HANDBOOK OF REFRACTORY CARBIDES AND NITRIDES

Properties, Characteristics, Processing and Applications

by

Hugh O. Pierson

Consultant and Sandia National Laboratories (retired)
Albuquerque, New Mexico

np NOYES PUBLICATIONS
Westwood, New Jersey, U.S.A.

 INNOSCIENCE EXHIBIT 1036

Copyright © 1996 by Noyes Publications
No part of this book may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission in writing from the Publisher.
Library of Congress Catalog Card Number: 96-12578
ISBN: 0-8155-1392-5
Printed in the United States

Published in the United States of America by
Noyes Publications
369 Fairview Avenue, Westwood, New Jersey 07675

10 9 8 7 6 5 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Pierson, Hugh O.
Handbook of refractory carbides and nitrides : properties, characteristics, processing, and applications / by Hugh O. Pierson.
p. cm.
Includes bibliographical references and index.
ISBN 0-8155-1392-5
1. Refractory transition metal compounds--Metallography.
2. Carbides. 3. Nitrides I. Title
TN693.T7P54 1996
666'.72--dc20 96-12578
CIP

MATERIALS SCIENCE AND PROCESS TECHNOLOGY SERIES

Editors

Rointan F. Bunshah, University of California, Los Angeles *(Series Editor)*
Gary E. McGuire, Microelectronics Center of North Carolina *(Series Editor)*
Stephen M. Rossnagel, IBM Thomas J. Watson Research Center
(Consulting Editor)

Electronic Materials and Process Technology

HANDBOOK OF DEPOSITION TECHNOLOGIES FOR FILMS AND COATINGS, Second Edition: edited by Rointan F. Bunshah

CHEMICAL VAPOR DEPOSITION FOR MICROELECTRONICS: by Arthur Sherman

SEMICONDUCTOR MATERIALS AND PROCESS TECHNOLOGY HANDBOOK: edited by Gary E. McGuire

HYBRID MICROCIRCUIT TECHNOLOGY HANDBOOK: by James J. Licari and Leonard R. Enlow

HANDBOOK OF THIN FILM DEPOSITION PROCESSES AND TECHNIQUES: edited by Klaus K. Schuegraf

IONIZED-CLUSTER BEAM DEPOSITION AND EPITAXY: by Toshinori Takagi

DIFFUSION PHENOMENA IN THIN FILMS AND MICROELECTRONIC MATERIALS: edited by Devendra Gupta and Paul S. Ho

HANDBOOK OF CONTAMINATION CONTROL IN MICROELECTRONICS: edited by Donald L. Tolliver

HANDBOOK OF ION BEAM PROCESSING TECHNOLOGY: edited by Jerome J. Cuomo, Stephen M. Rossnagel, and Harold R. Kaufman

CHARACTERIZATION OF SEMICONDUCTOR MATERIALS, Volume 1: edited by Gary E. McGuire

HANDBOOK OF PLASMA PROCESSING TECHNOLOGY: edited by Stephen M. Rossnagel, Jerome J. Cuomo, and William D. Westwood

HANDBOOK OF SEMICONDUCTOR SILICON TECHNOLOGY: edited by William C. O'Mara, Robert B. Herring, and Lee P. Hunt

HANDBOOK OF POLYMER COATINGS FOR ELECTRONICS, 2nd Edition: by James Licari and Laura A. Hughes

HANDBOOK OF SPUTTER DEPOSITION TECHNOLOGY: by Kiyotaka Wasa and Shigeru Hayakawa

HANDBOOK OF VLSI MICROLITHOGRAPHY: edited by William B. Glendinning and John N. Helbert

CHEMISTRY OF SUPERCONDUCTOR MATERIALS: edited by Terrell A. Vanderah

CHEMICAL VAPOR DEPOSITION OF TUNGSTEN AND TUNGSTEN SILICIDES: by John E. J. Schmitz

ELECTROCHEMISTRY OF SEMICONDUCTORS AND ELECTRONICS: edited by John McHardy and Frank Ludwig

HANDBOOK OF CHEMICAL VAPOR DEPOSITION: by Hugh O. Pierson

DIAMOND FILMS AND COATINGS: edited by Robert F. Davis

ELECTRODEPOSITION: by Jack W. Dini

HANDBOOK OF SEMICONDUCTOR WAFER CLEANING TECHNOLOGY: edited by Werner Kern

CONTACTS TO SEMICONDUCTORS: edited by Leonard J. Brillson

HANDBOOK OF MULTILEVEL METALLIZATION FOR INTEGRATED CIRCUITS: edited by Syd R. Wilson, Clarence J. Tracy, and John L. Freeman, Jr.

HANDBOOK OF CARBON, GRAPHITE, DIAMONDS AND FULLERENES: by Hugh O. Pierson

MOLECULAR BEAM EPITAXY: edited by Robin F. C. Farrow

HANDBOOK OF COMPOUND SEMICONDUCTORS: edited by Paul H. Holloway and Gary E. McGuire

HANDBOOK OF VACUUM ARC SCIENCE AND TECHNOLOGY: edited by Raymond L. Boxman, Philip J. Martin, and David M. Sanders

HIGH DENSITY PLASMA SOURCES: edited by Oleg A. Popov

DIAMOND CHEMICAL VAPOR DEPOSITION: by Huimin Liu and David S. Dandy

HANDBOOK OF MAGNETO-OPTICAL DATA RECORDING: edited by Terry McDaniel and Randall H. Victora

HANDBOOK OF REFRACTORY CARBIDES AND NITRIDES: by Hugh O. Pierson

ULTRA-FINE PARTICLES: edited by Chikara Hayashi, R. Ueda and A. Tasaki

Ceramic and Other Materials—Processing and Technology

SOL-GEL TECHNOLOGY FOR THIN FILMS, FIBERS, PREFORMS, ELECTRONICS AND SPECIALTY SHAPES: edited by Lisa C. Klein

FIBER REINFORCED CERAMIC COMPOSITES: edited by K. S. Mazdiyasni

ADVANCED CERAMIC PROCESSING AND TECHNOLOGY, Volume 1: edited by Jon G. P. Binner

FRICTION AND WEAR TRANSITIONS OF MATERIALS: by Peter J. Blau

SHOCK WAVES FOR INDUSTRIAL APPLICATIONS: edited by Lawrence E. Murr

SPECIAL MELTING AND PROCESSING TECHNOLOGIES: edited by G. K. Bhat

CORROSION OF GLASS, CERAMICS AND CERAMIC SUPERCONDUCTORS: edited by David E. Clark and Bruce K. Zoitos

HANDBOOK OF INDUSTRIAL REFRACTORIES TECHNOLOGY: by Stephen C. Carniglia and Gordon L. Barna

CERAMIC FILMS AND COATINGS: edited by John B. Wachtman and Richard A. Haber

CERAMIC CUTTING TOOLS: edited by E. Dow Whitney

Related Titles

CODE COMPLIANCE FOR ADVANCED TECHNOLOGY FACILITIES: by William R. Acorn

SEMICONDUCTOR INDUSTRIAL HYGIENE HANDBOOK: by Michael E. Williams and David G. Baldwin

Preface

The purpose of the *Handbook of Refractory Carbides and Nitrides* is to present in one volume a clear, objective and systematic assessment of the science and technology of these useful refractory materials. The technology and the applications have expanded greatly in the last three decades, stimulated by many major developments such as monolithic silicon nitride for gas turbine applications, coatings of titanium carbide and titanium nitride for cutting tools, silicon carbide fibers, silicon carbide semiconductor and optoelectronic devices, titanium nitride diffusion barriers, and many others.

With several of my colleagues, I felt the need for a systematic and objective review of these remarkable materials, one which would cover the scientific, engineering and applications viewpoints, coordinate the various trends, and promote interaction among researchers and users alike. This book should be useful to scientists, engineers, technicians, as well as production and marketing managers.

For many years, I headed the Chemical Vapor Deposition Group at Sandia National Laboratories, and then became a consultant to numerous organizations in the research and development of advanced materials. I had the opportunity to review and study the many aspects of refractory carbides and nitrides, including their chemistry, processing, equipment and applications, and thus obtain the necessary background for the preparation of this book.

I am particularly indebted to two old friends, Arthur Mullendore, retired from Sandia National Laboratories, and Jack Stiglich, formerly of Ultramet, for their ideas and comments and their thorough review of the manuscript. My many thanks also go to another old friend, George Narita, Executive Editor of Noyes Publications, for his help and patience in the preparation of this book.

Sandia Park, NM
June 1996

Hugh O. Pierson

NOTICE

To the best of our knowledge the information in this publication is accurate; however the Publisher does not assume any responsibility or liability for the accuracy or completeness of, or consequences arising from, such information. This book is intended for informational purposes only. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Publisher. Final determination of the suitability of any information or product for use contemplated by any user, and the manner of that use, is the sole responsibility of the user. We recommend that anyone intending to rely on any recommendation of materials or procedures mentioned in this publication should satisfy himself as to such suitability, and that he can meet all applicable safety and health standards.

Contents

1 Introduction 1

1.0 HISTORICAL PERSPECTIVE AND PRESENT STATUS OF REFRACTORY CARBIDES AND NITRIDES 1
2.0 CARBIDES AND NITRIDES AS REFRACTORY MATERIALS 2
3.0 BOOK OBJECTIVES 3
4.0 BOOK ORGANIZATION 4
5.0 GLOSSARY AND METRIC CONVERSION GUIDE 5
6.0 BACKGROUND READING 5
6.1 General References 5
6.2 Periodicals 6
6.3 Conferences 7

2 The Refractory Carbides 8

1.0 INTRODUCTION 8
2.0 DEFINITION AND CLASSIFICATION OF CARBIDES 8
2.1 Classification 9
2.2 Refractory Qualifications 9
2.3 Factors Controlling Carbide Formation 9
3.0 CARBIDE FORMATION AND ELECTRONEGATIVITY 9
3.1 Definition of Electronegativity 9
3.2 Comparison of Electronegativity 10

4.0 CARBIDE FORMATION AND ATOM SIZE 11
4.1 Atomic Radius 11
4.2 Carbide Formation and Ratio of Atomic Radii 12
5.0 THE ATOMIC BONDING OF CARBIDES 12
5.1 Ionic Bond 12
5.2 Covalent Bond 13
5.3 Metallic Bond 14
6.0 GENERAL CHARACTERISTICS OF CARBIDES 14
6.1 Interstitial Carbides 14
6.2 Covalent Carbides 14
6.3 Intermediate Carbides 15
6.4 Salt-Like Carbides 15
REFERENCES 16

3 Interstitial Carbides, Structure and Composition ... 17

1.0 DEFINITION AND GENERAL CHARACTERISTICS OF INTERSTITIAL CARBIDES 17
1.1 Definition 17
1.2 General Characteristics 18
2.0 ELECTRONIC STRUCTURE OF CARBON 18
2.1 Nucleus and Electronic Configuration of the Carbon Atom ... 19
2.2 Hybridization of the Carbon Atom 22
2.3 The sp^3 Bond 24
3.0 THE EARLY TRANSITION METALS 25
3.1 Definition of Transition Elements 25
3.2 Electronic Configuration of Early Transition Metals 26
4.0 CRYSTAL STRUCTURES 27
4.1 Close-Packed Crystalline Structures 27
4.2 Hexagonal Close-Packed (hcp) and Face-Centered Cubic Close-Packed (fcc) Structures 28
4.3 Body-Centered Cubic (bcc) and Simple Hexagonal Structures 31
4.4 Crystal Structures of Early Transition Metals 31
5.0 ATOMIC STRUCTURE OF INTERSTITIAL CARBIDES ... 34
5.1 Definition of Interstitial Structures 34
5.2 Atomic-Radii Ratio 34
5.3 Interstitial Sites 34
5.4 The Chromium Carbide Exception 36
6.0 CRYSTALLINE STRUCTURE AND COMPOSITION OF INTERSTITIAL CARBIDES 36
6.1 Crystalline Structure 36
6.2 Composition and Structure 37

6.3 Metal-to-Carbide Structural Switching 39
6.4 Density Considerations 40
7.0 ATOMIC BONDING OF INTERSTITIAL CARBIDES 41
7.1 Complexity of Bonding System 41
7.2 Overall Bonding Scheme 42
7.3 Thermal Properties Considerations 42
7.4 Ionic Bonding and Electronegativity 46
7.5 Covalent Bonding in Interstitial Monocarbides 46
7.6 Bonding and Atomic Spacing 47
7.7 Metallic Bonding 48
7.8 Band Structure 48
8.0 INTERSTITIAL CARBIDES AS DEFECT STRUCTURES . 48
8.1 Vacancies 48
8.2 Ordering of the Carbon Atoms 50
9.0 GENERAL REVIEW OF THE PROPERTIES OF INTERSTITIAL CARBIDES 51
9.1 Variations in Properties and Composition 51
9.2 General Characteristics 51
REFERENCES 52

4 Carbides of Group IV: Titanium, Zirconium, and Hafnium Carbides 55

1.0 GENERAL CHARACTERISTICS OF GROUP IV CARBIDES 55
2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP IV CARBIDES 56
2.1 Density and Melting Point 56
2.2 Thermal Properties 57
2.3 Thermodynamic Functions 58
2.4 Thermal Conductivity 58
2.5 Thermal Expansion 61
3.0 ELECTRICAL PROPERTIES OF GROUP IV CARBIDES .. 62
3.1 Electrical Conductivity 62
3.2 Hall Effect 64
4.0 MECHANICAL PROPERTIES OF GROUP IV CARBIDES 64
4.1 Property Variables 64
4.2 Summary of Mechanical Properties 65
4.3 Failure Mechanism 65
4.4 Ductile-Brittle Transition 66
4.5 Hardness 66
4.6 Transverse Rupture Strength 66

5.0 CHEMICAL PROPERTIES OF GROUP IV CARBIDES 68
5.1 Mutual Solubilities 68
5.2 Chemical Properties 68
6.0 CHARACTERISTICS AND PROPERTIES OF TITANIUM CARBIDE 68
6.1 Summary of Properties 68
6.2 Phase Diagram 72
6.3 Summary of Fabrication Processes 72
6.4 Summary of Applications and Industrial Importance 72
7.0 CHARACTERISTICS AND PROPERTIES OF ZIRCONIUM CARBIDE 73
7.1 Summary of Properties 73
7.2 Phase Diagram 74
7.3 Summary of Fabrication Processes 74
7.4 Summary of Applications and Industrial Importance 74
8.0 CHARACTERISTICS AND PROPERTIES OF HAFNIUM CARBIDE 76
8.1 Summary of Properties 76
8.2 Phase Diagram 77
8.3 Summary of Fabrication Processes 78
8.4 Summary of Applications and Industrial Importance 78
REFERENCES 78

5 Carbides of Group V: Vanadium, Niobium and Tantalum Carbides 81

1.0 GENERAL CHARACTERISTICS OF GROUP V CARBIDES 81
2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP V CARBIDES 82
2.1 Density and Melting Point 82
2.2 Thermal Properties 83
3.0 ELECTRICAL PROPERTIES OF GROUP V CARBIDES ... 87
4.0 MECHANICAL PROPERTIES OF GROUP V CARBIDES . 88
5.0 CHEMICAL PROPERTIES OF GROUP V CARBIDES 89
5.1 Mutual Solubilities 89
5.2 Chemical Properties 89
6.0 CHARACTERISTICS AND PROPERTIES OF VANADIUM CARBIDE 89
6.1 Summary of Properties 89
6.2 Phase Diagram 91
6.3 Summary of Fabrication Processes 92
6.4 Summary of Applications and Industrial Importance 92

7.0 CHARACTERISTICS AND PROPERTIES OF NIOBIUM CARBIDE 92
7.1 Summary of Properties 92
7.2 Phase Diagram 92
7.3 Summary of Fabrication Processes 95
7.4 Summary of Applications and Industrial Importance 95
8.0 CHARACTERISTICS AND PROPERTIES OF TANTALUM CARBIDE 95
8.1 Summary of Properties 95
8.2 Phase Diagram 97
8.3 Summary of Fabrication Processes 98
8.4 Summary of Applications and Industrial Importance 98
REFERENCES 98

6 Carbides of Group VI: Chromium, Molybdenum, and Tungsten Carbides 100

1.0 GENERAL CHARACTERISTICS OF GROUP VI CARBIDES 100
1.1 Common Features of Group VI Carbides 100
1.2 Refractory Characteristics 101
2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP VI CARBIDES 101
2.1 Density and Melting Point 102
2.2 Thermal Properties 102
3.0 ELECTRICAL PROPERTIES OF GROUP VI CARBIDES 104
4.0 MECHANICAL PROPERTIES OF GROUP VI CARBIDES . 106
5.0 CHEMICAL PROPERTIES OF GROUP VI CARBIDES ... 107
5.1 Mutual Solubilities 107
5.2 Chemical Properties 107
6.0 CHARACTERISTICS AND PROPERTIES OF CHROMIUM CARBIDE 107
6.1 Summary of Properties 107
6.2 Phase Diagram 107
6.3 Summary of Fabrication Processes 110
6.4 Summary of Applications and Industrial Importance 110
7.0 CHARACTERISTICS AND PROPERTIES OF MOLYBDENUM CARBIDE 110
7.1 Summary of Properties 110
7.2 Phase Diagram 110
7.3 Summary of Production Processes 112
7.4 Summary of Applications and Industrial Importance 112

8.0 CHARACTERISTICS AND PROPERTIES OF TUNGSTEN CARBIDE 113
8.1 Summary of Properties 113
8.2 Phase Diagram 114
8.3 Summary of Production Processes 115
8.4 Summary of Applications and Industrial Importance 116
REFERENCES 116

7 Covalent Carbides: Structure and Composition. 118

1.0 GENERAL CHARACTERISTICS OF COVALENT CARBIDES 118
2.0 ATOMIC STRUCTURE OF CARBON, BORON, AND SILICON 119
2.1 Electronic Configuration 119
2.2 Hybridized States 120
3.0 STRUCTURE AND COMPOSITION OF SILICON CARBIDE 121
3.1 The Carbon-Silicon Crystal Unit Cell 121
3.2 Covalent and Ionic Bonding 122
3.3 Beta Silicon Carbide 123
3.4 Alpha Silicon Carbide and Polytypes 123
3.5 Summary of Structural Data 124
3.6 Structural Correlation 127
3.7 Phase Diagram 127
4.0 STRUCTURE AND COMPOSITION OF BORON CARBIDE 128
4.1 The Boron Icosahedron 128
4.2 The Structure of Boron Carbide 130
4.3 Composition 132
4.4 The Boron-Carbon Bond 132
4.5 Summary of Structural Data for Boron Carbide 132
4.6 Phase Diagram 134
REFERENCES 135

8 Characteristics and Properties of Silicon Carbide and Boron Carbide 137

1.0 INTRODUCTION 137
2.0 CHARACTERISTICS AND PROPERTIES OF SILICON CARBIDE 137
2.1 Historical Background and Present Status 137
2.2 Summary of Properties 138

3.0 CHARACTERISTICS AND PROPERTIES OF BORON CARBIDE 142
3.1 Historical Background and Present Status 142
3.2 Summary of Properties 142
4.0 PHYSICAL AND THERMAL PROPERTIES OF THE COVALENT CARBIDES 144
4.1 Discussion and Comparison 144
4.2 Physical Properties 145
4.3 Thermal Properties 146
5.0 ELECTRICAL AND SEMICONDUCTOR PROPERTIES . 147
5.1 Electrical Properties 147
5.2 Semiconductor Properties 147
5.3 Boron Carbide as a Thermoelectric Material 149
6.0 MECHANICAL PROPERTIES 149
6.1 Property Variables 149
6.2 Summary of Mechanical Properties 149
6.3 Strength 149
6.4 Hardness 150
7.0 NUCLEAR PROPERTIES 151
8.0 SUMMARY OF FABRICATION PROCESSES 151
8.1 Silicon Carbide 151
8.2 Boron Carbide 152
9.0 SUMMARY OF APPLICATIONS AND INDUSTRIAL IMPORTANCE 152
9.1 Silicon Carbide 152
9.2 Boron Carbide 153
REFERENCES 154

