



Ceramics Science and Technology

Volume 1: Structures

Edited by
Ralf Riedel and I-Wei Chen



WILEY-VCH Verlag GmbH & Co. KGaA

This page intentionally left blank

**Ceramics Science
and Technology**

*Edited by
Ralf Riedel and I-Wei Chen*

Further Reading

W. Krenkel (Ed.)

Ceramic Matrix Composites

Fiber Reinforced Ceramics and their Applications

2008

ISBN: 978-3-527-31361-3

M. Scheffler, P. Colombo (Eds.)

Cellular Ceramics

Structure, Manufacturing, Properties and Applications

2005

ISBN: 978-3-527-31320-4

Ceramics Science and Technology

Volume 1: Structures

Edited by
Ralf Riedel and I-Wei Chen



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. Ralf Riedel

TU Darmstadt
Institut für Materialwissenschaften
Petersenstr. 23
64287 Darmstadt
Germany

Prof. Dr. I-Wei Chen

University of Pennsylvania
School of Engineering
3231 Walnut Street
Philadelphia, PA 19104-6272
USA

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <<http://dnb.d-nb.de>>.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Thomson Digital, Noida, India

Printing Strauss GmbH, Mörlenbach

Bookbinding Litges & Dopf GmbH, Heppenheim

Cover Design Schulz Grafik-Design, Fußgönheim

Printed in the Federal Republic of Germany

Printed on acid-free paper

ISBN: 978-3-527-31155-2

Contents

Preface	<i>XIII</i>
Dedication	<i>XV</i>
List of Contributors	<i>XIX</i>

I	Introduction	<i>1</i>
1	Modern Trends in Advanced Ceramics	<i>3</i>
	<i>Ralf Riedel, Emanuel Ionescu, and I.-Wei Chen</i>	
1.1	Advanced Ceramics	<i>3</i>
1.2	Conventional Synthesis and Processing of Advanced Ceramics	<i>3</i>
1.2.1	Synthesis of Ceramic Powders	<i>3</i>
1.2.2	Forming	<i>6</i>
1.2.3	Sintering	<i>7</i>
1.2.4	Finishing	<i>10</i>
1.3	Molecular Routes for the Synthesis and Processing of Advanced Ceramics	<i>11</i>
1.3.1	The CVD Process	<i>13</i>
1.3.2	The Sol–Gel Process	<i>15</i>
1.3.3	Polymer-Derived Ceramics (PDCs)	<i>18</i>
1.4	Methods for Characterization of Advanced Ceramic Materials	<i>21</i>
1.5	Applications of Advanced Ceramics	<i>27</i>
1.6	Outlook	<i>33</i>
	References	<i>34</i>
II	Structure of Ceramic Materials: Atomic Level	<i>39</i>
2	Modeling Amorphous Ceramic Structures	<i>41</i>
	<i>Peter Kroll</i>	
2.1	Introduction	<i>41</i>
2.2	Computational Approach	<i>43</i>

2.2.1	Bond Switching	43
2.2.1.1	The WWW-Method	43
2.2.1.2	Generation of Alternating Network Structures	45
2.2.1.3	Non-Tetrahedral Connectivity and Representation with Graphs	46
2.2.2	Network Algorithm	46
2.2.2.1	Interatomic Potential for Geometrical Relaxations	46
2.2.2.2	Simulated Annealing for Topological Relaxations	49
2.2.2.3	Tricks of the Trade	49
2.2.3	Density Functional Calculations	51
2.3	Results	52
2.3.1	a-SiO ₂	52
2.3.2	a-Si ₃ N ₄	56
2.3.3	a-SiNO	59
2.3.4	a-SiCO	60
2.3.5	a-SiCN	61
2.4	Summary and Conclusions	67
	References	68
3	Structural Chemistry of Ceramics	71
	<i>Rainer Pöttgen, Hubert Huppertz, and Rolf-Dieter Hoffmann</i>	
3.1	Introduction	71
3.2	Crystal Chemistry of Binary Oxides	73
3.2.1	The Structures of BeO and MgO	73
3.2.2	B ₆ O and the Modifications of Al ₂ O ₃	74
3.2.3	Rutile, Anatase, and Brookite	75
3.2.4	CeO ₂ , ThO ₂ , UO ₂ , and the Modifications of ZrO ₂ and HfO ₂	78
3.3	Complex Oxide Structures	80
3.3.1	Oxides with Perovskite-Related Structures	80
3.3.2	The Spinel Structure	82
3.3.3	Garnets	83
3.3.4	The Oxides Al ₂ TiO ₅ and BaFe ₁₂ O ₁₉	83
3.3.5	Structural Principles of Silicates	86
3.3.5.1	Zeolites	89
3.3.6	Structural Principles of Borates	89
3.4	Nitrides and Related Materials	92
3.4.1	AlN and the Modifications of Boron Nitride	92
3.4.2	The Modifications of Si ₃ N ₄	93
3.4.3	Structural Principles of Nitridosilicates	95
3.4.4	Sinoite	97
	References	98
4	Diffusion in Ceramics	105
	<i>Günter Borchardt, Karsten Gömann, Martin Kilo, and Harald Schmidt</i>	
4.1	General Introduction	105
4.2	Simple Oxides	108

