and nonstoichiometry (Chap. 6) and atom mobility (Chap. 7) were introduced. The chapter on glasses (Chap. 9) follows Chap. 8 since once again the notions introduced in Chaps. 6, 7, and 8 had to be developed in order to explain crystallization.

And while this is clearly not a ceramics handbook, I have included many important properties of binary and ternary ceramics collected over 10 years from numerous sources. In most chapters I also include, in addition to a number of well-tested problem sets with their numerical answers, worked examples to help the student through some of the trickier concepts. Whenever a property or phenomenon is introduced, a section clearly labeled experimental details has been included. It has been my experience that many students lacked a knowledge of how certain physical properties or phenomena are measured experimentally, which needless to say makes it rather fruitless to even try to attempt to explain them. These sections are *not* intended, by any stretch of the imagination, to be laboratory guides or procedures.

Finally, it should also be pointed out that Chaps. 2, 5, and 8 are by no means intended to be comprehensive — but are rather included for the sake of completion, and to highlight aspects that are referred to later in the book as well as to refresh the reader's memory. It is simply impossible to cover inorganic chemistry, thermodynamics, and phase equilibria in three chapters. It is in these chapters that a certain amount of prior knowledge by the reader is assumed.

I would like to thank Dr. Joachim Maier for hosting me, and the Max-Planck Institute fur Festkorperforchung in Stuttgart for its financial support during my sabbatical year, when considerable progress was made on the text. The critical readings of some of the chapters by C. Schwandt, H. Naefe, N. Nicoloso, and G. Schaefer is also gratefully acknowledged. I would especially like to thank Dr. Rowland M. Cannon for helping me sort out, with the right spirit I may add, Chaps. 10 through 12 — his insight, as usual, was invaluable.

I would also like to thank my colleagues in the Department of Materials Engineering and Drexel University for their continual support during the many years it took to finish this work. I am especially indebted to Profs. Roger Doherty and Antonious Zavaliangos with whom I had many fruitful and illuminating discussions. Finally I would like to take this opportunity to thank all those who have, over the many years I was a student, first at the American University in Cairo, Egypt, followed by the ones at the University of Missouri-Rolla and, last but not least, MIT, taught and inspired me. One has only to leaf through the book to appreciate the influence Profs. H. Anderson, R. Coble, D. Kingery, N. Kreidl, H. Tuller, D. Uhlmann, B. Wuench, and many others had on this book.

Comments, criticisms, suggestions, and corrections, from all readers, especially students, for whom this book was written, are most welcome. Please send them to me at the Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, or by e-mail at Barsoumw@drexel.edu.

Finally, I would like to thank my friends and family, who have been a continuous source of encouragement and support.

Michel W. Barsoum

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Chapter 1

Introduction

All that is, at all
Lasts ever, past recall,
Earth changes,
But thy soul and God stand sure,
Time's wheel runs back or stops:
Potter and clay endure.

Robert Browning

1.1 Introduction

The universe is made up of elements that in turn consist of neutrons, protons, and electrons. There are roughly 100 elements, each possessing a unique electronic configuration determined by its atomic number Z, and the spatial distribution and energies of their electrons. What determines the latter requires some understanding of quantum mechanics and is discussed in greater detail in the next chapter.

One of the major triumphs of quantum theory was a rational explanation of the **periodic table** (see inside front cover) of the elements that had been determined from experimental observation long before the advent of quantum mechanics. The periodic table places the elements in horizontal rows of increasing atomic number and vertical columns or **groups**, so that all elements in a group display similar chemical properties. For instance, all the elements of group VII B, referred to as halides, exist as diatomic gases characterized by a very high reactivity. Conversely, the elements of group VIII, the noble gases, are monoatomic and are chemically extremely inert.

A large majority of the elements are solids at room temperature, and because they are shiny, ductile, and good electrical and thermal conductors, they are considered *metals*. A fraction of the elements — most notably, N, O, H, the halides, and the noble gases — are gases at room temperature. The remaining elements are covalently bonded solids that, at room temperature, are either insulators (B, P, S, C[1]) or semiconductors (Si, Ge). These elements, for reasons that will become apparent very shortly, will be referred to as *nonmetallic elemental solids* (NMESs).

Very few elements are used in their pure form; most often they are alloyed with other elements to form engineering materials. The latter can be broadly classified as metals, polymers, semiconductors, or ceramics, with each class having distinctive properties that reflect the differences in the nature of their bonding.

In metals, the bonding is predominantly metallic, where delocalized electrons provide the "glue" that holds the positive ion cores together. This delocalization of the bonding electrons has far-reaching ramifications since it is responsible for properties most associated with metals: ductility, thermal and electrical conductivity, reflectivity, and other distinctive properties.

Polymers consist of very long, for the most part, C-based chains to which other organic atoms (for example; C, H, N, Cl, F) and molecules are attached. The bonding within the chains is strong, directional, and covalent, while the bonding between chains is relatively weak. Thus, the properties of polymers as a class are dictated by the weaker bonds, and consequently they possess lower melting points, higher thermal expansion coefficients, and lower stiffnesses than most metals or ceramics.

Semiconductors are covalently bonded solids that, in addition to Si and Ge already mentioned, include GaAs, CdTe, and InP, among others. The usually strong covalent bonds holding semiconductors together make their mechanical properties quite similar to those of ceramics (i.e.; brittle and hard).

Now that these distinctions have been made, it is possible to answer the non-trivial question: What is a ceramic?

1.2 Definition of Ceramics

Ceramics can be defined as *solid compounds that are formed by the application of heat, and sometimes heat and pressure, comprising at least two elements provided one of them is a non-metal or a nonmetallic elemental solid. The other element(s) may be a metal(s) or another nonmetallic elemental solid(s)*. A somewhat simpler definition was given by Kingery who defined ceramics as, "the art and science of making and using solid articles, which have, as their essential component, and are composed in large part of, inorganic nonmetallic materials". In other words, what is neither a metal, a semiconductor or a polymer is a ceramic.

[1] In the form of diamond. It is worth noting that although graphite is a good electrical conductor, it is not a metal since it is neither shiny nor ductile.