9 The Refractory Nitrides 156

1.0 INTRODUCTION 156
2.0 GENERAL CHARACTERISTICS OF NITRIDES 156
2.1 Definition and Classification 156
2.2 Refractory Qualifications 158
3.0 FACTORS CONTROLLING NITRIDE FORMATION 158
3.1 Nitride Formation and Electronegativity 158
3.2 Nitride Formation and Atom Size 159
3.3 The Electronic Bonding of Nitrides 159
4.0 GENERAL CHARACTERISTICS OF NITRIDES 159
4.1 Interstitial Nitrides 159
4.2 Covalent Nitrides 161
4.3 Intermediate Nitrides 161
4.4 Salt-Like Nitrides 161
REFERENCES 162

10 Interstitial Nitrides: Structure and Composition 163

1.0 DEFINITION AND GENERAL CHARACTERISTICS OF INTERSTITIAL NITRIDES 163
1.1 Definition 163
1.2 General Characteristics 164
2.0 ATOMIC STRUCTURE OF NITROGEN 165
2.1 Nucleus and Electronic Configuration of the Nitrogen Atom 165
2.2 Bonding and Hybridization 166
3.0 ATOMIC STRUCTURE OF INTERSTITIAL NITRIDES .. 168
3.1 Atomic Radii Ratio 168
3.2 Interstitial Sites 169
4.0 COMPOSITION AND CRYSTALLINE STRUCTURE OF INTERSTITIAL NITRIDES 169
4.1 Composition and Structure 169
4.2 Composition 171
4.3 Summary of Characteristics 172
4.4 Metal-to-Nitride Structural Switching 172
4.5 Density Considerations 174
5.0 ATOMIC BONDING OF INTERSTITIAL NITRIDES 174
5.1 Overall Bonding Scheme 174
5.2 Thermal Properties Considerations 176
5.3 Ionic Bonding and Electronegativity 179
REFERENCES 180

11 Interstitial Nitrides: Properties and General Characteristics 181

1.0 GENERAL PROPERTIES OF INTERSTITIAL NITRIDES 181
2.0 PHYSICAL AND THERMAL PROPERTIES OF INTERSTITIAL NITRIDES 181
2.1 Composition and Stoichiometry 182
2.2 Density and Melting Point 182
2.3 Thermal Properties 183
2.4 Thermal Conductivity 184
2.5 Thermal Expansion 185
3.0 ELECTRICAL PROPERTIES OF INTERSTITIAL NITRIDES 187
4.0 MECHANICAL PROPERTIES OF INTERSTITIAL NITRIDES 188
4.1 Summary of Mechanical Properties 189
4.2 Hardness 189

5.0 CHEMICAL PROPERTIES OF INTERSTITIAL NITRIDES 191
5.1 Mutual Solubilities 191
5.2 Chemical Properties 192
6.0 TITANIUM NITRIDE: SUMMARY OF PROPERTIES 193
6.1 Summary of Properties 193
6.2 Isomorphism 194
6.3 Phase Diagram 194
6.4 Summary of Fabrication Processes 195
6.5 Summary of Applications and Industrial Importance 195
7.0 ZIRCONIUM NITRIDE: SUMMARY OF PROPERTIES . 195
7.1 Summary of Properties 195
7.2 Isomorphism 195
7.3 Phase Diagram 195
7.4 Summary of Fabrication Processes 197
7.5 Summary of Applications and Industrial Importance 197
8.0 HAFNIUM NITRIDE. SUMMARY OF PROPERTIES 198
8.1 Summary of Properties 198
8.2 Isomorphism 199
8.3 Phase Diagram 199
8.4 Summary of Fabrication Processes 200
8.5 Summary of Applications and Industrial Importance 200
9.0 VANADIUM NITRIDE: SUMMARY OF PROPERTIES ... 200
9.1 Summary of Properties 200
9.2 Isomorphism 200
9.3 Phase Diagram 200
9.4 Summary of Fabrication Processes 200
9.5 Summary of Applications and Industrial Importance 202
10.0 NIOBIUM NITRIDE: SUMMARY OF PROPERTIES 202
10.1 Summary of Properties 202
10.2 Isomorphism 204
10.3 Phase Diagram 204
10.4 Summary of Fabrication Processes 204
10.5 Summary of Applications and Industrial Importance 205
11.0 TANTALUM NITRIDE. SUMMARY OF PROPERTIES .. 205
11.1 Summary of Properties 205
11.2 Isomorphism 205
11.3 Phase Diagram 205
11.4 Summary of Fabrication Processes 205
11.5 Summary of Applications and Industrial Importance 205
REFERENCES 207

12 Covalent Nitrides: Composition and Structure . 209

1.0 GENERAL CHARACTERISTICS OF COVALENT NITRIDES 209
2.0 ATOMIC STRUCTURE OF NITROGEN, BORON, ALUMINUM, AND SILICON 210
2.1 Electronic Configuration 210
2.2 Characteristics of the Elements Forming Covalent Nitrides 211
3.0 COMPOSITION AND STRUCTURE OF BORON NITRIDE 211
3.1 Composition 211
3.2 The Two Major Structures of Boron Nitride 212
3.3 Structure of Hexagonal Boron Nitride 213
3.4 Structure of Cubic Boron Nitride 214
3.5 Other Boron Nitride Structures 216
3.6 Summary of Structural Data of Boron Nitride 216
4.0 COMPOSITION AND STRUCTURE OF ALUMINUM NITRIDE 217
4.1 Composition 217
4.2 Structure 217
4.3 Bonding 218
4.4 Summary of Structural Data of Aluminum Nitride 218
5.0 COMPOSITION AND STRUCTURE OF SILICON NITRIDE 219
5.1 Composition 219
5.2 Structure 219
5.3 Bonding 220
5.4 Summary of Structural Data of Silicon Nitride 221
REFERENCES 222

13 Covalent Nitrides: Properties and General Characteristics 223

1.0 INTRODUCTION 223
2.0 PHYSICAL PROPERTIES OF THE COVALENT NITRIDES 223
2.1 Discussion and Comparison 223
2.2 Physical Properties 224
3.0 THERMAL AND ELECTRICAL PROPERTIES OF COVALENT NITRIDES 225
3.1 Thermal Properties 225
3.2 Electrical Properties 227

4.0 MECHANICAL PROPERTIES OF COVALENT NITRIDES 228
4.1 Property Variables 228
4.2 Summary of Mechanical Properties 229
4.3 Strength and Modulus 229
4.4 Hardness 232
5.0 CHEMICAL PROPERTIES OF COVALENT NITRIDES .. 232
6.0 CHARACTERISTICS AND PROPERTIES OF BORON NITRIDE 232
6.1 Historical Background and Present Status 232
6.2 Hexagonal Boron Nitride 232
6.3 Phase Diagram 234
6.4 CVD Boron Nitride 234
6.5 Cubic Boron Nitride 235
6.6 Chemical Resistance of Boron Nitride 236
7.0 CHARACTERISTICS AND PROPERTIES OF ALUMINUM NITRIDE 237
7.1 Historical Background and Present Status 237
7.2 Summary of Properties 237
7.3 Phase Diagram 237
7.4 Chemical Resistance of Aluminum Nitride 237
8.0 CHARACTERISTICS AND PROPERTIES OF SILICON NITRIDE 239
8.1 Historical Background and Present Status 239
8.2 Summary of Properties 240
8.3 Phase Diagram 240
8.4 Chemical Resistance of Silicon Nitride 240
8.5 Sialons 243
9.0 SUMMARY OF FABRICATION PROCESSES 243
9.1 Boron Nitride 243
9.2 Aluminum Nitride 243
9.3 Silicon Nitride 244
10.0 SUMMARY OF APPLICATIONS AND INDUSTRIAL IMPORTANCE 244
10.1 Boron Nitride 244
10.2 Aluminum Nitride 245
10.3 Silicon Nitride 245
REFERENCES 246

14 Processing of Refractory Carbides and Nitrides (Powder, Bulk, and Fibers) 248

1.0 INTRODUCTION 248
1.1 Synthesis Characteristics 248

1.2 Forms and Processing of Refractory Carbides and Nitrides 249
2.0 PRODUCTION OF REFRACTORY CARBIDE AND NITRIDE POWDERS 250
2.1 General Considerations 250
2.2 Chemical Preparation 250
2.3 Vapor-Phase Chemical Reactions 253
2.4 RF Plasma Torch 254
2.5 Self-Propagating High-Temperature Synthesis (SHS) 254
2.6 Sol-Gel 256
3.0 PRODUCTION OF BULK/MONOLITHIC SHAPES OF REFRACTORY CARBIDES AND NITRIDES 256
3.1 Powder Pressing 257
3.2 Sintering 257
4.0 FIBER PRODUCTION 262
4.1 State of the Art 262
4.2 Refractory-Carbide and Nitride Fibers by Sol-Gel 265
4.3 Silicon-Carbide Fibers by Chemical-Vapor Deposition (CVD) 268
4.4 Other Refractory-Fiber Materials 270
5.0 WHISKER PRODUCTION 271
5.1 Silicon Carbide Whiskers 271
5.2 Other Whisker Materials 272
REFERENCES 272

15 Processing of Refractory Carbides and Nitrides (Coatings) 276

1.0 COATING PROCESSES 276
1.1 Composite Nature of Coatings 276
1.2 Major Coating Processes 278
2.0 GENERAL CHARACTERISTICS OF CHEMICAL VAPOR DEPOSITION (CVD) 279
2.1 The CVD Process 279
2.2 General Characteristics 280
3.0 THE CVD OF REFRACTORY CARBIDES 280
3.1 Titanium Carbide 280
3.2 The CVD of Other Interstitial-Metal Carbides 284
3.3 The CVD of Silicon Carbide 286
3.4 The CVD of Boron Carbide 286
4.0 THE CVD OF REFRACTORY NITRIDES 287
4.1 The CVD of Titanium Nitride 287
4.2 The CVD of Other Interstitial Nitrides 288

4.3 The CVD of Aluminum Nitride 288
4.4 The CVD of Silicon Nitride 289
4.5. The CVD of Boron Nitride 290
5.0 PHYSICAL VAPOR DEPOSITION (PVD) 291
6.0 EVAPORATION 292
6.1 Principle of Evaporation 292
6.2 Reactive Evaporation 292
6.3 Reactive Evaporation of TiN 293
6.4 Plasma Evaporation 295
6.5 Molecular-Beam Epitaxy 295
6.6 Examples of Evaporated Films 295
7.0 SPUTTERING 295
7.1 Principle of Sputtering 295
7.2 Sputtering Techniques 297
7.3 Examples of Sputtered Films 297
8.0 ION PLATING 298
9.0 THERMAL SPRAY 300
9.1 Principle of Thermal Spray 300
9.2 Heat Sources 300
9.3 Reactive Thermal Spray 301
9.4 Examples of Thermal-Sprayed Coatings 302
REFERENCES 302

16 Applications of Refractory Carbides and Nitrides 309

1.0 OVERVIEW OF APPLICATIONS OF REFRACTORY CARBIDES AND NITRIDES 309
1.1 Applications Classification 309
1.2 Industrial Importance 310
1.3 Status of Industrial Production 311
2.0 AUTOMOTIVE AND AEROSPACE APPLICATIONS 312
2.1 Silicon Nitride in Automobile and Aircraft Engines 312
2.2 Aircraft Gas Turbines 314
2.3 High-Temperature and Oxidation Protection Applications .. 315
2.4 Ball Bearings 316
2.5 Composites 316
3.0 GENERAL INDUSTRIAL APPLICATIONS: MACHINERY AND EQUIPMENT 317
3.1 Machinery 318
3.2 Decorative Applications 319
3.3 Abrasives 319
4.0 CUTTING AND GRINDING TOOLS 319
4.1 Bulk Tungsten-Carbide Tools 320

4.2 TiN Coatings for Steel Tools 320
4.3 Bulk Silicon-Nitride Tools 320
5.0 ARMOR APPLICATIONS 321
6.0 NUCLEAR AND RADIATION APPLICATIONS 322
6.1 Nuclear Fission Applications 322
6.2 Nuclear Fusion Applications 322
7.0 ELECTRONIC AND OPTICAL APPLICATIONS 322
7.1 Titanium Nitride Diffusion Barrier 323
7.2 Silicon Nitride Electrical Insulation 324
7.3 Silicon Carbide Semiconductor 324
7.4 Aluminum Nitride Heat Sink 324
7.5 Thermoelectric Applications 324
7.5 Optical Applications 324
REFERENCES 325

Appendix: Conversion Guide 327

Index 331

1

Introduction

1.0 HISTORICAL PERSPECTIVE AND PRESENT STATUS OF REFRACTORY CARBIDES AND NITRIDES

Refractory carbides and nitrides are useful materials with numerous industrial applications and a promising future, in addition to being materials of great interest to the scientific community. Although most of their applications are recent, the refractory carbides and nitrides have been known for over one hundred years. Titanium and tungsten carbides were extracted from steel and properly identified around the middle of the nineteenth century. In 1890, E. G. Acheson produced the first silicon carbide, trademarked *Carborundum*, and by 1900 the French chemist Moissan had synthesized most other refractory carbides in his electric arc-furnace. Titanium carbonitride was first described in 1822 and identified by chemical analysis in 1850. Additional notes of historical interest will be presented in the relevant chapters.

The industrial importance of the refractory carbides and nitrides is growing rapidly, not only in the traditional and well-established applications based on the strength and refractory nature of these materials such as cutting tools and abrasives, but also in new and promising fields such as electronics and opto-electronics. Some typical applications are as follows:

- Silicon-nitride rotors, blades, rings, and burner tiles for gas turbines
- Tungsten-carbide cutting tools
- Titanium-nitride coatings on high-speed steel drill bits
- Silicon-carbide fibers and whiskers
- Boron-carbide abrasive blast nozzles
- Aluminum-nitride high thermal conductivity substrates for electronic circuits
- Silicon carbide burner tubes for gas furnaces
- Titanium nitride passivating and electrically insulating coatings for semiconductor devices
- Silicon carbide high-temperature semiconductor devices
- Silicon carbide blue light-emitting diode (LED)

Such a wide range of applications reflects the variety of these materials and the diversity of the industry, from small research laboratories developing new ideas to large plants manufacturing cutting tools, textile machinery, electronic and semiconductor components, and many other products. Together, these organizations form an essential part of the ceramic industry throughout the world.

2.0 CARBIDES AND NITRIDES AS REFRACTORY MATERIALS

The word *refractory* defines a material with a high melting point. In the context of this book, this means any carbide and nitride with a melting point arbitrarily selected as greater than 1800°C. In addition, to be considered refractory the material must have a high degree of chemical stability.

As shown in subsequent chapters, most elements form carbides and nitrides and these can be divided into several types with different physico-chemical structures and characteristics. Of these, however, only the interstitial and covalent materials meet the refractory qualification. This includes the carbides and nitrides of the nine transition elements of Groups IV, V, and VI and the 4th, 5th, and 6th Periods, the carbides and nitrides of boron and silicon, and aluminum nitride.

The carbides and nitrides of the lanthanides (the rare-earth elements) and actinides are well-defined and unique families of materials with promising applications, yet they cannot be considered refractory and are not included in this book.

Although carbides and nitrides as a group form the most refractory compounds, they are certainly not the only ones. Several borides, oxides, phosphides, silicides, and metals meet the refractory requirements mentioned above. To some degree, these materials complement the refractory carbides and nitrides and may be considered as competitors.

Why should the refractory carbides and nitrides be reviewed together in one book?

- They form two families of closely related materials which have similar atomic structures and chemistry
- Carbon and nitrogen are next to each other the second period of the Table of the Elements and, in many cases, the carbides and nitrides form solid solutions (known as *carbonitrides*)
- Many of their properties are similar
- They have essentially the same processing characteristics and basically the same applications
- In many respects, they complement each other

3.0 BOOK OBJECTIVES

A large body of information is available on the subject of refractory carbides and nitrides, including a number of books such as the ones listed in Sec. 6.0. These books provide excellent reviews but the authors have chosen to concentrate on the structural aspects and properties of carbides and nitrides, offering little information concerning processing and even less about applications. Moreover these studies were written several decades ago, and a large amount of research and development has taken place since. The basic understanding of these materials is gradually expanding. Technology is moving rapidly. Improvements in processing techniques appear regularly, and the scope of applications is constantly increasing and reaching into new fields such as aerospace, automotive, semiconductors, optics, and electronics.

With some of his colleagues, the author has felt the need for an updated and systematic review of refractory carbides and nitrides, which would summarize the scientific aspects of these materials and examine their relationship with the engineering, processing, and applications aspects, coordinate the divergent trends found today in industry and the academic community, and sharpen the focus of research and development by promoting interaction.

Industrial secrecy still prevails in many sectors. It is sometimes necessary but also often needlessly hampers progress. Interaction and coordination are limited even though the various technologies and applications share the same scientific basis, the same principles, the same chemistry, and often the same type of equipment. A purpose of this book is to bring these divergent areas together in one unified whole with the hope of providing a useful tool for engineers and scientists.

The main objectives of this book can be summarized as follows:

- Provide a complete review of the structures and properties of refractory carbides and nitrides
- Provide a thorough assessment of the technology, processing, and equipment and systems used in production and R&D, with emphasis on advanced designs
- Identify and describe the applications, particularly the new and emerging areas of semiconductors and electronics, optics, tool coatings, and wear, oxidation, or corrosion resistant products

4.0 BOOK ORGANIZATION

The book is organized in six basic sections:

1. Structure and properties of refractory interstitial carbides (Chs. 2–6)
2. Structure and properties of refractory covalent carbides (Chs. 7 and 8)
3. Structure and properties of refractory interstitial nitrides (Chs. 9–11)
4. Structure and properties of refractory covalent nitrides (Chs. 12 and 13)

5. Technology and processing (Chs. 14 and 15)
6. Applications (Ch. 16)

In the first eight chapters devoted to carbides, several basic principles are reviewed such as atomic and molecular structure, crystalline arrangement, type of bond, etc. These principles also apply to nitrides but are not repeated and only cross-referenced. Whenever possible, the relationship between structure, properties, and applications is stressed throughout the book.

5.0 GLOSSARY AND METRIC CONVERSION GUIDE

A glossary at the end of the book defines terms which may not be familiar to some readers. These terms are printed in *italics* in the text. All units in this book are metric, specifically the international system of units (SI) and a metric conversion guide is included at the end of the book.

6.0 BACKGROUND READING

The following is a representative list of the most important references, periodicals, and conferences dealing with carbides and nitrides.