4.2.1	Introduction	108
4.2.2	AO ₂ Systems: Fluorite Oxide ZrO ₂	109
4.2.2.1	Oxygen Diffusion	109
4.2.2.2	Cation Diffusion	112
4.2.3	A ₂ O ₃ Systems: Al ₂ O ₃	119
4.2.3.1	Oxygen Diffusion	120
4.2.3.2	Cation Diffusion	122
4.2.4	AO Systems: ZnO	123
4.2.4.1	Oxygen Diffusion	124
4.2.4.2	Zinc Diffusion	124
4.3	Diffusion in Complex Oxides	125
4.3.1	Introduction	125
4.3.2	Cation Volume Diffusion	126
4.3.2.1	Introduction	126
4.3.2.2	Cation Diffusion in Titanate Perovskites	126
4.3.2.3	Cation Diffusion in LnMO ₃ Perovskites	132
4.3.3	Anion Volume Diffusion	136
4.3.3.1	Introduction	136
4.3.3.2	Oxygen Diffusion in Titanate Perovskites	137
4.3.3.3	Oxygen Vacancy and Tracer Diffusion in LnMO ₃ Perovskites	141
4.4	Diffusion in Non-Oxide Ceramics	149
4.4.1	Introduction	149
4.4.2	Diffusion in Carbides	150
4.4.2.1	Silicon Carbide	150
4.4.2.2	Transition Metal Carbides	154
4.4.2.3	Actinide Carbides	155
4.4.3	Diffusion in Nitrides	155
4.4.3.1	Silicon Nitride	155
4.4.3.2	Transition Metal Nitrides	157
4.4.3.3	Actinide Nitrides	160
4.4.3.4	Silicon Carbonitrides	160
4.4.4	Hydrogen Diffusion in Si-Based Ceramics	163
4.4.5	Diffusion in Borides	165
	References	167

5 Structures of Ceramic Materials: Thermodynamics and Constitution 183

Matsvei Zinkevich and Fritz Aldinger

5.1	Introduction	183
5.2	Experimental Phase Studies	184
5.2.1	Determination of Phase Diagrams	184
5.2.2	Determination of Thermochemical Data	185
5.3	Methods of Computational Thermodynamics	187
5.3.1	Stoichiometric Phases	188
5.3.2	Solution Phases	189

5.3.3	The Compound Energy Formalism (CEF)	190
5.4	Case Studies	191
5.4.1	Thermodynamic Modeling of the Cerium–Oxygen System	191
5.4.2	Study of La_2O_3 – Ga_2O_3 System by Experiment and Thermodynamic Calculations	197
5.4.3	Modeling of Spinel Phases	202
5.4.4	Phase Equilibria in Ceramic Thermal Barrier Coatings	207
5.4.5	Phase Modeling in Si_3N_4 - and SiAlON-Based Ceramics	214
5.4.6	Phase Equilibria in the Si–B–C–N System	217
	References	226

III Structures of Ceramic Materials: Microstructural Level 231

6 Microstructural Design of Ceramics: Theory and Experiment 233

Gayle S. Painter and Paul F. Becher

6.1	Overview	233
6.2	An Introduction to Ceramics	236
6.3	Determinants of Ceramic Microstructure	241
6.3.1	Summary of Methods That Control Microstructure	243
6.3.1.1	Approaches to Tailor Ceramic Microstructure	243
6.4	Factors in Microstructural Design	244
6.4.1	Grain Size	245
6.4.2	Grain Reinforcement	245
6.4.3	Free Surface Phenomena	246
6.5	Amorphous Phases in Ceramics	246
6.5.1	Interfaces: Intergranular Films and Glassy Pockets	247
6.6	Silicon Nitride Ceramics: A Model System	250
6.6.1	Chemistry of Intergranular Films and Glasses	250
6.6.2	Adsorption Behavior of Rare Earth Additions	254
6.7	Theory and Modeling of Ceramics	258
6.7.1	Background	259
6.7.2	Continuum Modeling	260
6.7.3	Finite Element Modeling	261
6.7.4	Phase Field Method	262
6.7.5	Molecular Dynamics	265
6.7.6	Monte Carlo Methodology	268
6.7.7	First-Principles Density Functional Methods	268
6.7.8	Multiscale Methodologies	271
6.7.9	Comments on Methodology	277
6.8	A Case Study in Theory and Modeling: Intergranular Films in Silicon Nitride	278
6.9	Outlook	282
	References	285

