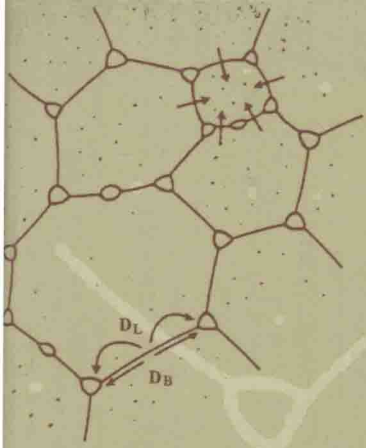

CERAMIC PROCESSING and SINTERING

M. N. RAHAMAN

CERAMIC PROCESSING and SINTERING

M. N. RAHAMAN

Department of Ceramic Engineering
University of Missouri-Rolla
Rolla, Missouri

MARCEL DEKKER, INC. NEW YORK • BASEL

Library of Congress Cataloging-in-Publication Data

Rahaman, M. N.
Ceramic processing and sintering / M.N. Rahaman.
p. cm. — (Materials engineering ; 10)
Includes index.
ISBN 0-8247-9573-3 (alk. paper)
1. Ceramics. 2. Sintering. I. Title. II. Series: Materials engineering (Marcel Dekker, Inc.) ; 10.
TP807.R28 1995
666—dc20 95-32195
CIP

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the address below.

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5

PRINTED IN THE UNITED STATES OF AMERICA

CERAMIC PROCESSING and SINTERING

MATERIALS ENGINEERING

1. Modern Ceramic Engineering: Properties, Processing, and Use in Design. Second Edition, Revised and Expanded, *David W. Richerson*
2. Introduction to Engineering Materials: Behavior, Properties, and Selection, *G. T. Murray*
3. Rapidly Solidified Alloys: Processes · Structures · Applications, *edited by Howard H. Liebermann*
4. Fiber and Whisker Reinforced Ceramics for Structural Applications, *David Belitskus*
5. Thermal Analysis of Materials, *Robert F. Speyer*
6. Friction and Wear of Ceramics, *edited by Said Jahanmir*
7. Mechanical Properties of Metallic Composites, *edited by Shojiro Ochiai*
8. Chemical Processing of Ceramics, *edited by Burtrand I. Lee and Edward J. A. Pope*
9. Handbook of Advanced Materials Testing, *edited by Nicholas P. Cheremisinoff and Paul N. Cheremisinoff*
10. Ceramic Processing and Sintering, *M. N. Rahaman*

Additional Volumes in Preparation

To
Vashanti, Lennard, and Ronald

Preface

Ceramics have been used since the earliest civilizations. The field of ceramic materials has its roots in the more traditional aspects of the subject such as clay-based ceramics and glasses. However, during the past few decades, new developments in the use of ceramics in more advanced technological applications have attracted considerable attention. In addition to the discovery of ceramic superconductors, the use of ceramics for heat-resistant tiles in the space shuttle, for optical fibers, and for components in high-temperature engines has generated considerable interest in the field.

The increasing use of ceramics in more advanced technological applications has resulted in a heightened demand for improvements in properties and reliability. In recent years there has been the realization that such improvements can be achieved only through careful attention to the fabrication process. The engineering properties of a polycrystalline ceramic are controlled by the microstructure, which in turn depends on the processing method used to fabricate the body. Therefore, the fabrication processes govern the production of microstructures with the desired properties. It is often stated that materials science is a field at the interface between the physical sciences (physics, chemistry, and mathematics) and engineering (such as electrical, mechanical, and civil engineering). In this view, the approach to the processing of ceramics is concerned with the understanding of fundamental issues and the application of that knowledge to the production of microstructures that have useful properties.

This book is concerned primarily with the processing of polycrystalline ceramics. Because of its importance and widespread use, the fabrication of ceramics by the firing of consolidated powders forms the focus of the book. The production of ceramics (and glasses) by the less conventional sol-gel route has been attracting considerable attention. A brief treatment of sol-gel processing is also included. The approach is to outline the fundamental issues of each process and show how they are applied to the practical fabrication of ceramics. Each fabrication route involves a number of processing steps, and each step has the potential for producing microstructural flaws that degrade the properties of the fabricated material. An important feature of the treatment is the attempt to show the importance of each step as well as the interconnection between the various steps in the overall fabrication route. Chapter 1 provides an introductory overview of the various methods that can be used for the production of ceramic materials. In the production of ceramics from powders and, to a lesser extent, the sol-gel route, the overview also forms the basis for the more detailed considerations later in the book. Chapters 2 to 12 form a logical development from the start of the fabrication route to the final fabricated microstructure.