6.1 General References

Storms, E. K., *The Refractory Metal Carbides*, Academic Press, New York (1967)

Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)

Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)

Kosolapova, T. Ya., *Carbides*, Plenum Press, New York (1971)

Samsonov, G., *Refractory Carbides*, Consultant Bureau, New York (1974)

Wehr, M. R., Richards, J. A., Jr. and Adair, T. W., III, *Physics of the Atom*, Addison-Wesley Publishing Co., Reading, MA (1978)

Evans, R. C., *An Introduction to Crystal Chemistry*, Cambridge Univ. Press, Cambridge (1979)

Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry,* Interscience Publishers, New York (1980)

Adams, D. M., *Inorganic Solids*, John Wiley & Sons, New York (1981)

Huheey, J. E., *Inorganic Chemistry*, Third Edition, Harper & Row, New York (1983)

March, J., *Advanced Inorganic Chemistry,* John Wiley & Sons, New York (1985)

Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)

Bunshah, R. F., *Handbook of Deposition Technologies for Films and Coatings,* 2nd ed., Noyes Publications, Park Ridge, NJ (1994)

6.2 Periodicals

Acta Crystallographica
Applied Physics Letters
Carbon
Ceramic Bulletin
Ceramic Engineering and Science Proceedings
Japanese Journal of Applied Physics
Journal of the American Ceramic Society
Journal of the American Chemical Society
Journal of Applied Physics
Journal of the Ceramic Society of Japan
Journal of Crystal Growth
Journal of the Electro-Chemical Society
Journal of the Less-Common Metals
Journal of Materials Research
Journal of Vacuum Science and Technology
Materials and Manufacturing Processes
Materials Engineering
Materials Research Society Bulletin
Nature
SAMPE Journal
SAMPE Quarterly
SPIE Publications
Science

6.3 Conferences

- International Conferences on chemical vapor deposition (CVD) of the Electrochemical Society (biennial)
- Composites and Advanced Ceramics Conferences of the American Ceramic Society (annual)
- Materials Research Society Conferences (annual)
- International Conference on Surface Modification Technologies (annual)

2

The Refractory Carbides

1.0 INTRODUCTION

The refractory carbides are hard and wear resistant, have high melting points, and are chemically inert. In a relatively short time, they have become major industrial materials with numerous applications such as cutting and grinding tools, bearings, textile-machinery components, oxidation-resistant gas burners, and many others.

This chapter is a general review of the structural characteristics of the refractory carbides, their classification, and general features. These materials can be divided into two major types: the interstitial carbides reviewed in Chs. 3 to 6, and the covalent carbides, reviewed in Chs. 7 and 8.

2.0 DEFINITION AND CLASSIFICATION OF CARBIDES

The element carbon forms coumpounds with most other elements (i.e., CO_2, CCl_4) but, by convention, the term *carbide* is only applied to those compounds formed by carbon and other elements of lower or about equal electronegativity.[1]

2.1 Classification

The carbides, as defined above, can be classified in four general categories which are commonly identified as:

1. Interstitial carbides (formed by the elements of Box A of Table 2.1)
2. Covalent carbides (formed by the elements of Box B of Table 2.1)
3. Intermediate carbides (formed by transiton metals of Groups VII and VIII)
4. Salt-like carbides (formed by the elements of Groups I, II, and III)

2.2 Refractory Qualifications

The term *refractory*, as stated in Ch. 1, means a material with a high melting point, arbitrarily fixed at >1800°C, and with a high degree of chemical stability. Only the interstitial and covalent carbides fulfill these two qualifications. The intermediate and salt-like carbides do not meet one or both of these conditions and cannot be considered as refractory, yet they are important materials and are briefly reviewed in Secs. 5.3 and 5.4.

2.3 Factors Controlling Carbide Formation

Three general and interrelated atomic characteristics play an essential part in the formation of carbides (and indeed of all compounds), i.e., the difference in electronegativity between carbon and the other element, the size of the respective atoms, and the bonding characteristics of these atoms. These factors are examined in the following three sections.

3.0 CARBIDE FORMATION AND ELECTRONEGATIVITY

3.1 Definition of Electronegativity

Electronegativity can be roughly defined as the tendency of an element to gain electrons and form negative ions. In the partial Periodic

Table shown in Table 2.1, the elements are listed with their electronegativity, calculated by using the values of Pauling and others. It should be noted that electronegativity of an element is not a fixed value but is dependent on its valence state. The table shows that carbon and nitrogen have higher electronegativity than any other elements to their left.[2][3]

3.2 Comparison of Electronegativity

The difference in electronegativity between carbon and the other element forming a carbide is an important factor in determining the nature of the compound. As shown in Table 2.1, that difference in the interstitial carbides is large (Box A) while it is much less pronounced in the covalent carbides (Box B).

Table 2.1: Periodic Table of the Elements Showing Their Electronegativity and Elements Forming Refractory Carbides

H																	
2.1											BOX B						
Li	Be										B	C	N	O	F		
1.9	1.5										2.0	2.5	3.0	3.5	4.0		
Na	Mg										Al	Si	P	S	Cl		
0.9	1.2		BOX A								1.5	1.8	2.1	2.5	3.0		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
0.9	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.0	1.6	1.6	1.8	2.0	2.4	2.8	
Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	
Ca	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	

Note: Elements in Box A form refractory interstitial carbides and elements in Box B form refractory covalent carbides

4.0 CARBIDE FORMATION AND ATOM SIZE

4.1 Atomic Radius

The second factor controlling carbide formation is the atomic radius of the constituent elements. The radii of elements forming carbides are listed in Table 2.2. A certain caution is in order when considering the radius of an element since the size of an atom is related to a wave function and it follows that no atom has a precise radius. Thus, the values given in Table 2.2 are essentially assumptions, yet they form an empirically useful set of values.[2] Moreover, the radius of an atom may change depending on the hybridization.

Table 2.2: Approximate Atomic Radius of Carbon and Selected Elements[4][5]

Element	Atomic Number	Atomic Radius (nm)	Type of Carbide
Boron	5	0.088*	C
CARBON	**6**	**0.078***	
Nitrogen	7	0.074*	
Oxygen	8	0.066*	
Aluminum	13	0.126*	S
Silicon	14	0.117*	C
Titanium	22	0.1467**	IS
Vanadium	23	0.1338**	IS
Chromium	24	0.1267**	IM
Manganese	25	0.1261**	IM
Iron	26	0.1260**	IM
Cobalt	27	0.1252**	IM
Nickel	28	0.1244**	IM
Zirconium	40	0.1597**	IS
Niobium	41	0.1456**	IS
Molybdenum	42	0.1386**	IS
Hafnium	72	0.1585**	IS
Tantalum	73	0.1457**	IS
Tungsten	74	0.1394**	IS

* Tetrahedral radii (sp^3)
** Coordination Number (CN)= 12

IS = interstitial carbide
C = covalent carbide
IM = intermediate carbide
S = salt-like carbide

The values of Table 2.2 are for the prevaling hybridization in carbide formation (see discussion of hybridization in Ch. 3). One should note that carbon is one of the smallest atoms. Table 2.2 also shows the type of carbide formed, i.e., interstitial (IS), covalent (C), intermediate (IM), or salt-like (S).

4.2 Carbide Formation and Ratio of Atomic Radii

The importance of the atomic radius will become evident as the structure of interstitial, intermediate, and covalent carbides is reviewed in Chs. 3 (intersitial carbides) and 7 (covalent carbides). Generaly speaking, when the difference is large, interstitial carbides are formed (i.e., TiC); when it is small, covalent carbides are formed (i.e., SiC).

5.0 THE ATOMIC BONDING OF CARBIDES

In addition to electronegativity and atomic size considerations, the other important factor governing the structure of carbides is the nature of the bond between the carbon atom and the other element forming the compound. One should note that bonding, electronegativity, and atom size are all interrelated.

A bond is the force of attraction that holds together the atoms of a molecule or a crystal. It is characterized by two factors: its length—determined by spectroscopic or diffraction techniques, and its strength—determined from quantitative energy measurements during bond formation or bond dissociation. The nature of the bond is a function of the electronic configuraton of the constituent elements, the types of orbitals available, and the bond polarity. Generally, short bonds are stronger than long bonds.[6]

The bonds in refractory carbides can be ionic, metallic, covalent, or combinations of these.[2]

5.1 Ionic Bond

An ionic bond is formed by transfer of valence electrons between two different atoms, resulting in a positive and a negative ion, and the resultant electrostatic attraction between these ions of unlike charges. Large differences in electronegativity favor ionic bonding. The archetypal ionic

material is sodium chloride (NaCl). Other examples of ionic bond are the salt-like carbides described in Sec. 5.4.

5.2 Covalent Bond

Covalent bonds are formed by the sharing of electrons (rather than transfer). Typically two atoms share a pair of electrons. A covalent structure, that of diamond, is shown schematically in Fig. 2.1.[7] The shaded regions designate a high probability of finding the shared electrons (see Sec. 3.3).

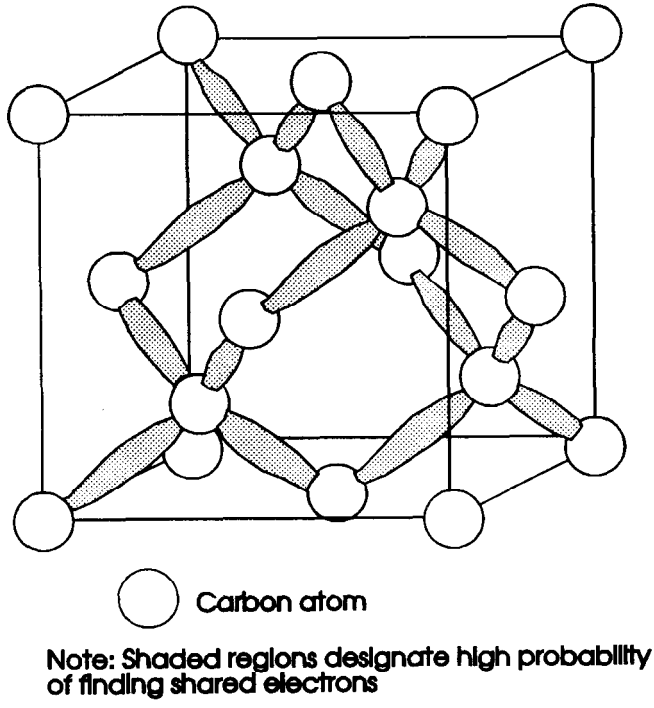


Figure 2.1: Schematic representation of the structure of the diamond crystal.

5.3 Metallic Bond

In a metallic bond, the atoms are considered to be ionized, with the positive ions arranged in the lattice positions. The electrons are *delocalized*, that is, they are able to move essentially freely throughout the lattice. The bonding occurs by the electrostatic attraction between the electrons and the positive metal ions. Most metals can be considered as close-packed arrays of atoms held together by these delocalized electrons. The metallic bond contributes to the bonding of interstitial carbides and is described in more detail in Ch. 3.

6.0 GENERAL CHARACTERISTICS OF CARBIDES

The characteristics of the four categories of carbides can be summarized as follows.

6.1 Interstitial Carbides

The difference in electronegativity between the two elements of the interstitial carbides is large. The carbon atom has a much smaller size than the other atom, allowing it to nest in the interstices of the lattice (hence the name interstitial). The bonding is partly covalent and ionic, but mostly metallic which explains why the interstital carbides closely resemble metals. Like metallic alloys, their composition is often indeterminate and their electrical and thermal conductivities are high. In addition, they have high melting points, high hardness and are chemically inert.[1] They fully meet the refractory criteria and are reviewed in detail in Chs. 3, 4, 5, and 6.

6.2 Covalent Carbides

The difference in electronegativity between the two elements of the covalent carbides is small. The carbon atom is only slightly smaller than the other atom. The bonding is essentially covalent.[1] Only two covalent carbides, silicon carbide and boron carbide, fully meet the refractory criteria. Other carbides such as beryllium carbide, Be_2C, are only partially covalent and, while they have a high melting point, are generally not chemically stable and are not considered here.

The refractory covalent carbides are reviewed in detail in Chs. 7 and 8.

6.3 Intermediate Carbides

Some transition metals of Groups VII and VIII such as manganese, iron, cobalt, and nickel, as well as chromium of Group VI also form carbides but, as shown in Table 2.2, their atomic radii are too small to accomodate the carbon atom in interstitial positions without severe distortion of the lattice. The carbon atoms are close enough for carbon-carbon bonds and carbon chains to form.[1] These carbides are not generally chemically stable. They are hydrolyzed by water or by dilute acids to produce hydrocarbons and hydrogen. An exception is chromium carbide, Cr_3C_2, which is a refractory border-line case. Yet, because of its interesting properties and commercial use, it is included in this study.

6.4 Salt-Like Carbides

The salt-like (or salinic) carbides are formed with carbon and the most electropositive elements, found in Groups I, II and III to the left of the Periodic Table (Table 2.1.). These elements have an electronegativity difference of about two or more which corresponds to an atomic bond that is at least 50% ionic.

These compounds have the characteristics of a salt, that is, they have a fixed composition; their physical properties are unlike those of their constituent elements; they are generally transparent to optical radiation and are good electrical insulators. They form transparent and colorless crystals. Some contain C^{4-} ions such as aluminum carbide (Al_4C_3) and beryllium carbide (Be_2C). They evolve methane when hydrolyzed and for that reason are usually known as methanides. Others contain C^2 ions such as calcium carbide (CaC_2); they yield acetylene when hydrolyzed and are known as acetylides.[1]

Although some of these salt-like carbides have high melting point (for instance beryllium carbide sublimes above 2100°C), they are decomposed readily by water and/or dilute acids at ordinary temperatures and thus do not meet the refractory criteria of this book. However, this does not necessarily detract from their usefulness. Aluminum and beryllium carbides, the three actinide carbides: ThC, UC and PuC, and several lanthanide (rare earth) carbides are important industrial materials in several areas such as atomic energy and others.[1][3]

REFERENCES

1. Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry*, Interscience Publishers, New York (1972)
2. Evans, R. C., *An Introduction to Crystal Chemistry*, Cambridge Univ. Press, Cambridge (1979)
3. Oyama, S. T., and Kieffer, R., in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4:841–860, John Wiley & Sons, New York (1993)
4. Wehr, M. R., Richards, J. A., Jr. and Adair, T .W., III, *Physics of the Atom*, Addison-Wesley Publishing Co., Reading, MA (1978)
5. March, J., *Advanced Inorganic Chemistry*, John Wiley & Sons, New York (1985)
6. Van Vlack, L. H., *Elements of Materials Science and Engineering*, 4th ed., Addison-Wesley Publishing Co., Reading, MA (1980)
7. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)

3

Interstitial Carbides, Structure and Composition

1.0 DEFINITION AND GENERAL CHARACTERISTICS OF INTERSTITIAL CARBIDES

As mentioned in the previous chapter, the refractory carbides consist of two structurally different types: the interstitial carbides and the covalent carbides. This chapter provides a general review of the structural characteristics of the interstitial carbides.

1.1 Definition

Interstitial carbides are crystalline compounds of a host metal and carbon. The host-metal atoms are generally arranged in a close-packed structure and the carbon occupies specific interstitial sites in that structure. Such a model sets size restrictions on the two elements in order for the carbon atom to fit into the available sites and the population of these sites (if all are occupied) determines the stoichiometry of the carbide.

Interstitial structures were formulated empirically by Hägg in 1931 and are also known as Hägg's structures. Hägg observed that the metals of

the nine early-transition elements fit the criteria for size and site availability and form interstitial carbides. These nine metals are:

	Group IV	Group V	Group VI
4th Period	Titanium	Vanadium	Chromium
5th Period	Zirconium	Niobium	Molybdenum
6th Period	Hafnium	Tantalum	Tungsten

1.2 General Characteristics

The interstitial carbides have several important characteristics in common.[1][2]

- They fully meet the refractory criteria
- Their interstitial structures lead to a combination of metallic, covalent, and ionic bonds
- They are primarily non-stoichiometric phases, and ordering of the carbon atoms is common
- They combine the physical properties of ceramics and the electronic properties of metals, i.e., high hardness and strength with high thermal and electrical conductivities
- They have the highest melting points of any group of materials
- They have high thermal and chemical stability

2.0 ELECTRONIC STRUCTURE OF CARBON

Carbides, like all materials, have a well-defined internal electronic structure which governs their behavior and controls their properties. This means that, in order to understand their mechanism of formation and their general characteristics and properties, it is essential to have a clear picture of the electronic configuration of their constituents. The element common to all carbides is, of course, carbon; a short review of its structure follows.[3]

2.1 Nucleus and Electronic Configuration of the Carbon Atom

Ground-State Configuration. The element carbon has the symbol C and an atomic number (or Z number) of 6, i.e., the neutral atom has six protons in the nucleus and correspondingly six electrons. In addition the nucleus includes six neutrons (for the carbon-12 isotope). The configuration of the six electrons is $1s^2 2s^2 2p^2$, that is two electrons are in the K shell ($1s$) and four in the L shell: two in the $2s$ orbital and two in the $2p$ orbital as shown in Fig. 3.1.

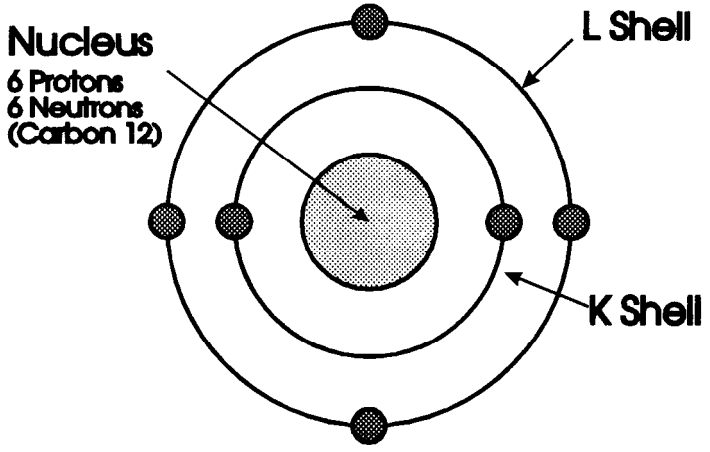


Figure 3.1: Schematic representation of the electronic structure of the carbon atom.

Quantum Numbers. The notation $1s^2$ (or $2s^2$, or $2p^2$) refers to the quantum numbers necessary to define an orbital.[4] The number "1" refers to the K or first shell (principal quantum number); the letter "*s*" refers to the subshell *s* (angular momentum quantum number) and the superscript numeral "2" refers to the number of atoms in that subshell. The K shell has only one orbital (the *s* orbital) and it cannot have more than two electrons. These two electrons, which have opposite spin, are the closest to the nucleus and have the lowest possible energy. The filled K shell is completely stable and its two electrons do not take part in any bonding.

The next two terms, $2s^2$ and $2p^2$, refer to the four electrons in the L shell. The L shell, when filled, can never have more than eight electrons; the element neon has a filled L shell. The L-shell electrons belong to two different subshells, the *s* and the *p*, and the 2*s* and the 2*p* electrons have different energy levels (the number "2" referring to the L or second shell, and the letters "*s*" and "*p*" to the orbitals or subshells). The two 2*s* electrons have opposite spin and the two 2*p* electrons parallel spin. This view of the carbon atom is represented schematically in Fig. 3.2.