7	Mesoscopic Ceramic Structures in One, Two, and Three Dimensions	297
	<i>Jörg J. Schneider and Jörg Engstler</i>	
7.1	Ceramics at the Mesoscale	297
7.1.1	The Scope of the Chapter	297
7.1.2	Introduction	297
7.2	Synthetic Routes to Mesoscaled Ceramic Structures	299
7.2.1	Electrochemical Approaches	299
7.2.2	Electrospinning	300
7.2.3	Electrophoretic Deposition	301
7.2.4	Sol-Gel Techniques	302
7.2.5	Fluidic Templating Techniques	303
7.2.6	Gas-Phase Techniques	306
7.3	One-Dimensional (1-D) Ceramic Structures	308
7.3.1	Ceramic Structures via Electrochemical Approaches	308
7.3.1.1	Tubes, Wires, and Rods	308
7.3.2	Ceramic Structures from Condensed Phase	310
7.3.2.1	Tubes, Wires, and Rods	311
7.3.3	Miscellaneous One-Dimensional Ceramics	318
7.4	Two-Dimensional (2-D) Ceramic Structures	328
7.4.1	Porous Ceramic Films from Condensed Phase (other than SiO ₂)	323
7.4.1.1	Templating Techniques for Non-Siliceous Ceramics	323
7.4.1.2	Templating Techniques using Monodisperse Spheres	328
7.4.2	Porous Ceramic Films via Electrochemical Approaches	329
7.5	Three-Dimensional (3-D) Ceramic Structures	332
7.5.1	Electrochemical and Condensed-Phase Routes to 3-D Ceramics	333
	References	338
8	Bulk Ceramic Nanostructures	347
	<i>Pavol Šajgalík, Ján Dusza, Zoltán Lenčák, Miroslav Hnatko, Dušan Galusek, and Katarína Ghillányová</i>	
8.1	Introduction	347
8.2	Materials and Related Nanocomposites	349
8.3	Formation of Nanoinclusions	352
8.3.1	Development of Nano/Microstructures	352
8.3.2	Interface Chemistry	353
8.3.3	SiC/Al ₂ O ₃ Nano/microcomposites	355
8.3.3.1	Solid-State Sintering of Crystalline Al ₂ O ₃ with Submicrometer Crystalline SiC	357
8.3.3.2	Sintering of Crystalline Al ₂ O ₃ with Addition of SiO ₂ + C	357
8.3.3.3	Liquid-Phase Sintering of Crystalline Al ₂ O ₃ with Submicrometer Crystalline SiC	358
8.3.3.4	Sintering of Crystalline Al ₂ O ₃ with Addition of Polycarbosilanes	358
8.3.4	SiC/Si ₃ N ₄ Nano/Microcomposites	360
8.3.4.1	Sintering of Amorphous SiCN Starting Powder	360

8.3.4.2	Sintering of Crystalline Si_3N_4 with Addition of Amorphous SiCN Powder [71–73]	360
8.3.4.3	Sintering of Crystalline Si_3N_4 with Addition of $\text{SiO}_2 + \text{C}$	360
8.3.4.4	SiC/ Si_3N_4 Nano/nanocomposite	361
8.4	Materials Preparation	361
8.4.1	Two-Step Sintering	361
8.4.2	Field-Activated Sintering (FAS), Spark Plasma Sintering (SPS), and Pulse Electric Current Sintering	362
8.4.3	<i>In-Situ</i> Reaction During the Densification Step	363
8.5	Properties of Ceramic Nanocomposites	364
8.5.1	Room Temperature Strengthening and Toughening	364
8.5.2	Hardness	365
8.5.3	Wear Resistance	366
8.6	High-Temperature Properties	366
8.6.1	Creep Resistance	366
8.6.1.1	SiC/ Si_3N_4 Nano/microcomposites	366
8.6.1.2	SiC/ Si_3N_4 Nano/nanocomposites	367
8.6.2	Thermal Shock Resistance of Ceramic Nanocomposites	368
8.7	Electrical Properties	369
	References	370
9	Glass Ceramics: Silica- and Alumina-Based	375
	<i>Christian Rüssel</i>	
9.1	Introduction	375
9.2	Theory of Nucleation and Crystal Growth	377
9.3	Glass Ceramics with Low Thermal Expansion Coefficients	381
9.4	Glass Ceramics for Mechanical Applications	383
9.4.1	Glass Ceramics with High Strength and High Hardness	384
9.4.2	Machinable Glass Ceramics	386
9.5	Bioglass Ceramics	388
9.5.1	Biocompatibility and Bioactivity	388
9.5.2	Biocompatible Glass Ceramics	389
9.5.3	Bioactive Glass Ceramics	391
9.6	Oriented Glass Ceramics	392
9.6.1	Routes to Oriented Glass Ceramics	392
9.6.2	Preparation by Thermodynamic Control	393
9.6.3	Preparation by Kinetic Control	393
9.6.4	Preparation by Shear Stress	396
9.7	Nano Glass Ceramics	400
	References	401
10	Cellular Structures	407
	<i>Paolo Colombo and Enrico Bernardo</i>	
10.1	Introduction	407
10.2	Structure	408