My intention has been to prepare a text that is suitable for a one-semester (or two-quarter) course in the processing of ceramics at the senior undergraduate level or the introductory graduate level. A background in the concepts and processing of traditional ceramics, typically obtained in lower-level undergraduate classes, is assumed. For a processing course, it may be advisable to omit Chapter 11, which covers some difficult issues of sintering in depth. The second half of the book (Chapters 7 to 12) may also be suitable for a one-semester course in sintering and microstructural control of ceramics at the introductory graduate level. It is hoped that the book will also be useful to researchers in industry who are involved in the production of ceramics or who wish to develop a background in the processing and sintering of ceramics.

I am greatly indebted to Dr. G. W. Scherer, who reviewed most of the chapters. His comments and constructive criticism saved me from perpetuating many mistaken ideas. Any remaining mistakes, however, are my own and I accept responsibility for them. I also wish to thank the many authors and publishers who have allowed me pemission to reproduce their figures in this book. Last but not least, I wish to thank my wife, Vashanti, for her unfailing support and her forbearance during my preoccupation with the completion of this book.

M. N. Rahaman

Contents

1

Ceramic Fabrication Processes: An Introductory Overview

1.1 INTRODUCTION

The subject of ceramics covers a wide range of materials. Recent attempts have been made to divide it into two parts: traditional ceramics and advanced ceramics. The use of the term "advanced" has, however, not received general acceptance, and other terms, including "technical," "special," "fine," and "engineering" will also be encountered. *Traditional ceramics* bear a close relationship to those materials that have been developed since the earliest civilizations. They are pottery, structural clay products, and clay-based refractories, with which we may also group cements and concretes and glasses. Whereas traditional ceramics still represent a major part of the ceramics industry, interest in recent years has focused on *advanced ceramics*, ceramics that, with minor exceptions, have been developed within the last 50 years or so. Advanced ceramics include ceramics for electrical, magnetic, electronic, and optical applications (sometimes referred to as *functional ceramics*) and ceramics for structural applications at ambient as well as elevated temperatures (*structural ceramics*). Although the distinction between traditional and advanced ceramics may be referred to in this book occasionally for convenience, we do not wish to overemphasize it. There is much to be gained through continued interaction between the traditional and advanced sectors.

Chemically, with the exception of carbon, ceramics are nonmetallic, inorganic compounds. Examples are the silicates such as kaolinite ($Al_2Si_2O_5(OH)_4$) and mullite ($Al_6Si_2O_{13}$), simple oxides such as alumina (Al_2O_3) and zirconia (ZrO_2), complex oxides other than the silicates such as barium titanate ($BaTiO_3$), and the superconducting material $YBa_2Cu_3O_{6+\delta}$($0 \leq \delta \leq 1$). In addition, there are nonoxides, including carbides such as silicon carbide (SiC) and boron carbide (B_4C), nitrides such as silicon nitride (Si_3N_4) and boron nitride (BN), borides such as titanium diboride (TiB_2), silicides such as molybdenum disilicide ($MoSi_2$), and halides such as lithium fluoride (LiF). There are also compounds based on nitride-oxide or oxynitride systems (e.g., β′-sialons with the general formula $Si_{6-z}Al_zN_{8-z}O_z$, where $0 < z < \approx 4$).

Structurally, all materials are either *crystalline* or *amorphous* (also referred to as *glassy*). The difficulty and expense of growing single crystals means that, normally, crystalline ceramics (and metals) are actually *polycrystalline*—they are made up of a large number of small crystals, or grains, separated from one another by grain boundaries. In ceramics as well as in metals, we are concerned with two types of structures, both of which have a profound effect on properties. The first type of structure is at the atomic scale: the type of *bonding* and the *crystal structure* (for a crystalline ceramic) or *amorphous structure* (if it is glassy). The second type of structure is at a larger scale: the *microstructure*, which refers to the nature, quantity, and distribution of the structural elements or phases in the ceramic (e.g., crystals, glass, and porosity).

It is sometimes useful to distinguish between the intrinsic properties of a material and the properties that depend on the microstructure. The *intrinsic properties* are determined by the structure at the atomic scale and are properties that are not susceptible to significant change by modification of the microstructure, properties such as the melting point, elastic modulus, coefficient of thermal expansion, and whether the material is brittle, magnetic, ferroelectric, or semiconducting. In contrast, many of the properties critical to the engineering applications of materials are strongly dependent on the microstructure (e.g., mechanical strength, dielectric constant, and electrical conductivity).