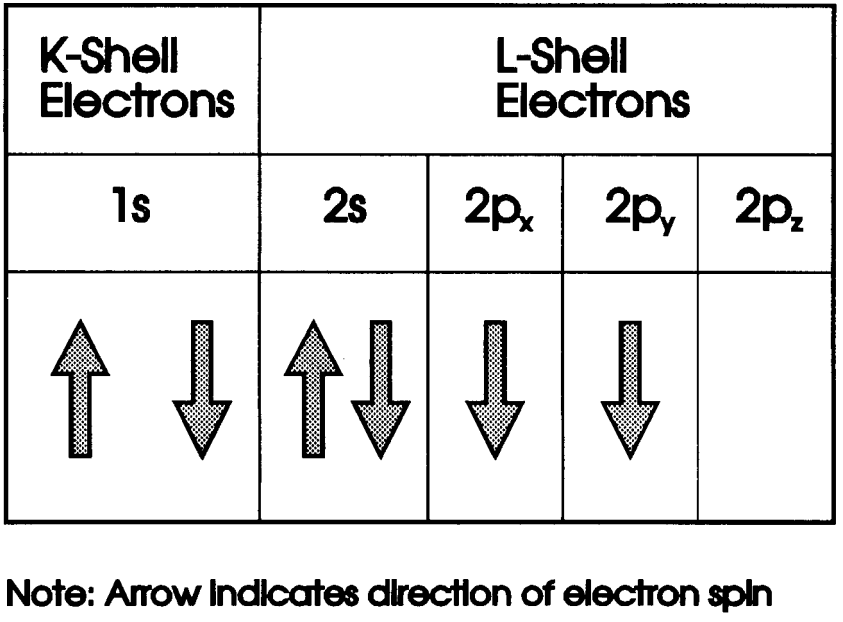


Figure 3.2: Diagram of the carbon atom in the ground state. Shaded areas indicate valence electrons.

Ground State. The configuration of the carbon atom described above refers to the configuration in its ground state, that is, the state where its electrons are in their minimum orbits, as close to the nucleus as they can be, with their lowest energy level, i.e., a single isolated atom.

Electron Wave Function. It should be stressed at this stage that no electron in an atom or a molecule can be accurately located. The electron wave function establishes the probability of an electron being located in a

given volume with the nucleus being the origin of the coordinate system. Mathematically speaking, this function has a finite value anywhere in space, but the value of the function becomes negligible at a distance of a few angstroms from the nucleus. For all practical purposes, the volume where the electron has the highest probability of being located is well defined and is usually represented as a small shaded volume.[5] The precise location within this volume is uncertain. A description of the modern view of the atom is found in Ref. 6.

Ground-State Orbitals. The carbon-atom orbitals in the ground state can be visualized as shown graphically in Fig. 3.3. The wave-function calculations represent the *s* orbital as a sphere with a blurred or fuzzy edge that is characteristic of all orbital representation. As a sphere, the *s* orbital is non-directional. The 2*p* orbital can be represented as an elongated barbell which is symmetrical about its axis and consequently is directional.

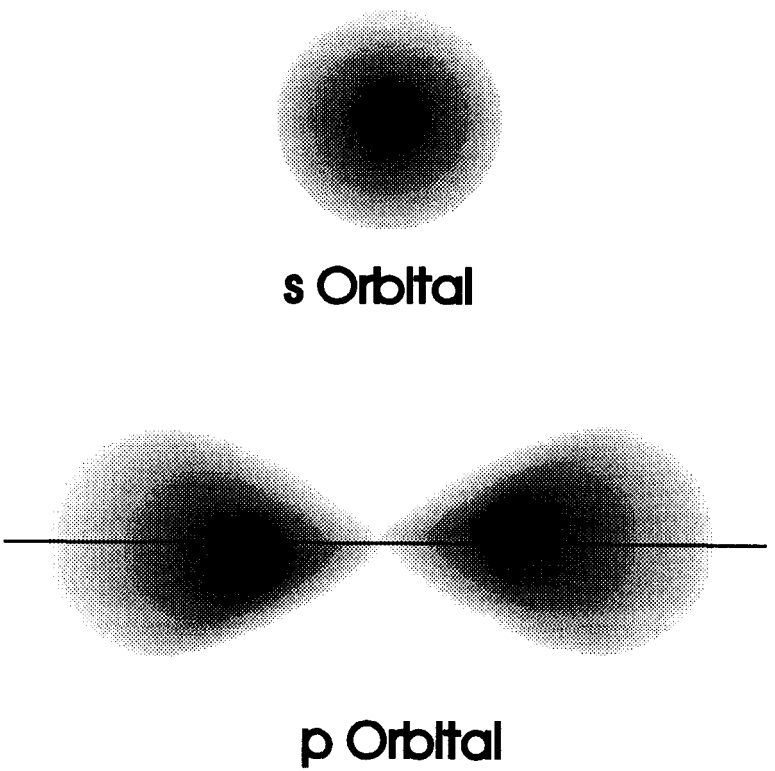


Figure 3.3: Schematic representation of the *s* and *p* orbitals.

Valence Electrons. In any given atom, the electrons located in the outer orbital are the only ones available for bonding to other atoms. These electrons are called the valence electrons. In the case of the carbon atom in the ground state, the valence electrons are the two $2p$ orbitals. Carbon in this state would then be divalent, since only these two electrons are available for bonding.

2.2 Hybridization of the Carbon Atom

This section and the next are a review of the ways carbon atoms bond to themselves or to other elements to form solids such as the carbides.

Carbon Hybrid Bonds. The $1s^2 2s^2 2p^2$ configuration of the carbon atom in the ground state described in the preceding section does not account for the various types of bonding found in carbon molecules or carbon compounds such as carbides, hydrocarbons, and many others. To account for these bonds, this ground state configuration must be altered to a state having four valence electrons instead of two, each in a separate orbital, and each with its spin uncoupled from the other electrons. This alteration occurs as a result of the formation of hybrid atomic orbitals. The hybridization can take one of three configurations, each with its own typical distribution of bonds in space: sp^3, sp^2, or sp. In carbide structures, most bonding occurs with the sp^3 configuration which can be summarized as follows (for a description of the sp^2 and sp orbitals and bonds see Ref. 3).

The Carbon Hybrid sp^3 Orbital. In the sp^3 hybrid configuration, the arrangement of the electrons of the L shell of the atom in the ground state is modified as one of the $2s$ electrons is promoted (or lifted) to the higher orbital $2p$ as shown in Fig. 3.4. These new orbitals are called hybrids since they combine the $2s$ and the $2p$ orbitals. They are labeled sp^3 since they are formed from one s orbital and three p orbitals.

In this hybrid sp^3 state, the carbon atom has four $2sp^3$ orbitals, instead of two $2s$ and two $2p$ of the ground-state atom. The valence state is raised from two to four and can accept four other electrons from another atom. The calculated sp^3 electron-density contour is shown in Fig. 3.5 and a graphic visualization of the orbital, in the shape of an electron cloud, is shown in Fig. 3.6.[7] This orbital is asymmetric, with most of it concentrated on one side and with a small tail on the opposite side. The lobes are labeled + or –. These refer to the sign of the wave function and not to any positive or negative charges since an electron is always negatively charged.

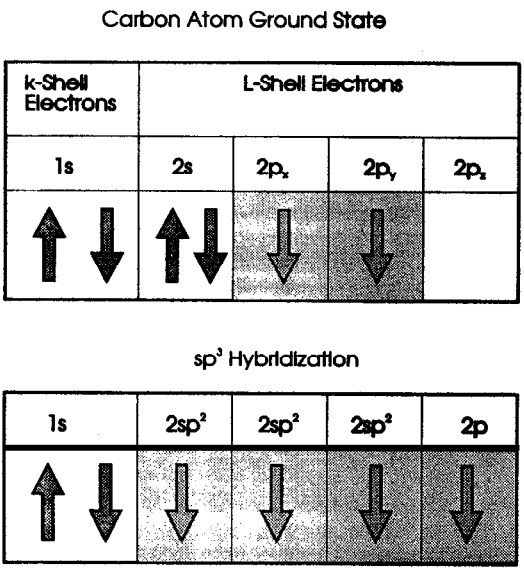


Figure 3.4: Diagram of the sp^3 hybridization of the carbon atom. Shaded areas indicate valence electrons. Arrows indicate direction of electron spin.

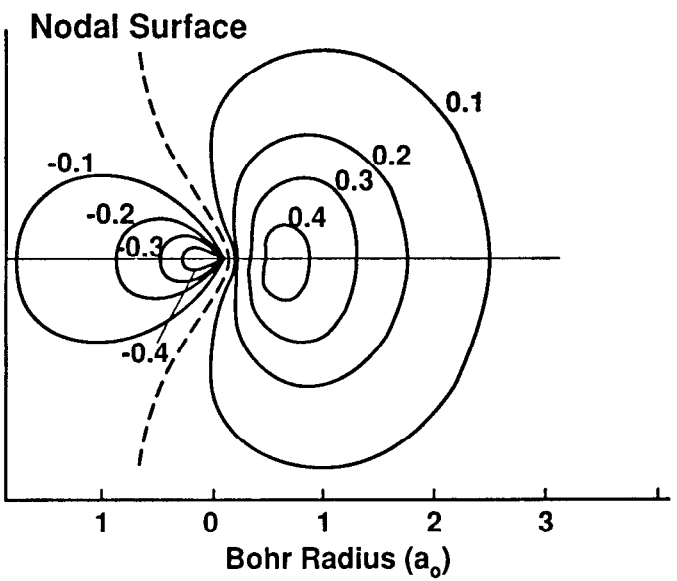


Figure 3.5: Calculated electron–density contours of the sp^3 hybridization of the carbon atom.

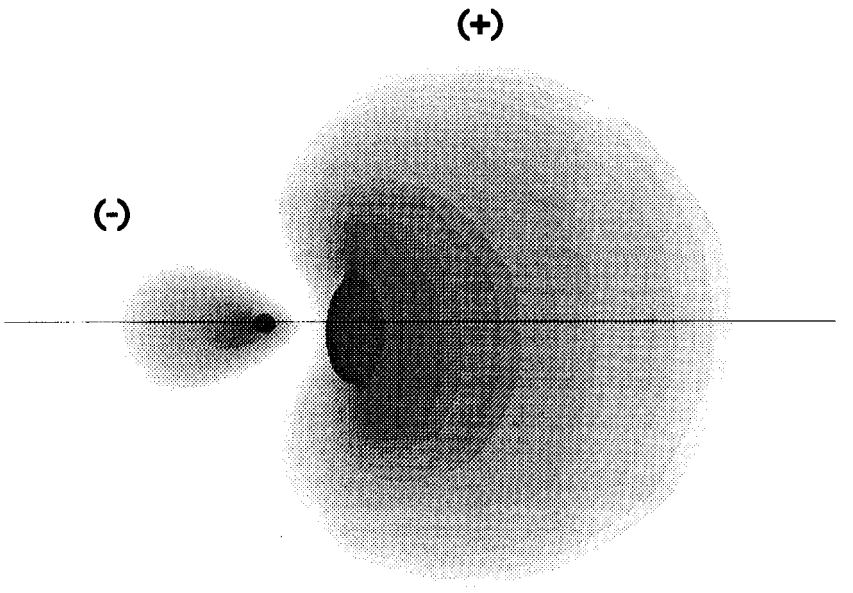


Figure 3.6: Cloud representation of the sp^3 hybrid orbital.

The energy required to accomplish the sp^3 hybridization and raise the carbon atom from the ground state to the corresponding valence state V_4 is 230 kJ mol^{-1}. This hybridization is possible only because the required energy is more than compensated by the energy decrease associated with forming bonds with other atoms.

2.3 The sp^3 Bond

The hybridized atom is now ready to form a set of bonds with other atoms. It should be stressed that these hybrid orbitals (and indeed all hybrid orbitals) are formed only in the bonding process with other atoms and are not representative of an actual structure of a free carbon atom.[8]

Bond Formation. The sp^3 bond formation is illustrated in Fig. 3.7. By convention, a directional (or stereospecific) orbital such as the sp^3 is called a sigma (σ) orbital, and the bond a sigma bond. The direction of the four bonds produces a tetrahedral symmetry which is found in structures such as diamond or silicon carbide where the carbon atom is bonded to four

other carbon atoms in the case of diamond, or to four atoms of silicon in the case of silicon carbide. In both cases, the four bonds are of equal strength.

Covalence. Carbon sp^3 bonding is covalent, that is, the atoms share a pair of electrons. Such covalent bonds are strong since the carbon atom is small and four of its six electrons (the four sp^3 valence electrons) form bonds. This is the case for the two covalent carbides, silicon carbide and boron carbide (see Ch. 7). The bonding in interstitial carbides is not as straightforward and is a combination of covalent, metallic, and ionic bonding as reviewed in Sec. 6.0.

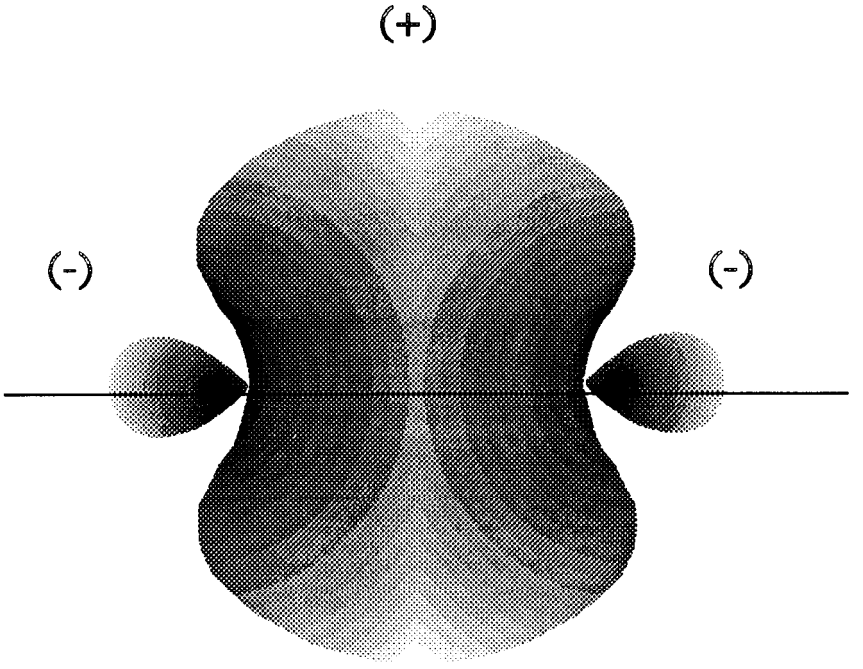


Figure 3.7: Cloud representation of the sp^3 hybrid orbital bonding (σ bond) showing covalent bonding

3.0 THE EARLY TRANSITION METALS

3.1 Definition of Transition Elements

The metals listed in Sec. 1.1 belong to a class of metallic elements known as transition elements which are characterized by their special

electronic arrangement. In the electronic configuration of other elements, the filling of an electronic shell occurs gradually and a shell must be full before the next one is occupied. This is not the case with transition elements, which can be broadly defined as elements having partially filled inner shells. Such a peculiar electronic structure plays an important role in the formation of interstitial carbides.[9]

3.2 Electronic Configuration of Early Transition Metals

The metals forming interstitial carbides are the early *d*-block transition elements. In these elements, the *d* shell is an inner shell and is only partially filled. The valence (bonding) electrons include not only the *s* electrons of the outermost shell but also the *d* electrons of that unfilled *d* shell. The bonding characteristics of these *d*-block elements are quite sensitive to the number and arrangement of the *d* electrons present.

The electronic configuration is shown in Table 3.1. One should note that the *d* shell is never more than half-full (a full *d* shell having 10 electrons).

The three metals of the fourth period (Ti, V, Cr) have a 3*d* inner subshell which is filled with a gradually increasing number of electrons while the outermost subshell 4*s* is virtually the same. They are known as 3*d* transition elements.

In the case of the three metals of the fifth period (Zr, Nb, Mo), it is the inner subshell 4*d* that is gradually filled with an increasing number of electrons; the 4*f* shell remains empty. They are known as 4*d* transition elements.

For the three metals of the sixth period (Hf, Ta, W), it is the inner shell 5*d* that is partially filled, while the 5*f* shell remains empty. They are known as 5*d* transition elements.

The 3*d*, 4*d*, and 5*d* subshells extend outward to the periphery of the atom (or ion) and are strongly influenced by other atoms (such as carbon) and vice versa. The number and location of these valence electrons affect the structure and characteristics of the respective carbides.[9][10]

Table 3.1: Electronic Configuration of Early Transition Metals[9]

		Shells and Subshells												
		K	L	M		N				O				P
		1*s*	2*s*	3*s*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*
Element	Z		2*p*	3*p*									5*g*	
Ti	22	2	8	8	**2**	2								
V	23	2	8	8	**3**	2	Note: incomplete *d* shells							
Cr	24	2	8	8	**5**	1	shown in bold							
Zr	40	2	8	8	10	2	6	**2**	–	2				
Nb	41	2	8	8	10	2	6	**4**	–	1				
Mo	42	2	8	8	10	2	6	**5**	–	1				
Hf	72	2	8	8	10	2	6	10	14	2	6	**2**	–	2
Ta	73	2	8	8	10	2	6	10	14	2	6	**3**	–	2
W	74	2	8	8	10	2	6	10	14	2	6	**4**	–	2

4.0 CRYSTAL STRUCTURES

The crystalline structure of early transition metals and their carbides belongs to one of the following types.

4.1 Close-Packed Crystalline Structures

A crystal can be defined as a solid in which the unit cells (atoms or molecules) have a three-dimensional periodic arrangement. In many crystalline systems, including interstitial carbides, the packing of atoms is such that they occupy a minimum of space and this is known as close packing.

In a close-packed structure, the atoms of the close-packed planes fit into the depressions of the adjacent planes and each atom is surrounded by six close neighbors in a hexagonal configuration as shown schematically in

Fig. 3.8, where atoms are represented as spheres. The interstices between the spheres are roughly triangular in cross section and can be divided into two groups, one pointing upwards (labeled *B*) and one pointing downwards (labeled *C*).

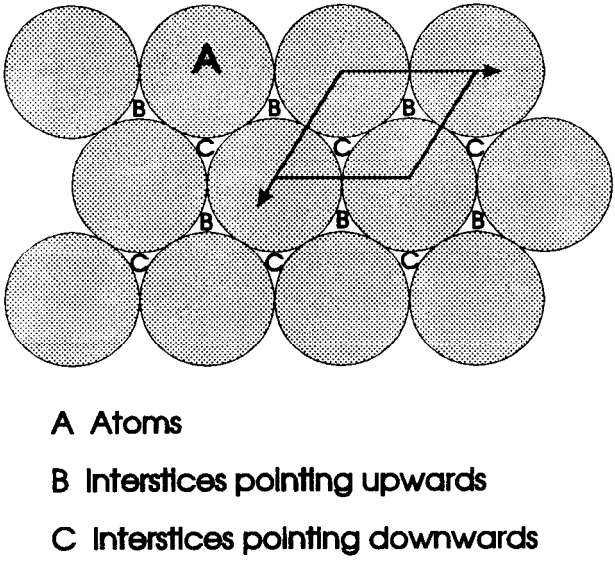


Figure 3.8: Schematic of the close packing of atoms

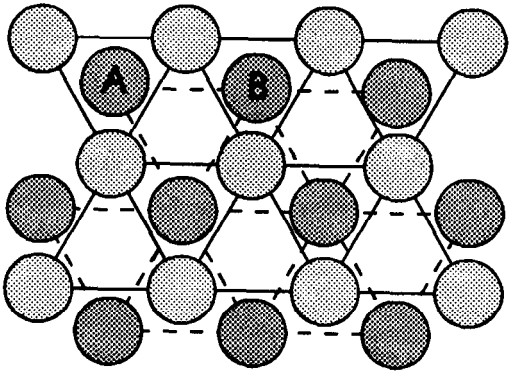
4.2 Hexagonal Close-Packed (*hcp*) and Face-Centered Cubic Close-Packed (*fcc*) Structures

The close-packed crystalline structures are either hexagonal close-packed (*hcp*) or face-centered cubic close-packed (*fcc*).[11][12] In a hexagonal close-packed structure, the atoms of the first layer are directly over those of the third layer and this planar arrangement is shown in Fig. 3.9a and 3.9b. The layer sequence is expressed as *ABAB* and the resulting crystal has a hexagonal symmetry.