10.3	Properties	410
10.3.1	Mechanical Properties	410
10.3.2	Thermal Properties	420
10.3.3	Electrical Properties	424
10.3.4	Acoustic Properties	427
10.3.5	Permeability	428
10.4	Fabrication Methods	432
10.5	Applications	436
10.6	Summary	438
	References	439
11	Ceramic Thin Films	443
	<i>Theodor Schneller, Subhasish B. Majumder, and Rainer Waser</i>	
11.1	Introduction	443
11.2	Fundamentals of the Chemical Solution Deposition Process	444
11.2.1	The Chemical Solution Route	444
11.2.1.1	Alkoxides	446
11.2.1.2	Carboxylates	447
11.2.1.3	β -Diketonates	448
11.2.1.4	Heteroleptic Precursors	448
11.2.2	Thin/Thick Film Synthesis	449
11.2.2.1	Sol–Gel Processes	449
11.2.2.2	Metallo–Organic Decomposition Routes	452
11.2.2.3	Hybrid Approaches	453
11.2.2.4	Diol and Suspension Processes	456
11.2.2.5	Nitrate, Citrate, and Pechini Routes	456
11.2.2.6	Mesoscopic Thin Film Synthesis Using a Microemulsion-Mediated Technique	457
11.2.3	Phase Formation and Film Densification	459
11.2.3.1	Thermal Processing	460
11.2.3.2	General Thermodynamic Aspects	464
11.3	Structure–Property Relationships	467
11.3.1	Microstructure and Texture Control	469
11.3.2	Three-Dimensional Nanostructures	473
11.4	The Application of CSD-Derived Ceramic Films	480
11.4.1	Integrated or Embedded Capacitors	481
11.4.2	Coated Conductors	482
11.4.3	Microwave Dielectric Thin Films	483
11.4.3.1	Low-Frequency Dielectric Properties	483
11.4.3.2	Phase-Shifter Characteristics at Microwave Frequencies	485
11.4.3.3	Uniform and Graded Doped Mn:BST 50/50 Films	486
11.4.4	Thin Film Electrodes for Li Ion Rechargeable Batteries	488
11.4.4.1	Positive Electrode Materials	488
11.4.4.2	Kinetic Analysis for Li ⁺ Intercalation Behavior in Thin Film Electrodes: LiMn ₂ O ₄ Electrode as a Case Study	489

11.4.5	Multiferroic Thin Films	493
11.4.6	Piezoelectric Films for MEMS	496
11.5	Conclusions	498
	References	499
12	Multiphase Fiber Composites	511
	<i>Dietmar Koch, Ralf Knoche, and Georg Grathwohl</i>	
12.1	Introductory Remarks	511
12.2	Fibers for Ceramic Composites	512
12.2.1	General Features and Basic Considerations	512
12.2.2	Oxide Fibers	514
12.2.3	Si-Based Non-Oxide Fibers	516
12.2.4	Carbon Fibers	520
12.3	Processes to Fabricate Ceramic Fiber Composites	523
12.3.1	Fiber Preforms	523
12.3.2	Fiber Integration in the Matrix	527
12.3.2.1	Liquid Polymer Infiltration (LPI)	528
12.3.2.2	Liquid Silicon Infiltration (LSI)	529
12.3.2.3	Chemical Vapor Infiltration (CVI)	532
12.3.2.4	Further Integration Techniques	536
12.3.3	Concluding Remarks	538
12.4	Non-Brittle Composites and Associated Mechanisms	538
12.4.1	Weak Interface Composites (WIC)	539
12.4.2	Weak Matrix Composites (WMC)	545
12.5	Properties of Ceramic Fiber Composites	548
12.5.1	Stiffness, Strength, and Toughness	548
12.5.2	High-Temperature and Long-Term Properties	555
12.5.3	Fatigue	562
12.6	Applications of Ceramic Fiber Composites	564
12.6.1	Space-Related Applications	564
12.6.2	Energy-Related Applications	567
12.6.3	Friction-Related Applications	570
12.6.3.1	Bearings	570
12.6.3.2	Brakes and Clutches	570
12.6.4	Ballistic Armor Applications	572
12.6.5	Other Applications	574
	References	574
	Index	583

Preface

Besides metals and polymers, advanced ceramics are one of the most promising classes of materials for the key technologies of the 21st century. Recent developments in the field of ceramics include a selection of synthesis, processing and sintering techniques applied for the production of novel structural and functional ceramics and ceramic composites. Significant progress has been made in the past two decades with respect to the production of novel multifunctional ceramics with a tailor made micro- and/or nanoscale structure reflecting the increasing technological importance of advanced ceramic materials.

The 4-volume series of *Ceramics Science & Technology* covers various aspects of modern trends in advanced ceramics reflecting the status quo of the latest achievements in ceramics science and development. The contributions highlight the increasing technological significance of advanced ceramic materials and present concepts for their production and application. Volume 1 deals with structural properties of ceramics by considering a broad spectrum of length scale, starting from the atomic level by discussing amorphous and crystalline solid state structural features, and continuing with the microstructural level by commenting on microstructural design, mesoscopic and nano structures, glass ceramics, cellular structures, thin films and multiphase (composite) structures. Volume 2 will focus on (i) the distinct ceramic materials classes, namely oxides, carbides and nitrides and (ii) physical and mechanical properties of advanced ceramics. The series will be continued by Volume 3 with chapters related to modern synthesis and processing techniques used for the production of engineering ceramics and will be completed by Volume 4 which will be devoted to application.

Quo vadis ceramics? The 4-volume series also intends to provide comprehensive information relevant to the future direction of advanced or engineering ceramics. The present book series evidences technologically important trends related to the further development of this fascinating class of materials. Latest examples of technological achievements already commercialized include piezoelectric ceramics based on PZT ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) used e.g. for common rail diesel engines, Si_3N_4 -based ball bearings and glow plugs for diesel engines, carbon fiber reinforced silicon carbide (C/SiC) brake, luminescent ceramics based on sialon derivatives for LED applications, GaN-based ceramics for optoelectronics, and many others.