Intrinsically, ceramics usually have high melting points and are therefore generally described as highly refractory. They are also usually hard, brittle, and chemically inert. This chemical inertness is usually taken for granted, for example, in ceramic and glass tableware and in the bricks, mortar, and glass of our houses. However, when used at high temperatures, as in the chemical and metallurgical industries, this chemical inertness is severely tried. The electrical, magnetic, and dielectric behavior covers a wide range—for example, in the case of electrical behavior, from insulators to conductors. The applications of ceramics are many. Usually, for a given application one property may be of particular importance, but, in fact, all relevant properties need to be considered. We are therefore usually interested in combinations of properties. For traditional ceramics and glasses, familiar applications include structural building materials (e.g., bricks and roofing tile), refractories for furnace linings, tableware

Table 1.1 Applications of Advanced Ceramics Classified by Function

Function	Ceramic	Application
Electric	Insulation materials (Al_2O_3, BeO, MgO)	Integrated circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate
	Ferroelectric materials ($BaTiO_3$, $SrTiO_3$)	Ceramic capacitor
	Piezoelectric materials (PZT)	Vibrator, oscillator, filter, etc.
		Transducer, ultrasonic humidifier, piezoelectric spark generator, etc.
	Semiconductor materials ($BaTiO_3$, SiC, ZnO-Bi_2O_3, V_2O_5 and other transition metal oxides)	NTC thermistor: temperature sensor, temperature compensation, etc.
		PTC thermistor: heater element, switch, temperature compensation, etc.
		CTR thermistor: heat sensor element
		Thick-film thermistor: infrared sensor
		Varistor: noise elimination, surge current absorber, lighting arrestor, etc.
		Sintered CdS material: solar cell
		SiC heater: electric furnace heater, miniature heater, etc.
	Ion-conducting materials (β-Al_2O_3, ZrO_2)	Solid electrolyte for sodium battery
		ZrO_2 ceramics: oxygen sensor, pH meter fuel cells
Magnetic	Soft ferrite	Magnetic recording head, temperature sensor, etc.
	Hard ferrite	Ferrite magnet, fractional horse power motors, etc.
Optical	Translucent alumina	High-pressure sodium vapor lamp
	Translucent Mg-Al spinel, mullite, etc.	For a lighting tube, special-purpose lamp, infrared transmission window materials
	Translucent Y_2O_3-ThO_2 ceramics	Laser materials
	PLZT ceramics	Light memory element, video display and storage system, light modulation element, light shutter, light valve

Table 1.1 *Continued*

Function	Ceramic	Application
Chemical	Gas sensor (ZnO, Fe_2O_3, SnO_2)	Gas leakage alarm, automatic ventilation fan, hydrocarbon, fluorocarbon detectors, etc.
	Humidity sensor ($MgCr_2O_4$-TiO_2)	Cooking control element in microwave oven, etc.
	Catalyst carrier (cordierite)	Catalyst carrier for emission control
	Organic catalyst	Enzyme carrier, zeolites
	Electrodes (titanates, sulfides, borides)	Electrowinning aluminum, photochemical processes, chlorine production
Thermal	ZrO_2, TiO_2	Infrared radiator
Mechanical	Cutting tools (Al_2O_3, TiC, TiN, others)	Ceramic tool, sintered CBN; cermet tool, artificial diamond; nitride tool
	Wear-resistant materials (Al_2O_3, ZrO_2)	Mechanical seal, ceramic liner, bearings, thread guide, pressure sensors
	Heat-resistant materials (SiC, Al_2O_3, Si_3N_4, others)	Ceramic engine, tubine blade, heat exchangers, welding burner nozzle, high-frequency combustion crucibles
Biological	Alumina ceramics implantation, hydroxyapatite bioglass	Artificial tooth root, bone, and joint
Nuclear	Nuclear fuels (UO_2, UO_2-PuO_2)	
	Cladding materials (C, SiC, B_4C)	
	Shielding materials (SiC, Al_2O_3, C, B_4C)	

Source: Ref. 1, with permission.

and sanitaryware, electrical insulation (e.g., electrical porcelain and steatite), glass containers, and glasses for building and transportation vehicles. The applications for which advanced ceramics have been developed or proposed are already very diverse, and this area is expected to continue to grow at a reasonable rate. Table 1.1 illustrates some of the applications for advanced ceramics [1].