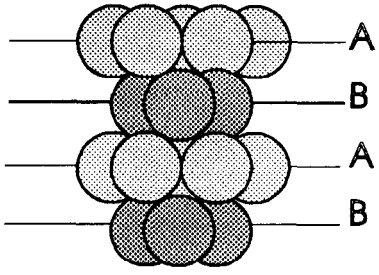
In a face-centered cubic close-packed structure, the successive layers are repeated in the layer sequence *ABCABC* as shown in Fig. 3.10a and 3.10b.

Another view of these two structures, hcp and fcc, is illustrated in Fig. 3.11.[10] In both cases, each packing atom has twelve equidistant nearest

neighbors (i.e., its coordination number is 12). These structures are compact with a volume per atom of only 5.66 R^3, R being the radius of the spherical atom.[12]

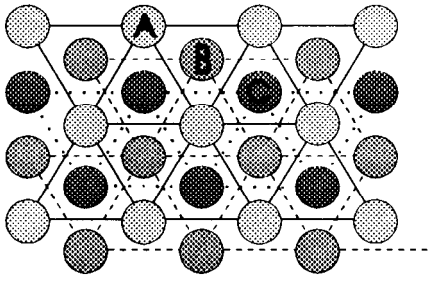


(a)

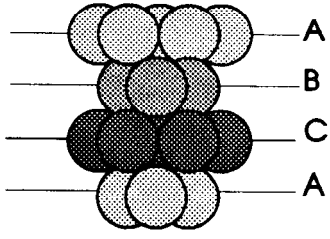


(b)

Figure 3.9: Schematic of a hexagonal close–packed (hcp) crystal structure. *(a)* Layer sequence viewed in the {001} direction. Two layers are shown. Note: (001) plane is expanded by a factor of two while diameter of atom is kept constant to show layer sequence. *(b)* Layer sequence viewed perpendicular to the {001} direction.



(a)



(b)

Figure 3.10: Schematic of a face–centered close–packed (fcc) crystal structure. *(a)* Layer sequence viewed in the {001} direction. Two layers are shown. Note: (001) plane is expanded by a factor of two while diameter of atom is kept constant to show layer sequence. *(b)* Layer sequence viewed perpendicular to the {001} direction.

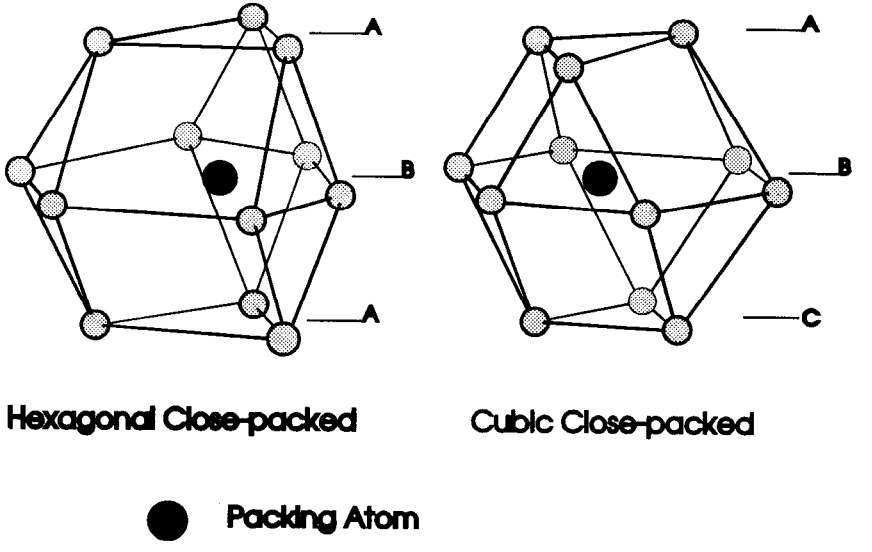


Figure 3.11: Schematic of the arrangement of the 12 nearest neighbors around one packing atom.

4.3 Body-Centered Cubic (*bcc*) and Simple Hexagonal Structures

Two other crystalline structures which are not close-packed must be mentioned here: the body-centered cubic (*bcc*) and the simple hexagonal (*hex*). The bcc structure is a common structure of early transition metals and is shown in Fig. 3.12. Each atom has only eight equidistant nearest neighbors instead of twelve for close-packed systems (coordination number = 8), and the structure has a lower density with a volume per atom of $6.16\ R^3$.[12][13]

The simple hexagonal (hex) unit cell is shown in Fig. 3.13 typically represented by the WC structure (see Sec. 5.0).

4.4 Crystal Structures of Early Transition Metals

The crystalline structures and lattice parameters of the early transition metals are shown in Table 3.2.

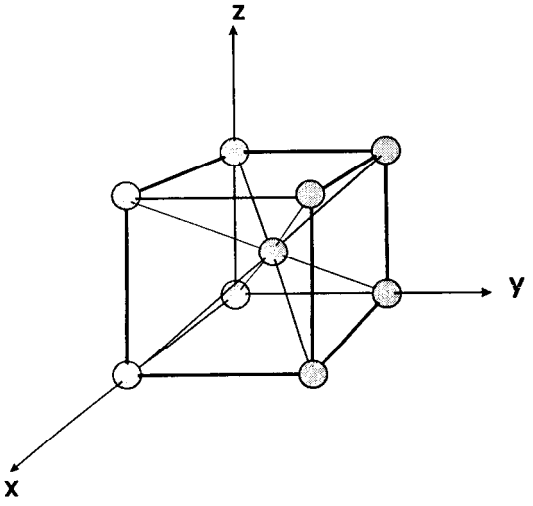


Figure 3.12: Schematic of the unit cell of a cubic body–centered (bcc) crystal structure.

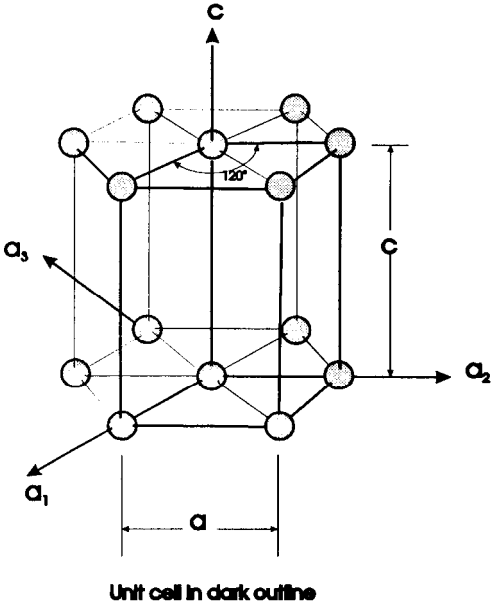


Figure 3.13: Schematic of the unit cell of a simple hexagonal (hex) crystal structure.

Table 3.2: Crystal Structure of Early Transition Metals

	Group IV Metals
Titanium	αTi: hcp (a_o = 0.2950, c_o = 0.4686), low-temp. form
	βTi: bcc (a_o = 0.3307), high-temp. form
	(transition temperature: 880°C)
Zirconium	αZr: hcp (a_o = 0.3232, c_o = 0.5147), low-temp. form
	βZr: bcc (a_o = 0.362), high-temp. form
	(transition temperature 750°C)
Hafnium	αHf: hcp (a_o = 0.3197, c_o = 0.5058), low-temp. form
	βHf: bcc
	(transition temperature 1750°C)
	Group V Metals
Vanadium	bcc (a_o = 0.3024)
Niobium	bcc (a_o = 0.3300)
Tantalum	bcc (a_o = 0.3306)
	Group VI Metals
Chromium	αCr bcc (a_o = 0.2884)
	βCr fcc (a_o = 0.368)
	γCr hcp (a_o = 0.2722, c_o = 0.4427)
Molybdenum	bcc (a_o = 0.3147)
Tungsten	bcc (a_o = 0.3165)

Note: Lattice parameters, expressed in nm, are shown in brackets

The metals of Group IV have two structures, a low-temperature one (α) which is hcp and a high-temperature one (β) which is bcc. Those of Group V and VI (with the exception of chromium) have only one structure.

5.0 ATOMIC STRUCTURE OF INTERSTITIAL CARBIDES

5.1 Definition of Interstitial Structures

An interstitial structure is one in which the ions or atoms of a nonmetallic element, typically carbon for carbides, nitrogen for nitrides, or hydrogen for hydrides, occupy certain interstitial sites within a metal lattice. Expressed in geometrical terms, the ratio of the radius of the interstitial atom to the radius of the atom of the host metal must be less than 0.59 for an interstitial structure to be formed.[12]

5.2 Atomic-Radii Ratio

As shown in Table 3.3, the nine early transition elements qualify as host structures for interstitial carbides, with the borderline exception of chromium. The radii ratio is smallest for the carbides of Group IV and highest for those of Group VI.[2,12]

Table 3.3: Carbon/Metal Atomic Radii Ratio of Interstitial Carbides

Group IV		Group V		Group VI	
Ti-C	0.526	V-C	0.576	Cr-C	0.609
Zr-C	0.483	Nb-C	0.530	Mo-C	0.556
Hf-C	0.486	Ta-C	0.529	W-C	0.553

Limit for interstitial formation: 0.59

5.3 Interstitial Sites

The metal atoms of a close-packed crystal structure, visualized as solid spheres, obviously cannot fill all the space available. The volumes (or voids) between them are known as interstitial sites. The polyhedron formed by connecting the centers of the spheres surrounding the void is either tetrahedral or octahedral (the void itself is not). A tetrahedron has four

plane faces and a tetrahedral site is shown in Fig. 3.14. An octahedron has eight plane faces and an octahedral site is shown in Fig. 3.15.

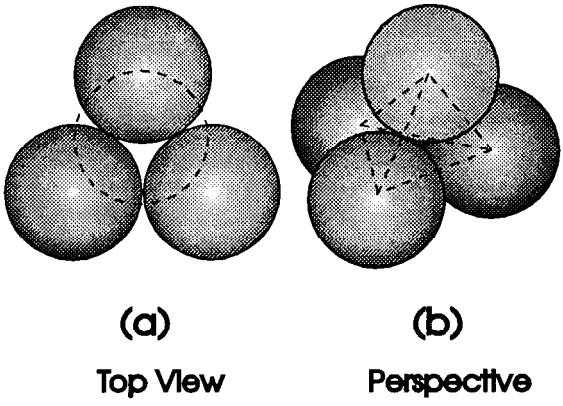


Figure 3.14: Schematic of a tetrahedral site formed by close–packed spheres.

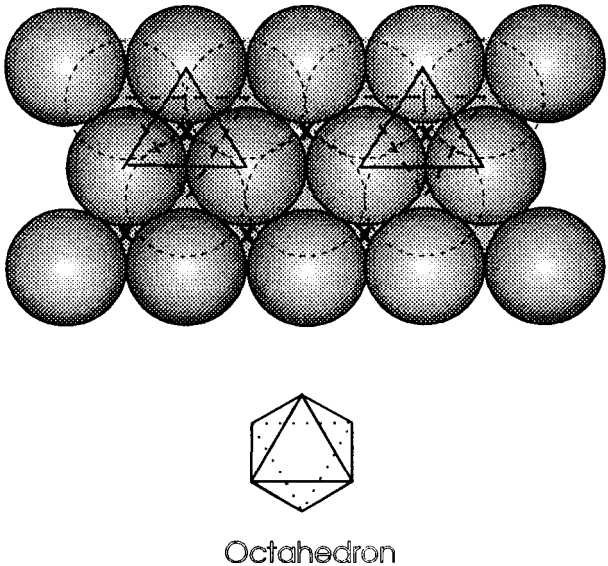


Figure 3.15: Diagram showing the location of the octahedral sites (x) between layers of close–packed spheres.

Tetrahedral interstitial sites are small and the largest atom able to fit into them without distorting the host lattice must have a radius no larger than 0.225 R, R being the radius of the metal atom. Octahedral interstitial sites are much larger and the largest atom able to fit into them without distorting the lattice can have a radius up to 0.59 R as mentioned in the previous section.

Closed-Packed Structures. In a close-packed interstitial carbide, the carbon atom is far too large to occupy a tetrahedral site and can only fit into an octahedral site. In these sites, it is octahedrally coordinated with the six metal atoms that surround it and thus achieves the highest possible coordination number. Since there is only one octahedral site per metal atom and if all are occupied by a carbon atom, a stoichiometric monocarbide is formed.

Simple Hexagonal Structures. Another site for the carbon atom is found in the simple hexagonal structure of tungsten carbide (WC) and chromium carbide (Cr_3C_2). This is a special case where metal-atom layers are not displaced laterally but are stacked directly over one another forming a sequence of layers *AA* or *BB*. Such structures are not close-packed and do not form octahedral sites; the available interstitial sites are trigonal prisms as shown in Fig. 3.16. To form a simple hexagonal structure, the ratio of the carbon atom radius to the metal atom radius must be greater than 0.53 (but less than 0.59); this is only possible with the carbides of Group VI as shown in Table 3.3.[12]

5.4 The Chromium Carbide Exception

Chromium carbide, with a carbon/metal atomic-radii ratio of 0.61, is a borderline case and, strictly speaking, belongs to the intermediate class of carbides (reviewed in Ch. 2, Sec. 5.3). Yet, unlike other intermediate carbides, it meets the refractory criteria and is a material of major industrial importance. For these reasons, it is included in this book (see Ch. 7).

6.0 CRYSTALLINE STRUCTURE AND COMPOSITION OF INTERSTITIAL CARBIDES

6.1 Crystalline Structure

As shown in the previous section, the ratio of the atomic radii of the elemental components (R_C/R_M) determines the suitability of a system to

form interstitial structures. It is also a factor in determining the type of crystal structure that the compound will adopt.

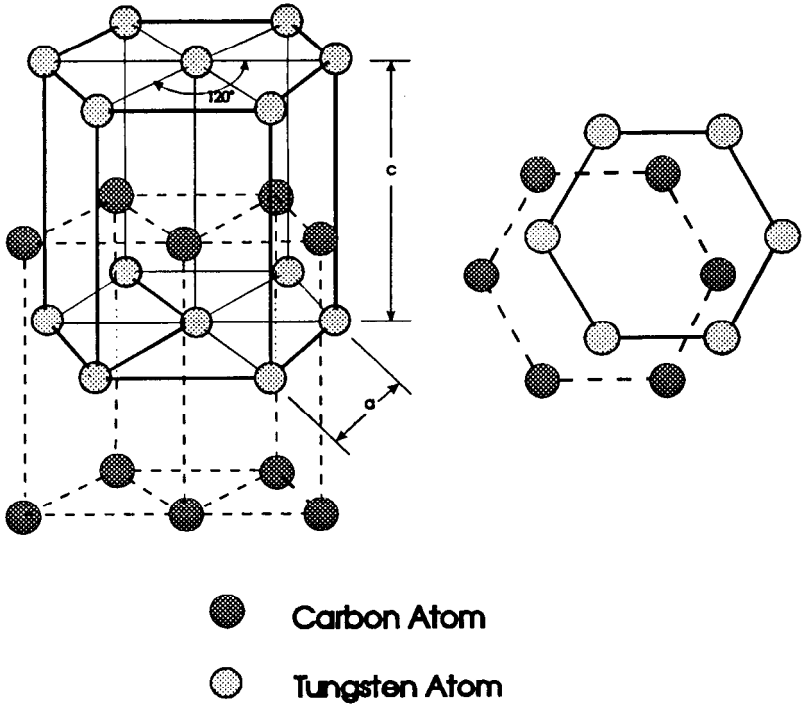


Figure 3.16: Schematic representation of the simple hexagonal (hex) structure of the tungsten carbide crystal.

6.2 Composition and Structure

The major compositions and structures of interstitial carbides are summarized in Table 3.4, and are reviewed in more detail for each carbide in Chs. 5, 6, and 7.[2][13]

The table shows that the structure and composition of interstitial carbides increase in complexity with increasing group number, but are generally similar within each group; it also shows that all monocarbides have a fcc structure and that the carbon to metal ratio is one or less.

The characteristics of each group are summarized in Table 3.5.

Table 3.4: Major Compositions and Structures of Interstitial Carbides

Group IV	Group V	Group VI
TiC_{1-x} (fcc)	V_2C (hcp) V_4C_3* V_6C_5* V_8C_7* VC (fcc)	$Cr_{23}C_6$ (fcc) Cr_7C_3* Cr_3C_2 (hex)
ZrC_{1-x} (fcc)	Nb_2C (hcp) Nb_3C_2* Nb_4C* NbC (fcc)	Mo_2C (hcp) Mo_3C_2* MoC (hex)
HfC_{1-x} (fcc)	Ta_2C (hcp) Ta_3C_2* Ta_4C_3* TaC (fcc)	W_2C (hcp) WC (hex)

fcc = face-centered cubic close packed
hcp = hexagonal close packed
hex = simple hexagonal
* unidentified

Table 3.5: Known Phases and Structures of Interstitial Carbides

Group IV Carbides

- Lowest carbon/metal atomic radii ratio
- Composition is monocarbide with carbon atoms in all octahedral sites (at stoichiometry)
- fcc structure (NaCl) only
- Structure of host metal is either hcp or bcc

Group V Carbides

- Intermediate carbon/metal atomic radii ratio
- Major composition is M_2C composition (stable phase) with carbon atoms occupying half the octahedral sites
- hcp and fcc structures
- Host metal has only one structure: bcc

Group VI Carbides

- Highest carbon/metal atomic radii ratio
- Several compositions
- fcc, hcp, and hexagonal structures
- Host metal has only one structure: bcc

6.3 Metal-to-Carbide Structural Switching

As shown in Table 3.2, most early transition metals have a bcc structure which is not geometrically suitable to accommodate the carbon atoms in its interstices. Consequently, in order to form a carbide, the metal must switch to a close-packed structure (fcc or hcp), which provides octahedral sites large enough for the carbon atoms and is in turn stabilized by them. The switch can be seen by comparing Tables 3.2 and 3.4.

This switch is accompanied by an increase of a few percent in the distance between the metal atoms, as shown in Table 3.6. This table compares the metal-to-metal (M-M) atomic spacing of the pure metals of Group IV and V and their M-M spacing within their monocarbide (MC) structure.[2][15] In every case, the M-M spacing increases when going from the pure metal to the carbide. The increase is more pronounced with the carbides of Group V than for those of Group IV. This factor influences the metallic bonding as reviewed in the following section.

Table 3.6: Atomic Spacing of Pure Metal and Monocarbide Host Metal

Carbide	M-M Spacing as Pure Metal* (nm)	M-M Spacing as Host Metal (nm)	Change (%) **
TiC	0.2934	0.3065	+ 4.46
ZrC	0.3194	0.3324	+ 3.91
HfC	0.3170	0.3294	+ 3.76
VC	0.2676	0.2923	+ 8.79
NbC	0.2912	0.3147	+ 7.46
TaC	0.2914	0.3131	+ 6.93

* For coordination number = 12

** Change going from the pure metal to the host metal in the carbide

This switch in the metal structure occurring when an interstitial carbide is formed has been used to assert that these compounds are not truly interstitial structures since the basic metal framework is modified.[15] This interpretation may be semantically correct but the use of the term interstitial is widespread and, if not entirely accurate, provides a visual and easy-to-grasp representation of the structure.