Furthermore, a variety of application fields are emerging in which novel ceramics are required and are expected to be established and commercialized in the near future. This technologically driven process requires a long-term alignment and a strong basis in continued fundamental research in ceramics science and technology. The 4-volume series would like to contribute to this development by providing the latest knowledge in ceramics science suitable for students specializing in ceramics as well as for university and industrial research.

We wish to thank all contributing authors for their great enthusiasm in compiling excellent manuscripts in their respective area of expertise. We also acknowledge the support of Karen Böhling who proofread each manuscript with due accuracy and patience. Last not least we thank the Wiley-VCH editors, Martin Ottmar and Rainer Münz, for their continuous encouragement to work on the book project.

Darmstadt and Philadelphia
December 2007

Ralf Riedel
I-Wei Chen

Dedication

Volume 1 of the Ceramic Science & Technology series is dedicated to Prof. Sir Richard Brook

It gives me great pleasure to dedicate *Ceramics Science and Technology Vol I* to Prof. Sir Richard Brook on the occasion of his 70th birthday.



Prof. Sir Richard Brook (source: Leverhulme Trust)

With respect to his remarkable lifework, this handbook covers many aspects of modern trends in advanced ceramics, a research interest passionately pursued by Prof. Brook.

Born in Leeds/UK on 12th March 1938, he has enjoyed a profound education in materials science and a long and distinguished research career in the field of engineering ceramics. After graduating in Ceramics at Leeds University in 1962, he continued his studies at the Massachusetts Institute of Technology in Boston, where he completed a thesis on “Nickel-ferrite thin films” and was conferred a ScD degree in 1966. Afterwards, as an Assistant Professor of Materials Science at the University of Southern California, he conducted research activities focusing on defect chemistry of oxides, the electrical properties of insulators and the kinetics of microstructure development in ceramics. In 1970 he returned to the UK to embark on more in-depth studies into the general processing of ceramics at the Atomic Energy Authority in Harwell. In his capacity as Head of the Department of Ceramics at Leeds University from 1974 he emerged as a leading figure in technological advances related to the fabrication of oxide and non-oxide ceramics. In recognition of his dedicated services to science, he received the award of Officer of the Order of the British Empire in 1988. In the same year he moved to Stuttgart after accepting an offer to become a Director of the Max-Planck-Institute for Metals Research, where he was conferred an Honorary Professorship at the University of Stuttgart. During the time he spent at the Max-Planck-Institute he gained further inspiration from distinguished scientists from all over the world. In 1991 he then went back to the UK initially joining Oxford University as Cookson Chair of Materials Science and subsequently taking on the role of Chief Executive of the Engineering and Physical Sciences Research Council. In 2001 he took up the Directorship of the Leverhulme Trust with the role of making awards for the support of research and education. His career then culminated in his receiving a knighthood in the same year for services to Science and Engineering. Particularly noteworthy is the great importance he attaches to the fact that his work in ceramics has its roots in the ancient tradition of pottery. This awareness has had an enduring influence on his ambition to systematically understand the sintering mechanisms as well as microstructure property relation associated with the processing of ceramics as a fundamental basis to develop novel structural and functional ceramics for both domestic and high-tech applications. In addition to his position at Leverhulme Trust he has enthusiastically worked as the main Editor for the *Journal of the European Ceramic Society* for many years. Under his editorship, the Journal emerged as one of the most important scientific ceramic journals.

I am glad that I had the chance to work with Prof. Sir Richard Brook and to share thoughts and scientific discussions with him during his time at the Powder Metallurgical Laboratory (PML) of the Max-Planck-Institute for Metals Research. In particular, our joint organization of the scientific workshop entitled “Powder-Free-Processing of Ceramics” held in 1990 at Schloß Ringberg in Germany was a fundamental step in the further development of the polymer-derived ceramics field I have been involved in.

On behalf of the co-editor, Prof. I-Wei Chen, I extend my best wishes and warmest greetings to Prof. Sir Richard Brook on his 70th birthday. As a prolific teacher and researcher, author of countless scientific papers, recipient of numerous prestigious awards and member of internationally acclaimed research societies and editorial boards, Prof. Sir Richard Brook has won great admiration from the materials science community while playing an influential and truly innovative role in technological advances in ceramics science and technology.

Ralf Riedel
Institut für Materialwissenschaft
Technische Universität Darmstadt
64832 Darmstadt
Germany

This page intentionally left blank

List of Contributors

Fritz Aldinger

Heraeus Sensor Technology
Reinhard-Heraeus-Ring 23
63801 Kleinostheim
Germany

Paul F. Becher

Materials Science and Technology
Division
Oak Ridge National Laboratory
Oak Ridge
Tennessee 37831-6114
USA

Enrico Bernardo

Università di Padova
Dipartimento di Ingegneria Meccanica –
Settore Materiali
Via Marzolo, 9
35131 Padova
Italy

Günter Borchardt

Tu Clausthal
Institut für Metallurgie
Robert-Koch-Strasse 42
38678 Clausthal-Zellerfeld
Germany

I.-Wei Chen

University of Pennsylvania
School of Engineering
3231 Walnut Street
Philadelphia, PA 19104-6272
USA

Paolo Colombo

Università di Padova
Dipartimento di Ingegneria Meccanica –
Settore Materiali
Via Marzolo, 9
35131 Padova
Italy
and
The Pennsylvania State University
Department of Materials Science and
Engineering
University Park
PA 16801
USA

Ján Dusza

Slovak Academy of Sciences
Institute of Materials Research
Košice
Slovakia

Jörg Engstler

Eduard-Zintl-Institute of Inorganic
and Physical Chemistry
Department of Chemistry
Petersenstrasse 18
64287 Darmstadt
Germany

Dušan Galusek

Slovak Academy of Sciences
Institute of Inorganic Chemistry
Dubravská cesta 9
SK-845 36 Bratislava 45
Slovakia

Katarína Ghillányová

Slovak Academy of Sciences
Institute of Inorganic Chemistry
Dubravská cesta 9
SK-845 36 Bratislava 45
Slovakia

Karsten Gömann

University of Tasmania
Central Science Laboratory
Private Bag 74
Hobart, TAS 7001
Australia

Georg Grathwohl

Universität Bremen
Keramische Werkstoffe und Bauteile
Am Biologischen Garten 2 IW 3
28359 Bremen
Germany

Miroslav Hnatko

Slovak Academy of Sciences
Institute of Inorganic Chemistry
Dubravská cesta 9
SK-845 36 Bratislava 45
Slovakia

Rolf-Dieter Hoffmann

Westfälische Wilhelms-Universität
Münster
Institut für Anorganische und
Analytische Chemie
Corrensstrasse 30
48149 Münster
Germany

Hubert Huppertz

Ludwig-Maximilians-Universität
München
Department Chemie und Biochemie
Butenandtstrasse 5–13 (Haus D)
81377 München
Germany

Emanuel Ionescu

TU Darmstadt
Institut für Materialwissenschaft
Petersenstrasse 23
64287 Darmstadt
Germany

M. Kilo

TU Clausthal
Institut für Metallurgie
Robert-Koch-Strasse 42
38678 Clausthal-Zellerfeld
Germany

Ralf Knoche

Universität Bremen
EADS Astrium GmbH
Hünefeldstr. 1-5
28199 Bremen
Germany

Dietmar Koch

Universität Bremen
Keramische Werkstoffe und Bauteile
Am Biologischen Garten 2 IW 3
28359 Bremen
Germany

Peter Kroll

University of Texas at Arlington
Department of Chemistry and
Biochemistry
700 Planetarium Pl.
Arlington, TX 76019-0065
USA

Zoltán Lenčák

Slovak Academy of Sciences
Institute of Inorganic Chemistry
Dubravská cesta 9
SK-845 36 Bratislava 45
Slovakia

Subhasish B. Majumder

Indian Institute of Technology
Materials Science Centre
Kharagpur 721 302
India

Gayle S. Painter

Materials Science and Technology
Division
Oak Ridge National Laboratory
Oak Ridge
Tennessee 37831-6114
USA

Rainer Pöttgen

Westfälische Wilhelms-Universität
Münster
Institut für Anorganische und
Analytische Chemie
Corrensstrasse 30
48149 Münster
Germany

Ralf Riedel

TU Darmstadt
Institut für Materialwissenschaft
Petersenstrasse 23
64287 Darmstadt
Germany

Christian Rüssel

Otto-Schott-Institut
Chemische Fakultät
der Friedrich-Schiller-Universität
Fraunhoferstr. 6
07743 Jena
Germany

Pavol Šajgalík

Slovak Academy of Sciences
Institute of Inorganic Chemistry
Dubravská cesta 9
SK-845 36 Bratislava 45
Slovakia

Harald Schmidt

TU Clausthal
Institut für Metallurgie
Robert-Koch-Str. 42
38678 Clausthal-Zellerfeld
Germany

Jörg J. Schneider

Eduard-Zintl-Institute of Inorganic
and Physical Chemistry
Department of Chemistry
Petersenstrasse 18
64287 Darmstadt
Germany

Theodor Schneller

RWTH Aachen
Institut für Werkstoffe der
Elektrotechnik II
Sommerfeldstr. 24
52074 Aachen
Germany

Rainer Waser

Institut für Werkstoffe der

Elektrotechnik II

RWTH Aachen

Sommerfeldstr. 24

52074 Aachen

Germany

and

Forschungszentrum Jülich

Institut für Festkörperforschung

52425 Jülich

Germany

Matsvei Zinkevich

Heraeus Sensor Technology

Reinhard-Heraeus-Ring 23

63801 Kleinostheim

Germany

I

Introduction

This page intentionally left blank

1

Modern Trends in Advanced Ceramics

Ralf Riedel, Emanuel Ionescu, and I.-Wei Chen

1.1

Advanced Ceramics

Ceramics are defined as inorganic, non-metallic materials which are typically crystalline in nature and contain metallic and non-metallic elements such as Al_2O_3 , CaO , ZrO_2 , SiC , and Si_3N_4 . There are several broad categories of ceramics classifying the industrial products as follows: clay products, white ware, refractories, glasses, cements, abrasives, and advanced ceramics.