6.4 Density Considerations

Table 3.7 compares the density of the metals of Groups IV, V, and VI with the density of the corresponding interstitial carbides (for materials closest to stoichiometry) and the difference between the two in percent.[1][2]

Table 3.7: Density of Metals and Corresponding Interstitial Carbides

	Carbide	Carbide Density (g/cm^3)	Metal Density (g/cm^3)	Change (%) *
Group IV	TiC	4.91	4.54	+ 8.1
	ZrC	6.59	6.51	+ 1.2
	HfC	12.67	13.36	- 5.1
Group V	VC	5.65	6.11	- 7.5
	NbC	7.79	8.56	- 9.0
	TaC	14.5	16.6	- 12.6
Group VI	Cr_3C_2	6.68	7.20	- 7.2
	Mo_2C	9.06	10.22	- 11.3
	WC	15.8	19.3	- 18.1

* Change in density going from the host metal to the carbide

TiC and ZrC both have higher density than their respective metals, whereas the other carbides have lower density, possibly corresponding to a larger increase in M-M spacing occuring during formation of the monocarbide noted in Table 3.6.

7.0 ATOMIC BONDING OF INTERSTITIAL CARBIDES

7.1 Complexity of Bonding System

As shown in the preceding section, the spatial arrangement of interstitial carbides is relatively well established. How the carbon and metal atoms are held together is more uncertain. The subject is still controversial and a definite unified bonding scheme has yet to be devised. However, the understanding of this bonding, theoretically and experimentally, is progressing, particularly with the monocarbides which have been more thoroughly investigated than the other compositions. A point of general agreement is that the bonding system is complex.

The structural characteristics and properties of interstitial carbides are generally different from those one might expect from a simple solution of carbon atoms in the interstices of the transition metal, reflecting an obvious change in the atomic bonding.[12] Some of the major differences between the host metal and the carbide are as follows:

- The carbides are hard and brittle while the host metals are malleable and much softer
- The carbides have a high bond strength which exceeds by far the strength characteristics of the host metal[16]
- The melting point of the carbides is generally much higher than that of the parent metal (see Sec. 6.2 and Fig. 3.10)[17]
- A switch to a more stable structure occurs in every case when going from the metal to the carbide, as mentioned in Sec. 5.3

These differences indicate that interstitial carbides are held together by considerably stronger bonds than the purely metallic bonds of the parent metals. Indeed, it would be unreasonable not to expect metal-carbon bonding to contribute to the strength and stability of the structure.

7.2 Overall Bonding Scheme

The carbon atoms in an interstitial carbide can be considered as isolated atoms nesting, so to speak, within the framework of the metal atoms and with essentially no carbon-to-carbon bond since the spacing between carbon atoms is too large for any significant atomic interaction resulting from overlapping electron shells. The overall bonding scheme is then limited to metal-to-metal (M-M) and metal-to-carbon (M-C) bonds and combines the three types of bonding: ionic, covalent, and metallic, described in Ch. 2, Sec. 5.2.[18][19] It can be summarized as follows:

a. Ionic bonding resulting from a transfer of electrons from the metal to the carbon atom,

b. Metallic bonding with a finite density of states at the Fermi-energy level E_f,

c. Covalent bonding between metal *d*-state and the carbon *p*-state, with some metal-to-metal interaction.

These bonding schemes are examined in the following sections.

An accurate determination of the electronic band structure and density of states is essential to obtain a precise representation of structure of these carbides and understand their bonding mechanisms and the relation between bonding characteristics and properties. The band structure is usually well characterized and experimental observations are fairly extensive for the simpler carbides such as the carbides of Groups IV (Ti, Zr, Hf) and the monocarbides of Group V (V, Nb, Ta). However, the band structure for other compositions and non-stoichiometric compounds is not as thoroughly investigated and is not as well determined.[18][20]

7.3 Thermal Properties Considerations

Comparisons of the melting points of interstitial carbides and their host metals and the bond energies of these carbides give a qualitative view of the M-M and M-C bonds.

Comparison of Melting Point. The melting points are shown in Table 3.8 and Fig. 3.17. The Group IV carbides have much a higher melting point than their host metals. The differences are smaller for those of Group V, while in Group VI the reverse occurs as the metals have higher melting points than the corresponding carbides. Table 3.8 also shows the bonding energies of the monocarbides (Groups IV and V) are high, a fact that is

reflected by the high melting points of these materials.[14] Table 3.8 also compares the changes in density going from the carbide to the host metal as reported in Table 3,7. A point of interest is that the ratio of melting points (MP_c/MP_m) and the density changes (from metal density to carbide density) gradually and fairly evenly diminishes going from group IV to group VI.

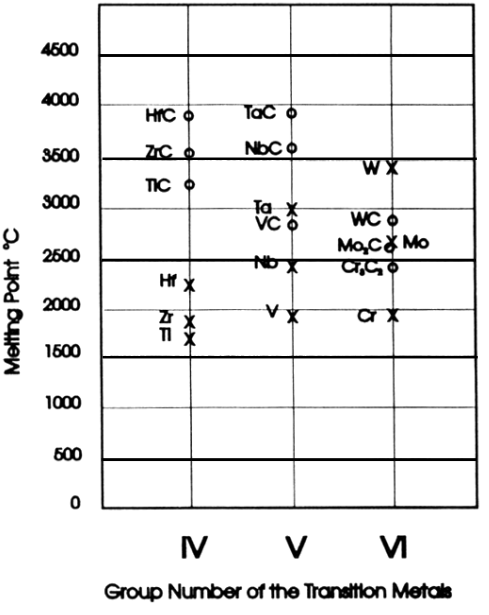


Figure 3.17: Comparison of melting points of interstitial carbides and their host metals

Assuming that the melting point of the metal can be used as a gauge of the M-M bond strength, i.e., the higher the melting point the higher the M-M bond strength, and the melting point of the carbide to gauge the M-C bond strength, the following qualitative trend can be established:[1]

Group IV	M-M bond weak	—	M-C bond very strong
Group V	M-M bond strong	—	M-C bond strong
Group VI	M-M bond very strong	—	M-C bond weak

Table 3.8: Bond Energy and Melting Point of Interstitial Carbides and their Host Metals

		Bond Energy E_o, eV	Melting Point (°C) Carbide	Metal	MP_c/MP^m	Density Change,%*
Group IV	TiC	14.66	3067	1660	1.9	+8.1
	ZrC	15.75	3420	1850	1.9	+1.2
	HfC	17.01	3928	2230	1.77	-5.1
Group V	VC	13.75	2830	1890	1.5	-7.5
	NbC	16.32	3600	2468	1.46	-9
	TaC	16.98	3950	2996	1.32	-12.6
Group VI	Cr_3C_2	-	1810	1865	0.97	-7.2
	Mo_2C	-	2520	2620	0.96	-11.3
	WC	-	2870	3410	0.84	-18.1

* Change in density going from the host metal to the carbide

Note: Variations in the thermal properties of interstitial carbides are often found in the literature, reflecting the difficulty of these measurements at such high temperatures and the essentially non-stoichimetric nature of interstitial carbides. The values given here are a general average.[13][14][16][17]

Heat of Formation. Properties such as heat of formation and standard entropy are important factors in determining the bonding nature of solids in general and carbides in particular.[2][18] Figure 3.18 shows the heat of formation of the transition metal carbides for near-stoichiometry compositions. Within each group, the absolute values are relatively close but decrease markedly when going from Group IV to Group VI.

These characteristics of the melting point and heat of formation show the greater stability of the carbides of Group IV which would imply that the bonding portions of their electron band structure are filled (i.e., a half-filled *d*-shell). The carbides of Group V and especially those of Group VI are less stable which may be related to the gradual filling of the antibonding portion of the bond.

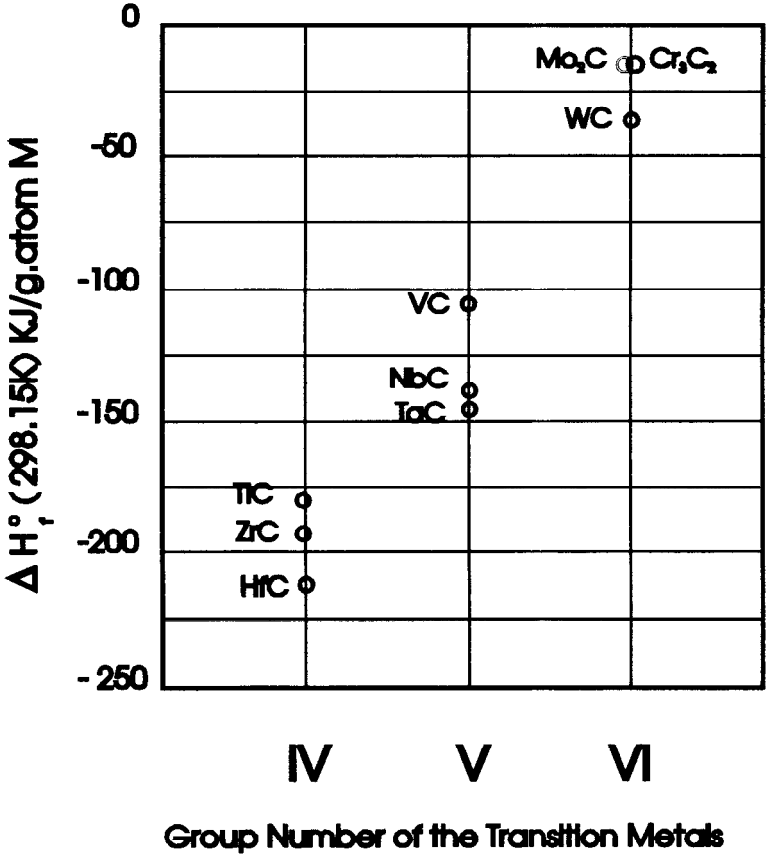


Figure 3.18: Heats of formation of interstitial carbides.

7.4 Ionic Bonding and Electronegativity

As mentioned in Ch. 2, electronegativity is the tendency of an element to gain electrons and form negative ions. The electronegativity of carbon is high while that of the early transition metals is low (see Ch. 2, Table 2.1). The differences are shown in Table 3.9.

Table 3.9: Difference in Electronegativity Between Carbon and Host Metal

Group IV		Group V		Group VI	
C-Ti	1.0	C-V	0.9	C-Cr	0.9
C-Zr	1.1	C-Nb	0.9	C-Mo	0.7
C-Hf	1.2	C-Ta	1.0	C-W	0.8

Ionic bonding results from the transfer of electrons from one atom to the other leading to an electrostatic interaction. A qualitative relationship between the difference in electronegativity and the ionic character of the bond is well recognized, the greater the difference, the greater the ionicity. For an electronegativity difference of one, the percentage ionic character is estimated at about 20%.[12] However, such estimation is valid for purely ionic structures and may not be entirely applicable to interstitial carbides.[21]

An ionic bonding contribution has definitely been established, particularly for TiC. It indicates a charge transfer from the titanium to the carbon, $M \rightarrow C$, of about half an electron, resulting in the formation of M^+ and C^- ions. This ionic bonding would be expected to be similar for the other carbides of Group IV and those of Group V but less significant for those of Group VI as the electronegativity difference decreases.[19][21]

7.5 Covalent Bonding in Interstitial Monocarbides

As opposed to ionic bonding which involves electron transfer, covalent bonding means the sharing of electrons. Interstitial carbides have some degree of covalent bonding (M-C and M-M) resulting mostly from interaction between the $2p$ state of the carbon (see Ch. 2, Sec. 3.1) and the d state of the metal (the unfilled d orbitals mentioned in Sec. 2.2), and also from interaction between metal atoms.[19]

In order to form a monocarbide, the valence electrons of the carbon atom hybridize with the *spd* band of the metal atom. It is likely that the metal orbitals are the d^2sp^3 hybridization since the typical octahedral grouping of the metal atoms centered on the carbon atom has six bonds to the six corners of the octahedron, thus favoring the M-C bond. Indeed, the d^2sp^3 hybridization is common in the Group IV metals (Ti, Zr, Hf).[12][21]

7.6 Bonding and Atomic Spacing

By using the geometrical constants of the structure of the interstitial monocarbides and of the individual atoms, Kisly has proposed a relative contribution of each bonding component, ionic and covalent, as shown in Table 3.10.[15]

Table 3.10: Metal-Carbon Bond Length and Deviation from Sum of Covalent (ΔC) and Ionic (ΔJ) Radii of Components

Carbide	Metal/Carbon Bond Length (nm)	Sum of Covalent Radii (nm)	ΔC (%)*	Sum of Ionic Radii (nm)	ΔJ (%)**
TiC	0.2158	0.2227	3.2	0.1437	-33.4
ZrC	0.2341	0.2467	5.4	0.1580	-32.5
HfC	0.2319	0.2432	4.9	0.1572	-32.2
VC	0.2059	0.2131	3.5	0.1321	-35.8
NbC	0.2216	0.2327	5.0	0.1458	-34.2
TaC	0.2205	0.2314	4.5	0.1444	-34.5

* % change going from M-C bond length to sum of covalent radii

** % change going from M-C bond length to sum of ionic radii

In this table, the measured length of the metal-carbon bond of each monocarbide is compared to the sum of the covalent radii of the metal and carbon atoms. The change, ΔC, is expressed in percentage. As can be seen,

it is small and does not exceed 5%. On the other hand, the difference between the M-C bond length and the sum of the ionic radii of the constituent (ΔJ) is considerably larger, the ionic radius being over 30% smaller in all observed cases. This would indicate that the M-C bond is much more covalent than ionic.

7.7 Metallic Bonding

The metallic character of the bond is partially retained as evidenced by a degree of metallic bonding (M-M) with a finite density of states at the Fermi energy and an appreciable electron density in the unit cell.[18] As a result, some properties such as thermal and electrical conductivity have strong metallic characteristics (see following three chapters).

7.8 Band Structure

Detailed reviews of the band structure of interstitial carbides were made by Schwarz,[19] Calais,[20] Neckel,[22] Ivanovsky,[23] and Redinger.[24] The band structure can be summarized as follows. The electronic energy spectra of these carbides are similar and contain bands of C2*s*, C2*p*–M*d,s,* and M*d,s,p* states (M = metal). When the valence concentration (VEC) in the elementary cell of the carbide is ≈ 8 (TiC, ZrC, and HfC), the Fermi level is found in the region of the density-of-state minimum between *p-d* and *d*-like bands. With VEC > 8 (carbides of Groups V and VI), the Fermi level is in the low-energy region of the metal states band.

8.0 INTERSTITIAL CARBIDES AS DEFECT STRUCTURES

8.1 Vacancies

Interstitial carbides are stable over a broad range of composition and can be considered to be essentially non-stoichiometric materials in which stoichiometry is rarely, if ever, reached. In other words, there are vacancies, that is, missing atoms within the lattice. These missing atoms are mostly carbon and only rarely are metal vacancies present. The amount of carbon vacancies can be considerable, reaching 50% in some cases. An example is given in Fig. 3.19 which represents the phase diagram of the binary system Ti-C.[2] The extensive homogeneity range is shown in the

shaded portion of the diagram. As a result of such a wide range of stable compositions, the interstitial carbides are usually considered as defect structures.

The lattice parameter varies with the composition as shown in the typical case of titanium carbide in Fig. 3.20.[1] One should note that the highest value of a_o occurs at a carbon/titanium ratio of approximately 0.85 and not at stoichiometry. This is also where the melting point is the highest.

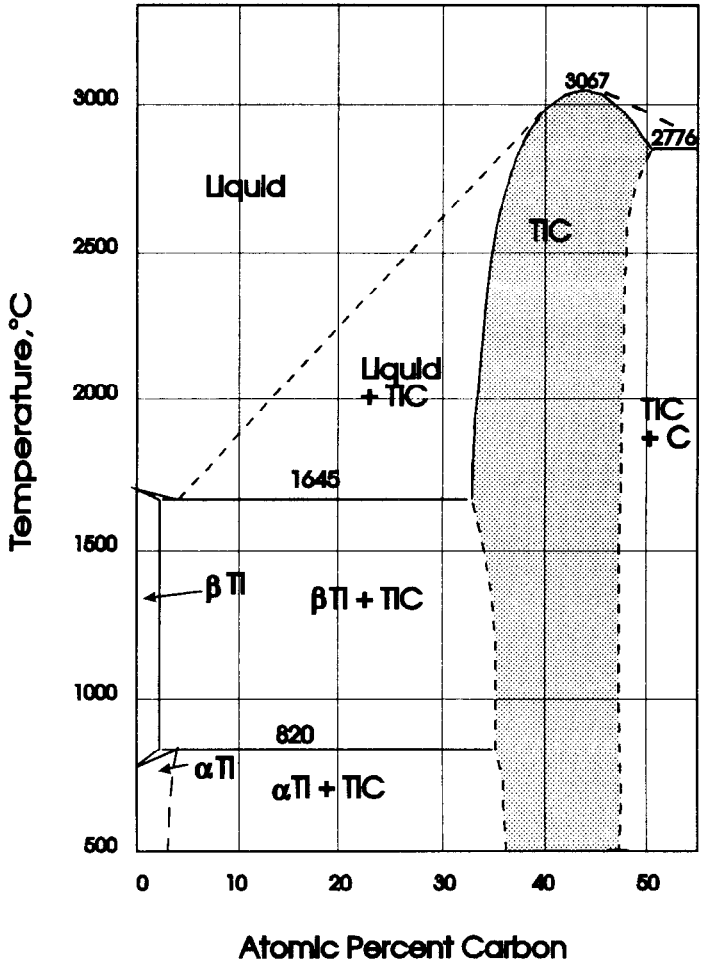


Figure 3.19: Carbon–titanium phase diagram. Homogeneity range shown in shaded section.[25]

8.2 Ordering of the Carbon Atoms

When the concentration of carbon-atom vacancies is high, a long-range ordering in their arrangement within the metal lattice is usually observed. The effect of this ordering on the structure and physical properties of the carbide may be considerable in some cases but the mechanisms of formation, the structural and bonding arrangement are still not well defined.[2][25][26]

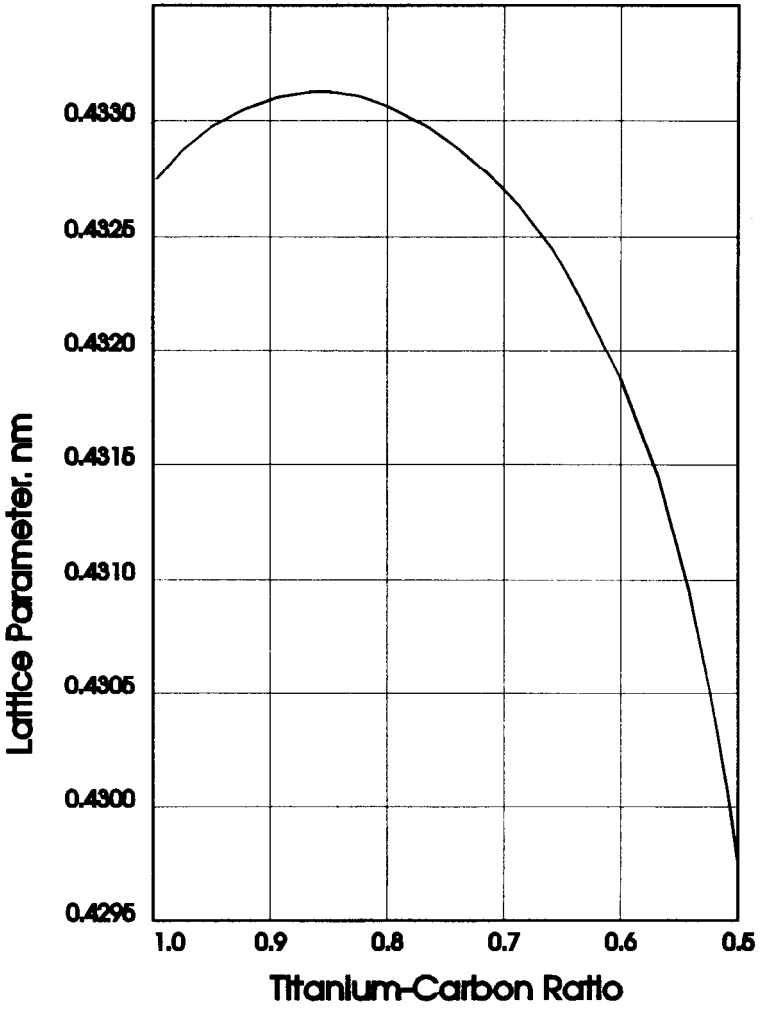


Figure 3.20: Lattice parameter of TiC as a function of composition.