Advanced ceramics are materials tailored to possess exceptional properties (superior mechanical properties, corrosion/oxidation resistance, thermal, electrical, optical or magnetic properties) by controlling their composition and internal structure. They are subdivided into *structural ceramics* (wear parts, cutting tools, engine components and bioceramics), *electrical ceramics* (capacitors, insulators, substrates, integrated circuit packages, piezoelectrics, magnets and superconductors), *ceramic coatings* (engine components, cutting tools and industrial wear parts) and *chemical processing* and *environmental ceramics* (filters, membranes, catalysts and catalyst supports).

As an example of advanced ceramics, silicon carbide (SiC) bearings for chemical plants are shown in Figure 1.1. This type of device must withstand aggressive chemical environments, show high compressive strength, high stiffness, low density, high fracture resistance, and remain stable under thermal stress.

1.2

Conventional Synthesis and Processing of Advanced Ceramics

1.2.1

Synthesis of Ceramic Powders

The preparation of ceramic products typically involves heating processes of ceramic powders which must undergo special handling in order to control purity, particle

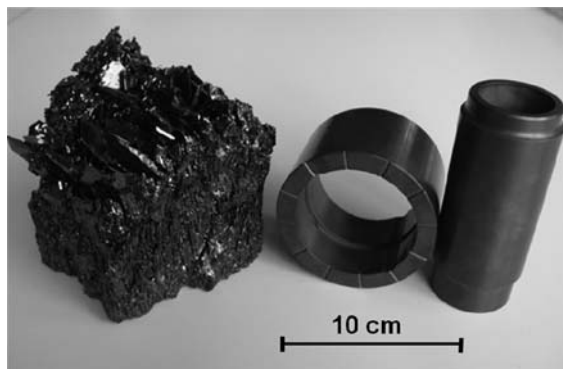


Figure 1.1 High-temperature and corrosion-resistant silicon carbide (SiC) advanced ceramic (right) produced from silicon carbide raw material (left) obtained by the reaction of silica with carbon at temperature $>2000^{\circ}\text{C}$, according to the Acheson process.

size, particle size distribution, and heterogeneity. These factors play an important role in the properties of the finished ceramic part. In principle, it is possible to distinguish finished ceramics made of naturally harvested materials from fully synthetically prepared starting materials. While most of the binary oxide ceramics such as alumina or silica can be processed from natural sources, non-oxide ceramics and more complex oxides such as high-temperature superconductors must be obtained by complex synthetic routes. Both the natural products and the synthetic materials must be controlled in terms of their chemical compositions and homogeneity, specific shape, particle size, and particle size distribution (Figure 1.2).

There are several synthetic methods for the preparation of ceramic powders. *Solid-state reactions* are the most widely used processes as they are suitable for the

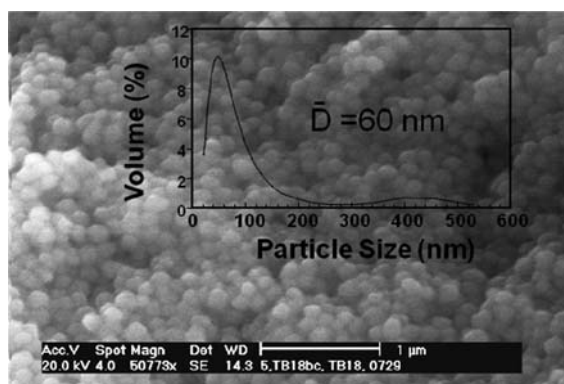


Figure 1.2 SEM image of a sol-gel-derived silicon carbide/nitride-based composite powder. The particle size distribution of the powder is shown in the inset.

mass-production of cost-efficient powders. Highly pure ultrafine powders are synthesized via *gas-phase reactions*. *Liquid-phase synthesis* for producing homogeneous fine ceramic powders involves the co-precipitation method and a hydrothermal synthesis. In most synthesis routes, temperature is the main reaction-controlling parameter. In recent approaches related to the search for new synthetic compounds, pressure has been used in addition to temperature for the synthesis of novel nitrides such as γ - Si_3N_4 or cubic Hf_3N_4 and Zr_3N_4 . Laser-heated diamond anvil cell and multi anvil techniques have been successfully applied for basic high-pressure ceramic synthesis studies (Figures 1.3 and 1.4) [1,2].