9.0 GENERAL REVIEW OF THE PROPERTIES OF INTERSTITIAL CARBIDES

9.1 Variations in Properties and Composition

The relationship between structure and properties is often difficult to establish since the effects of atomic size, valencies, bond length, bond strength, stoichiometry, vacancies, and vacancy ordering are yet to be fully determined. A great deal of work is still needed.

Variations in composition and the presence of defects and vacancies may considerably alter the properties and behavior of these materials. This is reflected by the high spread of values found in the literature. In order to be meaningful, a property should be associated with the composition of the carbide being tested; this is often not the case and, although a great deal of information is available, the reported values are sometimes questionable. The data listed in the following chapters must be viewed with this in mind.

A reason for the high spread is, in addition to the variation in composition and other factors mentioned above, the paucity of large single crystals of high quality and uniformity. Measurements made on polycrystals and films have to contend with grain boundaries, grain growth, voids, and other defects which impart an additional measure of uncertainty in the results.[25]

Another reason is the effect of impurities, especially dissolved oxygen. Oxygen is difficult to remove altogether and may affect the physical properties of the material, particularly measurements of the lattice parameters.[1]

9.2 General Characteristics

As seen above, the atomic structure of interstitial carbides is a mixture of ionic, covalent, and metallic bonding. As a result, the properties of these compounds reflect this structural mix and combine metallic and ceramic characteristics as summarized in Table 3.11.

Table 3.11: General Properties of Interstitial Carbides as Related to Structural Bonding

Metallic bonding (metal-like properties)

- high thermal conductivity
- high electrical conductivity
- Hall constant close to host metal
- opacity and typical lustre
- indeterminate composition (like alloys)
- sequence of distinct phases

Covalent bonding (ceramic-like properties)

- high hardness
- high bond strength and brittleness
- very high melting point and refractoriness

Ionic bonding

- chemical behavior of ionic crystals
- high electron energy level
- electrodiffusion

Note: The properties of each interstitial carbide are reviewed in the following three chapters.

REFERENCES

1. Storms, E. K., *The Refractory Metal Carbides*, Academic Press, New York (1967)
2. Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)
3. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)
4. Wehr, M. R., Richards, J. A., Jr., and Adair, T. W., III, *Physics of the Atom*, Addison-Wesley Publishing Co., Reading, MA (1978)

5. Cram, D. J., and Hammond, G. S., *Organic Chemistry*, McGraw-Hill Book Co., New York (1964)
6. Eggers, D. F., et. al., *Physical Chemistry,* John Wiley & Sons, New York (1964)
7. Huheey, J. E., *Inorganic Chemistry*, Third Edition, Harper & Row, New York (1983)
8. March, J., *Advanced Inorganic Chemistry,* John Wiley & Sons, New York (1985)
9. Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry*, Interscience Publishers, New York (1980)
10. Adams, D. M., *Inorganic Solids*, John Wiley & Sons, New York (1981)
11. Pandey, D. and Krishna, P., Polytypism in Close-Packed Structures, in *Current Topics in Materials Science,* (E. Kaldis, ed.), pp. 415-491, North Holland Pub. Co., Amsterdam (1982)
12. Evans, R. C., *An Introduction to Crystal Chemistry*, Cambridge Univ. Press, Cambridge (1979)
13. Galasso, F. S., *Structure and Properties of Inorganic Solids*, Pergamon Press, New York (1970)
14. Kosolapova, T. Ya., *Carbides*, Plenum Press, New York (1971)
15. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd., Bristol, UK (1984)
16. Zhurakovskii, E. A., and Vasilenko, N. N., The State of the Carbon Atom in Transition Metal Carbides, in *Refractory Carbides,* (G. V. Sansanov, ed.), Consultant Bureau, New York (1974)
17. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
18. Fernandez Guillermet, A., and Grimvall, G., Cohesive Properties and Vibrational Entropy of 3d-Transition Metal Carbides, *J. Phys. Chem. Solids,* 53(1):105–125 (1992)
19. Schwarz, K., and Neckel, A., Chemical Bonding in Refractory Transition Metal Compounds, in *Science of Hard Materials* (E. A. Almond et al, eds.), Institute of Physics Conference Series No. 75, Adam Hilger Ltd., Bristol, UK (1984)
20. Calais, J. L., Band Structure of Transition Metal Compounds, *Advances in Physics*, 26(6):847-885 (1977)
21. Oyama, S. T., Crystal Structure and Chemical Reactivity of Transition Metal Carbides and Nitrides, *J. Solid State Chem.*, 96:442-445 (1992)

22. Neckel, A., Recent Investigations on the Electronic Structure of the 4th and 5th Group Transition Metal Monocarbides, Mononitrides, and Monoxides, *Int. J. of Quantum Chemistry*, Vol. XXIII, pp. 1317-1353 (1983)

23. Ivanovsky, A. L., Anisimov, V. I., and Gubanov, V. A., The Influence of Structural Defects on the Electronic Properties of Interstitial Alloys, *J. Phys. Chem. Solids,* 50(9):883-892 (1989)

24. Redinger, J., et. al., Vacancy Induced Changes in the Electronic Structure of Titanium Carbide, *J. Phys. Chem. Solids*, 36(3):383-393 (1985)

25. Sundgren, J. E., et. al., TiN_x Atomic Arrangement and Electronic Structure, *Am. Inst. of Physics Conf. Series* No. 149, New York (1986)

26. Moisy-Maurice, V, et. al., Neutron Scattering Studies of the Defect Structures in TiC_{1-x} and NbC_{1-x}, in *Science of Hard Materials*, (R. K. Viswanadham, ed.), Plenum Press, New York (1981)

4

Carbides of Group IV: Titanium, Zirconium, and Hafnium Carbides

1.0 GENERAL CHARACTERISTICS OF GROUP IV CARBIDES

This chapter is a review of the characteristics and properties of the interstitial carbides formed by the metals of Group IV: titanium, zirconium, and hafnium. The rationale for reviewing these compounds together in one chapter is their similarity in atomic bonding, composition, and crystallography as shown in Ch. 3 and summarized as follows:

- The metal-to-metal bond is relatively weak and the metal-to-carbon bond is strong
- The only stable composition is the monocarbide with carbon atoms in all octahedral sites (at stoichiometry)
- The major crystalline structure is ccp with a fcc B1 symmetry (NaCl)

These carbides also have similar properties and characteristics. Of the three, titanium carbide has been more investigated and is the most important from an application standpoint. It is produced industrially on a large scale in the form of powders, molded shapes, and thin films. The

fabrication processes and the applications of these three carbides are summarized in Secs. 6, 7, and 8 and reviewed in more detail in Chs. 14, 15, and 16.

2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP IV CARBIDES

In this section and the next three, the properties and characteristics of the interstitial carbides of Group IV are reviewed and compared with those of the host metals, the corresponding interstitial nitrides, as well as those of another refractory group: the borides of the Group IV metals . The values given are those for composition as close to stoichiometry as possible.[1]–[6] As mentioned in Ch. 3, Sec. 8.1, interstitial carbides are essentially non-stoichiometric compounds and the variations in the reported property values often found in the literature reflect this characteristic. The values given here are an average.[7]–[12]

2.1 Density and Melting Point

Density and melting point are shown in Table 4.1,

Table 4.1: Density and Melting Point of Group IV Interstitial Carbides and Other Refractory Compounds

Material	Density (g/cm^3)	Melting Point °C
TiC	4.91	3067
ZrC	6.59	3420
HfC	12.67	3928
Ti	4.54	1660
Zr	6.51	1850
Hf	13.36	2230
TiN	5.40	2950
ZrN	7.32	2980
HfN	13.8	3387
TiB_2	4.52	2980
ZrB_2	6.09	3040
HfB_2	11.20	3250

As could be expected, the density increases considerably with the increasing atomic number of the metal. The melting points of these carbides are higher in all cases than those of the other compounds and particularly those of the host metals.

2.2 Thermal Properties

The thermal properties are shown in Table 4.2.

Table 4.2: Thermal Properties of Group IV Interstitial Carbides and Other Refractory Materials

Material	Specific Heat at 298 K (J/mole·K)	Thermal Conductivity at 20°C (W/m·K)	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
TiC	33.8	21.0	7.4
ZrC	37.8	20.5	6.7
HfC	33.4	20.0	6.6
Ti	25.05	21.9	8.5
Zr	26.05	22.7	
Hf	26.27	23.0	6.0
TiN	33.74	19.2	9.3
ZrN	40.39	20.5	7.2
HfN	38.01	21.7	6.9
TiB_2	44.29	24.3	6.6
ZrB_2	48.26	24.3	6.6
HfB_2	49.77		6.8

Of note are the higher specific heats and thermal conductivities of the borides.

2.3 Thermodynamic Functions

The heat of formation and the standard entropy were reported in Ch. 3, Sec. 6.3 and Fig. 3.18 (see also Secs. 3, 4, and 5). High-temperature enthalpy data may be calculated by the following equation:

Eq. (1) $$H°_T - H°_{298.15K} = A + BT + CT^2 + DT^3 + (E/T)$$

The values of *A*, *B*, *C*, *D*, and *E* for TiC, ZrC, and HfC are given in Table 4.3.

Table 4.3: Thermodynamic Values of Group IV Carbides

	TiC	ZrC	HfC
A	-5.0007×10^{3}	-5.4298×10^{3}	-3.8886×10^{3}
B	+13.296T	+14.228T	+10.526T
C	$-9.7189\times10^{-4}T^2$	$-1.5583\times10^{-3}T^2$	$+1.0963\times10^{-3}T^2$
D	$+3.8451\times10^{-7}T^2$	$+4.6364\times10^{-7}T^3$	$-1.0149\times10^{-7}T^3$
E	$+4,2124\times10^{5}/T$	$+4.6364\times10^{5}/T$	$+1.9539\times10^{5/T}$

from 298–3000 K, in cal/mole ±0.5 %

The specific heat (C_p) of the Group IV carbides as a function of temperature is shown in Fig. 4.1.[13] C_p is also expressed as the first derivation of Eq. 1 above. Other thermal functions are detailed in Ref. 5.

2.4 Thermal Conductivity

The thermal conductivity or *k* (i.e., the time rate of transfer of heat by conduction) of interstitial carbides is different from that of most other refractory materials as *k* increases with increasing temperature as shown in Fig. 4.2.[13] Typically, the mechanism of thermal conductivity involves two components: electron thermal conductivity k_e and phonon (lattice) conductivity k_p. As shown in Fig. 4.3 (in this case for titanium carbide), k_e increases markedly with temperature. This behavior is believed to be the

result of strong scattering of electrons and phonons by carbon vacancies in addition to the scattering of electrons by polar optical phonons and the scattering of phonons by the conduction electrons.[9]–[12]

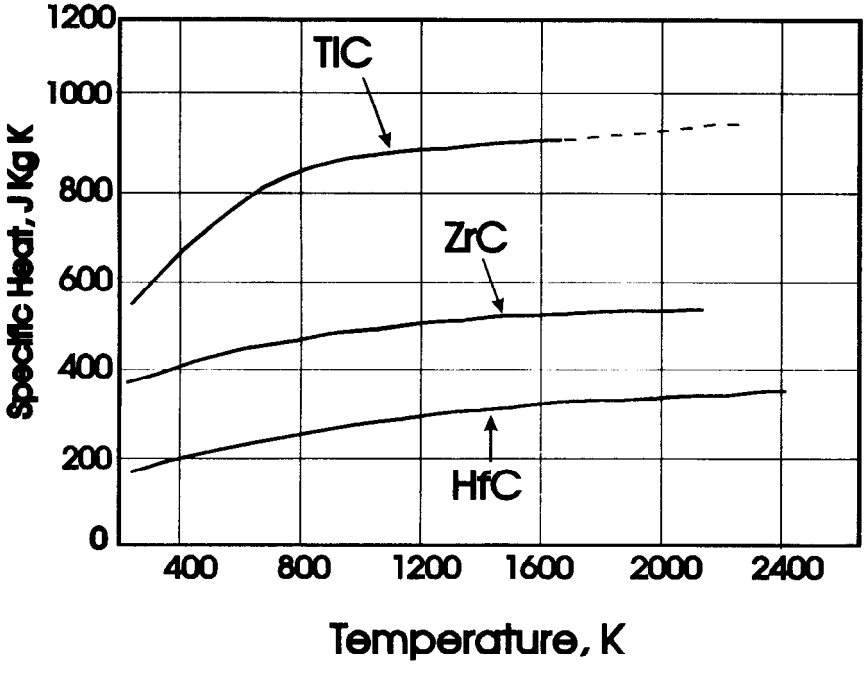


Figure 4.1: Specific heats of Group IV carbides as a function of temperature.[13]

As can be seen in Table 4.2, the thermal conductivities of the Group IV carbides, nitrides, and borides are relatively close. They are also similar to those of the host metals and, from this standpoint, reflect the metallic character of these compounds. However, their conductivities are much lower than that of the best conductors such as Type II diamond (2000 W/m·K), silver (420 W/m·K), copper (385 W/m·K), beryllium oxide (260 W/m·K), and aluminum nitride (220 W/m·K).[14]

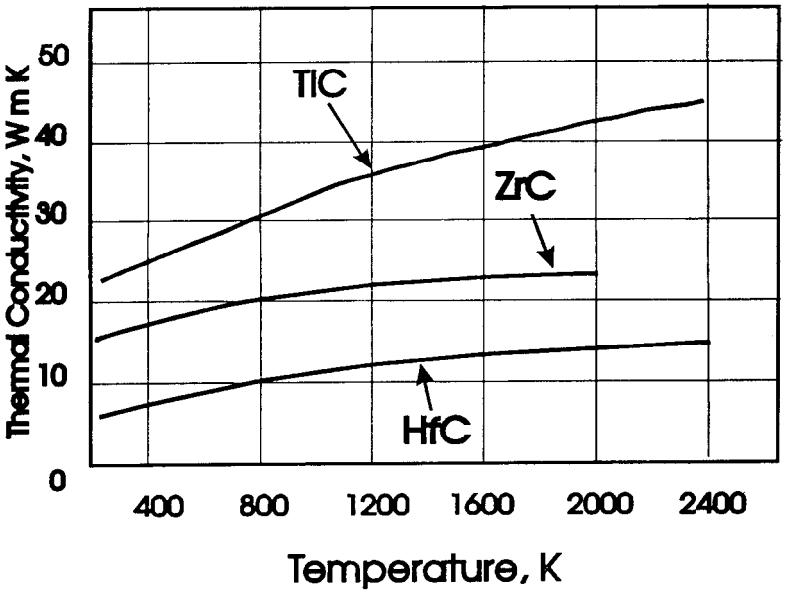


Figure 4.2: Thermal conductivities of Group IV carbides as a function of temperature.[13]

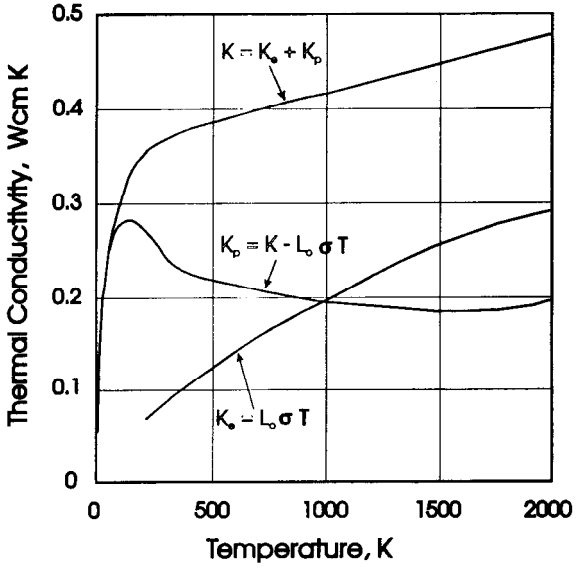


Figure 4.3: Thermal conductivity components of titanium carbide as a function of temperature: k_e = electron conductivity; k_p = phonon conductivity.

2.5 Thermal Expansion

The interatomic spacing between the atoms of a carbide (as with any other material) is a function of temperature. At zero degree K (-273°C), these atoms have their lowest energy position, that is, they are in the ground state (see Ch. 3, Sec. 2.1). The increased energy resulting from increasing temperature causes the atoms to vibrate and move farther apart. In other words, the mean interatomic spacing increases and the result is thermal expansion. In strongly bonded solids such as the carbides, the amplitude of the vibrations is small and the dimensional changes remain small. As shown in Table 4.4, the higher the bond energy, the lower the expansion. This correlation is also observed with the carbides of Group V (See Ch. 5, Sec. 2).

Table 4.4: Bond energy and Thermal Expansion of Group IV Carbides

Carbide	Bond Energy E_o, eV	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
TiC	14.20	7.4
ZrC	15.58	6.7
HfC	16.45	6.6

As shown in Fig. 4.4,[13] thermal expansion increases with increasing temperature but this increase is not linear and is slightly more rapid at high temperature.

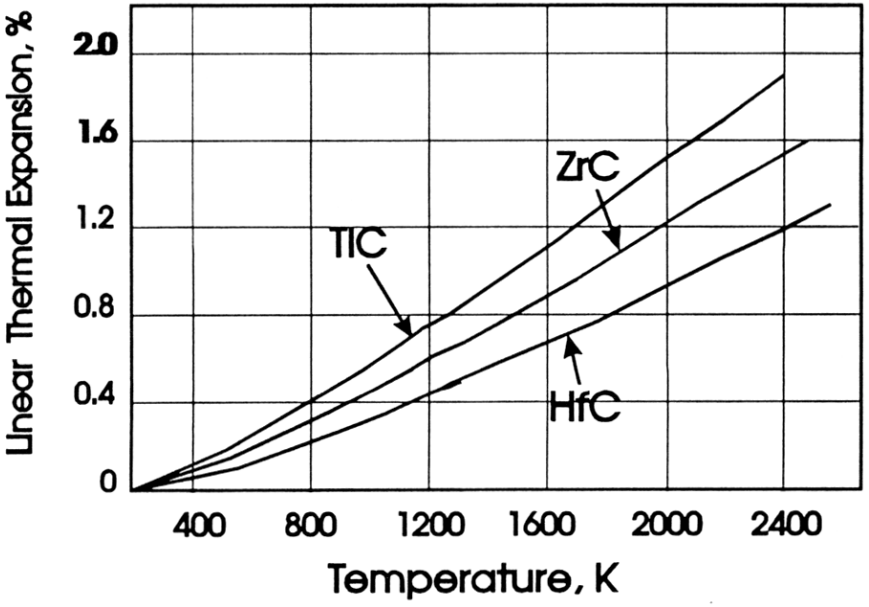


Figure 4.4: Linear thermal expansions of Group IV carbides as a function of temperature.