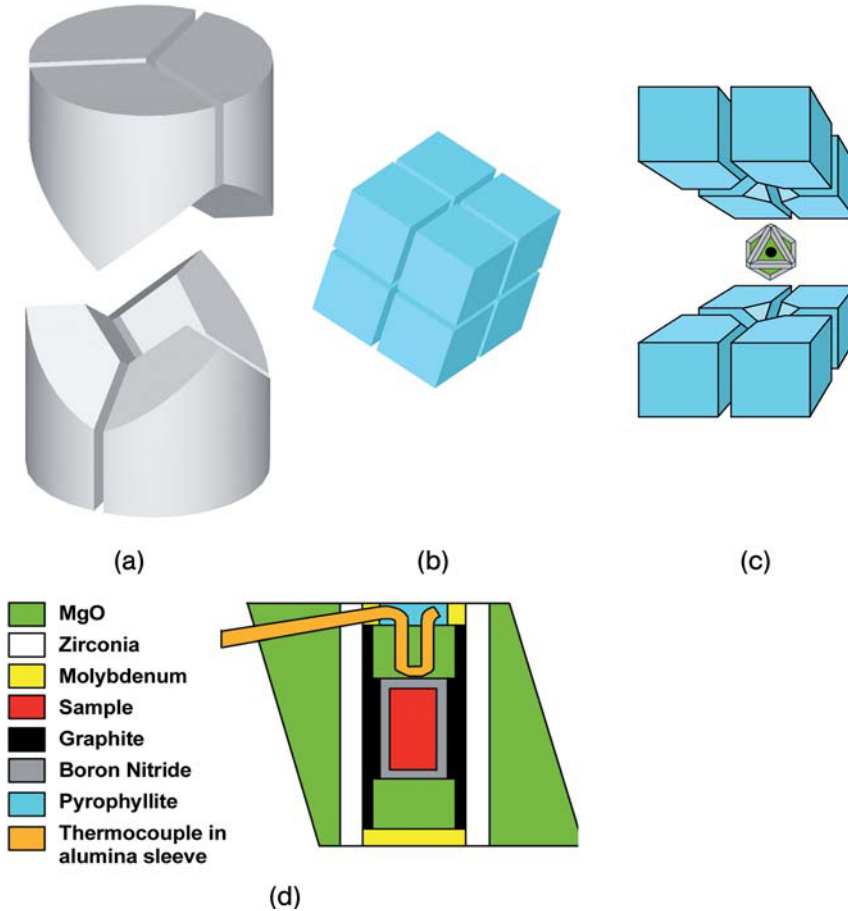


Figure 1.3 Schematic drawing of a multi anvil (MA) apparatus for high-pressure/high-temperature materials synthesis. (a) Walker-type module. (b) Eight tungsten carbide cubic anvils. (c) Schematics of compression of the octahedral pressure cell between eight truncated tungsten carbide anvils. (d) Cross-section of the octahedral pressure cell. The MA cell can be operated up to 25 GPa pressure and up to 2400 °C.

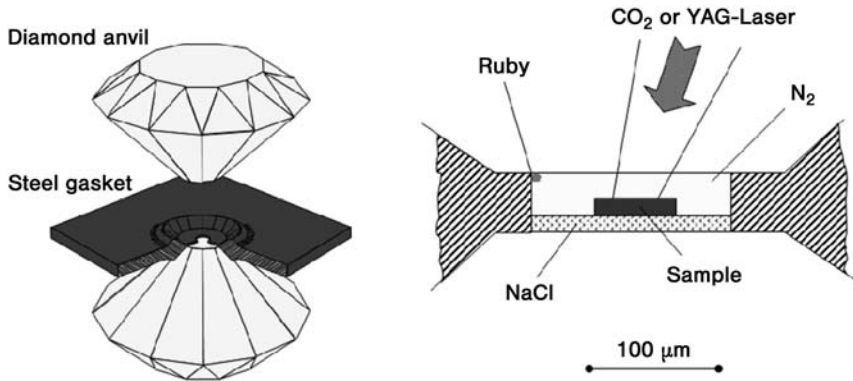


Figure 1.4 Schematic drawing of a laser-heated diamond anvil cell (LH-DAC) for the high-pressure and high-temperature materials synthesis (left). The inset on the right shows the sample holder device. The LH-DAC can be operated at pressures up to 100 GPa and 7000 °C. For further details, see Refs. [1,2].

1.2.2

Forming

Forming processes involve a mix, slip, or plastic material which is formed into a shape. It is generally desirable to have high green densities, as this factor acts against the firing shrinkage. This leads also to reduced rejects and lower firing temperatures.

There are several forming processes for advanced ceramics. Some of these are classified as traditional, namely die pressing or cold isostatic pressing (CIP). Slip casting and extrusion, tape casting and injection-molding processes are classified as wet and high-tech forming processes.

Die pressing is by far the most frequently used forming process for advanced ceramics, and involves the uniaxial compaction of a granulated powder during confined compression in a die. The pressed green bodies can be then fired directly or after isostatic pressing.

Isostatic pressing involves the shaping of granular powders in a flexible, air-tight container placed in a closed vessel filled with pressurized liquid. This method assures a uniform compaction of the powders into a green body that retains the general shape of the flexible container and any internal tooling profile.

Slip casting of ceramics is a technique that has long been used for manufacturing traditional ceramics. The advantages of slip casting include its ability to form green bodies of a complex shape, without expensive tooling. The bodies produced are almost invariably thin-walled with a uniform thickness. It is an inexpensive process when compared with other ceramic manufacturing techniques. A slip is prepared by ball-milling the appropriate powders along with binders, plasticizers, deflocculants, etc., in a solvent or water. In order to reproduce the castings, it is essential that the