3.0 ELECTRICAL PROPERTIES OF GROUP IV CARBIDES

3.1 Electrical Conductivity

In electrical conductors such as metals, the attraction between the outer electrons and the nucleus of the atom is weak; the outer electrons can move readily and, since an electric current is essentially a flow of electrons, metals are good conductors of electricity. In electrical insulators (or dielectrics), electrons are strongly bonded to the nucleus and are not free to move. The electrical properties of Group IV carbides are shown in Table 4.5.[5][6][15]

Table 4.5: Electrical Properties of Group IV Interstitial Carbides and Other Refractory Compounds

Compound	Electrical Resistivity at 20°C ($\mu\Omega$·cm)	Hall Constant at 20°C 10^{-4} $cm^3/A{\cdot}s$	Magnetic Susceptibility 10^{-6} emu/mol
TiC	68	-15.0	-7.5
ZrC	43	-9.41	-30
HfC	37	-12.4	-37
Ti	43	-0.2	
Zr	43	+0.3	
Hf	35		
TiN	20–25	- 0.7 ±0.02	+38
ZrN	7–21	-1.3	+22
HfN	33		
TiB_2	9–15	-2.4	
ZrB_2	7–10		
HfB_2	10–12		

As shown in the above table, the Group IV carbides (and Groups V and VI carbides as well) are good electrical conductors and have an electrical resistivity only slightly higher than that of the parent metals, reflecting the metallic character of these compounds. The nitrides and especially the borides have even lower resistivity. The large spread in the reported values may be attributed to differences in composition and the presence of defects and impurities.

The magnetic susceptibility is strongly affected by the metal-to-carbon ratio, and the values listed here are extrapolated to stoichiometric composition.[5]

3.2 Hall Effect

The Hall effect occurs when a current-carrying conductor is placed in a magnetic field and is related to the difference between electron conduction and positive-hole conduction. Electron conduction is the dominant factor in the transition metal carbides which, with the exception of WC, all have a negative Hall constant. A discussion of the Hall effect in interstitial carbides is found in Ref. 15.

4.0 MECHANICAL PROPERTIES OF GROUP IV CARBIDES

4.1 Property Variables

The mechanical properties and the failure mechanisms of transition-metal carbides are reviewed in detail by Toth.[5] Generally, large spreads in the reported values found in the literature are common. This is particularly true in older reports which were mostly performed on sintered materials. More recently, testing has been switched to single crystals or polycrystalline materials obtained from the melt or by thin-film deposition. These are believed to yield more accurate and consistent information. Yet, any test must be carefully characterized in order to be meaningful. The following factors influence mechanical testing.[16][17]

- Stoichiometry
- Impurities particularly oxygen and nitrogen
- Grain size and morphology
- Grain orientation
- Structural defects (vacancies, dislocations)
- Presence of different phases

Transition metal carbides are often processed by sintering with a metal binder such as cobalt and nickel. The mechanical properties of such composites are often quite different from those of single crystal or polycrystalline materials.[18] This often adds to the confusion when quoting property values (see Ch. 17).

4.2 Summary of Mechanical Properties

The mechanical properties of Group IV carbides are summarized in Table 4.6. The values are average values reported in the recent literature.[1][16][17][19]–[21]

4.3 Failure Mechanism

Interstitial carbides are strong materials especially at high temperature. However, like most ceramics, they are intrinsically brittle. For example, metals have a fracture toughness that is generally some forty times greater than conventional ceramics. This brittleness of carbides is related on the atomic level to their strong hybrid ionic-covalent bonds which, as mentioned above, means a relatively weak metal-to-metal bond but a strong metal-to-carbon bond. These strong bonds prevent plastic deformation such as occurs in ductile metals. No plastic deformation means catastrophic brittle failure since applied stresses tend to concentrate at the sites of flaws such as voids or chemical impurities at grain interfaces. It follows that, if ceramics could be made without such flaws, they would be far more resistant to cracking. In reality, the actual strength of ceramics is only a small fraction of the theoretical strength.

Table 4.6: Mechanical Properties of Group IV Interstitial Carbides and Other Refractory Compounds at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)	Transverse Shear Modulus (GPa)	Rupture Strength (MPa)
TiC	28–35	410–510	186	240–390
ZrC	25.9	350–440	172	
HfC	26.1	350–510	193	
TiN	18–21	251		
ZrN	15.8	397		
HfN	16.3			
TiB2	15–45	480–563		240
ZrB_2	22.5			
HfB_2	29.0			

4.4 Ductile-Brittle Transition

The transition-metal carbides have the ability to deform plastically above a given temperature, i.e., the ductile-to-brittle transition temperature. Below that temperature, the carbides fail in a brittle manner while above it, they show a ductile behavior and undergo plastic deformation.[5] The transition temperature is not a fixed value but depends on several factors such as grain size, composition, and impurity content.[19] It is usually about 800°C.

4.5 Hardness

Hardness is a complex property which involves elastic and plastic deformation, crack initiation, and the development of new surfaces. It can be defined in terms of bonding energy, covalency level, atomic spacing, and by the parameters of fracture and deformation characteristics.[20] Hardness is dependent on the fabrication process, composition, and the presence of impurities. Table 4.6 shows that all the compounds of Group IV metals are hard, the carbides being the hardest, followed by the borides and the nitrides. The Group IV carbides have higher hardness than those of Groups V and VI (see Chs. 5 and 6). This reflects the greater strength of M-C bonds found in these carbides.

Hardness vs. Composition. Hardness varies with composition as shown in Fig. 4.5.[1] For the Group IV carbides, it appears to increase gradually until stoichiometry is reached. The Group V carbides have a different behavior and their hardness reaches a maximum somewhat below stoichiometry.

Hardness vs. Temperature. Hardness decreases rapidly with increasing temperature as shown in Fig. 4.6.[4][18] The exception is WC which maintains a high hardness until about 800°C (See Ch. 6, Sec. 8).

4.6 Transverse Rupture Strength

In the testing of tensile properties of brittle materials such as carbides, it is difficult to obtain perfect grip alignment without bending stresses that tend to give premature fracture. For that reason, tensile testing is not truly representative of the strength of these materials as it is in metals. Transverse bending (and particularly the 4-point bending test) is preferred.[22] As with

other properties, strength may vary considerably depending on the composition, the microstructure, the fabrication process, and other variables.

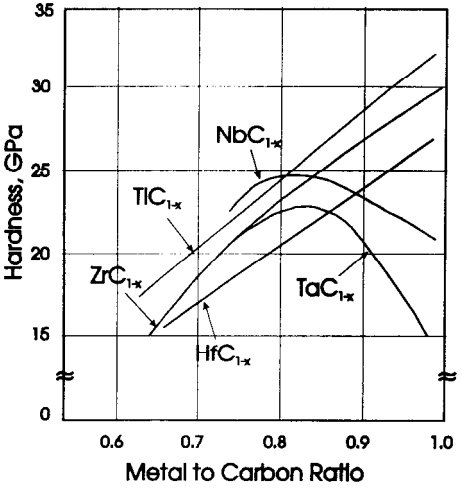


Figure 4.5: Hardnesses of refractory carbides as a function of metal–to–carbon ratio.

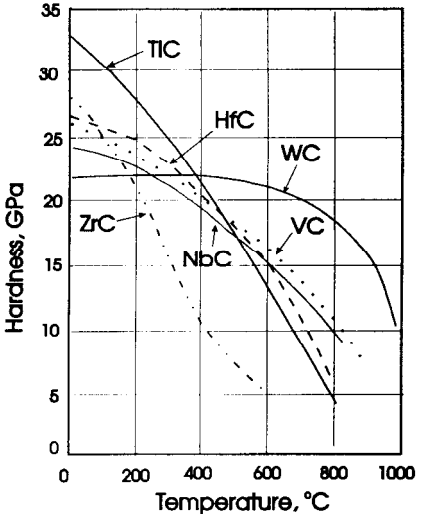


Figure 4.6: Hardnesses of refractory carbides as a function of temperature.

5.0 CHEMICAL PROPERTIES OF GROUP IV CARBIDES

5.1 Mutual Solubilities

A characteristic of the carbides of Group IV and the monocarbides of Group V is their mutual solubility as shown in Fig. 4.7.[1][4] This solubility is complete between each of the carbides of Group IV; it is also complete between those of Group V. Intergroup solubility (i.e., between Group IV and V) is also complete with the exception of VC which is only a partial solvent for the Group IV carbides and which, interestingly enough, has the largest carbon/metal atomic radii ratio (see Table 3.3 of Ch. 3). The solubility between the carbides of Groups IV and V and those of Group VI is reviewed in Ch. 6, Sec. 5.1. The carbides and the mononitrides of Group IV and V are also mutually soluble as shown in Fig. 4.8.[23]

Many ternary carbides and nitrides are known and some of these compounds have excellent properties. For instance, the hardness of ternary-carbide systems of the same group (Group IV or Group V) is considerably higher than the hardness of the binary constituents.[1] A hardness of approximately 43.1 GPa is reported for the compound $Ti_{0.6}Hf_{0.4}C$ as shown in Fig. 4.9, making it one of the hardest materials known. The system Ti(C,N) has also been extensively investigated and is a useful coating for wear resistance applications (see Ch. 16).

The study of these ternary (and quaternary) systems is an extensive and promising area but outside the scope of this book (for a general review of these systems, see Ref. 24).

5.2 Chemical Properties

The Group IV carbides are generally chemically inert[3] (see following three sections).

6.0 CHARACTERISTICS AND PROPERTIES OF TITANIUM CARBIDE

6.1 Summary of Properties

The characteristics and properties of titanium carbide are summarized in Table 4.7.

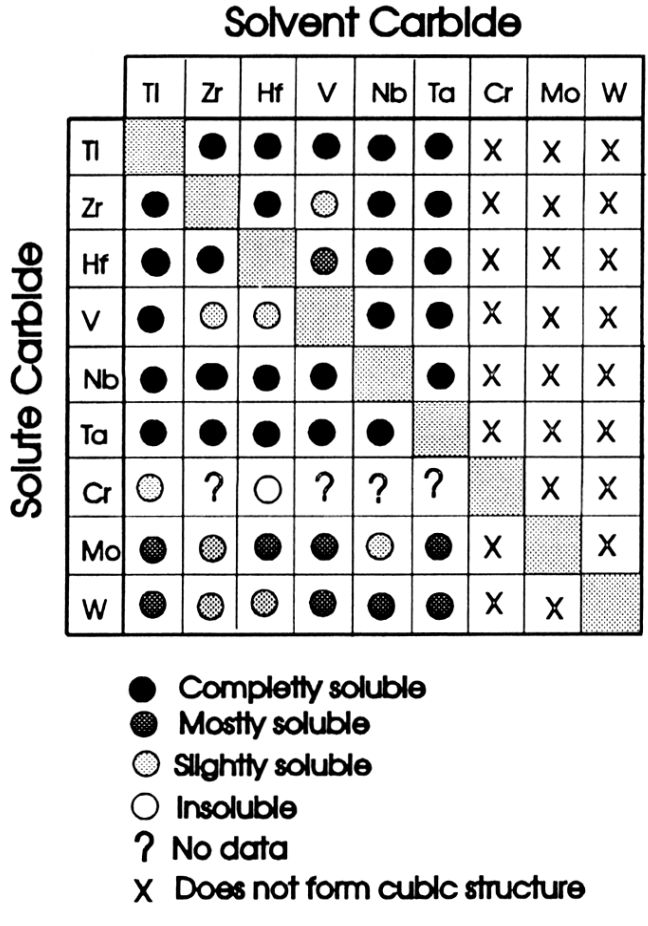


Figure 4.7: Mutual solubilities of refractory carbides.

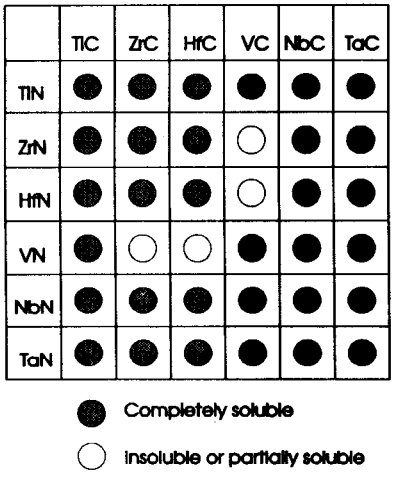


Figure 4.8: Mutual solubilities of Group IV and Group V carbides and nitrides.

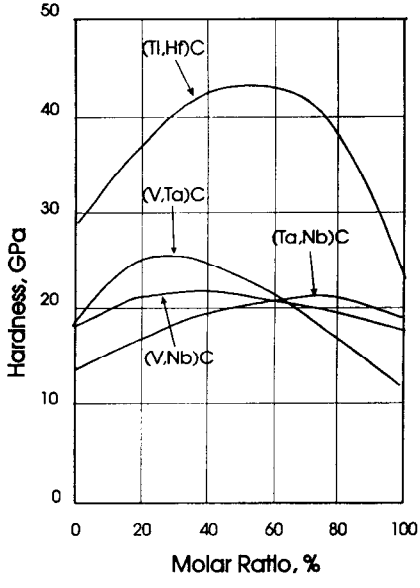


Figure 4.9: Hardnesses of ternary refractory carbides as a function of composition.

Table 4.7: Summary of Characteristics and Properties of Titanium Carbide. Note: Test temperature is 20°C unless otherwise stated.

Structure: cubic close packed (fcc. B1, NaCl)[25]
Lattice Parameter: 0.4328 nm
Space Group: *Fm3m*
Pearson Symbol: cF8
Composition: $TiC_{0.47}$ to $TiC_{0.99}$
Molecular Weight: 59.91 g/mol
Color: silver gray
X-ray Density: 4.91 g/cm^3

Melting Point: 3067°C (does not decompose)
Debye Temperature: 614 K
Specific Heat (C_p): 33.8 J/mole·K
Heat of Formation, -ΔH, at 298 K (kJ/g-atom metal): 184.6[5]
Thermal Conductivity (K): 21 W/m·°C (see Fig. 4.2 & 4.3)
Thermal Expansion: 7.4 x 10^{-6}/°C (see Fig.4.4)

Electrical Resistivity: 50 ± 10 μΩ·cm
Superconductive Transition Temperature: 1.15K
Hall Constant: - 15.0 × 10^{-4} cm·A·s
Magnetic Susceptibility: + 6.7 × 10^{-6} emu/mol

Vickers Hardness: 28–35 GPa
Modulus of Elasticity: 410–510 GPa
Shear Modulus: 186 GPa
Bulk Modulus: 240–390 GPa
Poisson's Ratio: 0.191
Transverse Rupture Strength: 240–390 MPa
Coefficient of Friction: 0.25 (on tool steel, 50% humidity)[26]

Oxidation Resistance: Oxidizes slowly in air at 800°C

Chemical Resistance: Resistant to most acids. Attacked by HNO_3 and HF. Attacked by the halogens. Can be heated in hydrogen to its melting point without decomposition.

Isomorphism: TiC is isomorphous with TiN and TiO. Thus oxygen and nitrogen as impurities, or as deliberate addition, can substitute for carbon to form binary and ternary solid solutions over a wide range of homogeneity. These solutions may be considered as Ti(C,N,O) mixed crystals. TiC forms solid solutions with the other monocarbides of Group IV and V. It is the host lattice for WC (see Ch. 6, Sec. 8).

6.2 Phase Diagram

The C-Ti phase diagram is shown in Fig. 3.12 of Ch. 3.[27][28]

6.3 Summary of Fabrication Processes

Titanium carbide powder is prepared by the reaction of TiO_2 with carbon at 2000°C or above in hydrogen; by the carburization of titanium sponge; by the auxiliary bath technique, or by plasma-CVD. Titanium carbide coatings are deposited by CVD, evaporation or sputtering (see Chs. 14 and 15).

6.4 Summary of Applications and Industrial Importance

Titanium carbide is extremely hard with high strength and rigidity and outstanding wear resistance. It has a low coefficient of friction and resists cold welding. It also has good stability at high temperature. For these reasons it has become a major industrial material as a secondary carbide in cemented tungsten-carbide cutting and grinding tools. It is also used as a coating for these tools, and in other mechanical and abrasive wear applications. However it is susceptible to chemical attack and is not a good diffusion barrier.

The following is a summary of applications of titanium carbide in production or development. More details are given in Ch. 16.

- Secondary carbide in cemented carbides
- Coatings for cutting and milling tools and inserts
- Coatings for stamping, chamfering and coining tools
- Ball-bearing coatings[29]
- Coatings for extrusion and spray gun nozzles
- Coatings for pump shafts, packing sleeves, and feedscrews for the chemical industry
- Coatings for molding tools and kneading elements for plastic processing
- Molded bipolar plates for high-voltage battery and fuel power sources[30]
- Coatings for fusion-reactor applications[31]

7.0 CHARACTERISTICS AND PROPERTIES OF ZIRCONIUM CARBIDE

7.1 Summary of Properties

The characteristics and properties of zirconium carbide are summarized in Table 4.8.

Table 4.8: Characteristics and Properties of Zirconium Carbide.
Note: Test temperature is 20°C unless otherwise stated.

Structure: cubic close packed (fcc B1, NaCl)
Lattice Parameter: 0.4698 nm
Space Group: *Fm3m*
Pearson Symbol: cF8
Composition: $ZrC_{0.55}$ to $ZrC_{0.99}$
Molecular Weight: 104.91 g/mol
Color: silver gray
X-ray Density: 6.59 g/cm^3

Melting Point: 3420°C (melts without decomposition)
Debye Temperature: 491 K
Specific Heat (C_p): 37.8 J/mole·K
Heat of Formation, -ΔH, at 298 K (kJ/g-atom metal): 196[5]
Thermal Conductivity: 20.5 W/m·°C (see Fig. 4.2)
Thermal Expansion: 6.7×10^{-6}/°C (see Fig.4.4)

Electrical Resistivity: 45 ± 10 μΩ·cm
Superconductive Transition Temperature: < 1.2 K
Hall Constant: -9.42×10^{-4} cm·A·s
Magnetic Susceptibility: -23×10^{-6} emu/mol

Vickers Hardness: 25.5 GPa
Modulus of Elasticity: 350–440 GPa
Shear Modulus: 172 GPa
Bulk Modulus: 207 GPa
Poisson's Ratio: 0.191

Table 4.8: *(Cont'd)*

Oxidation Resistance: Oxidizes in air at 800°C

Chemical Resistance: Not as chemically resistant as TiC. Dissolved by cold HNO_3 and by a cold mixture of H_2SO_4 and H_3PO_4. Reacts readily with the halogens. Can be heated in hydrogen to its melting point without decomposition.

Isomorphism: Like TiC, ZrC forms solid solutions with oxygen and nitrogen which have a wide range of composition. The lattices of ZrC, ZrN, and ZrO are isotypical. ZrC forms solid solutions with the other monocarbides of Group IV and V.

7.2 Phase Diagram

The Zr-C phase diagram is shown in Fig. 4.10.[27][28]

7.3 Summary of Fabrication Processes

Zirconium carbide powder is prepared by the reaction of ZrO_2 with carbon at 1800–2400°C in hydrogen; by the carburization of zirconium sponge; by the auxiliary bath technique, or by plasma-CVD. Zirconium carbide coatings are deposited by CVD, evaporation or sputtering (see Chs. 14 and 15).

7.4 Summary of Applications and Industrial Importance

Zirconium carbide is a highly refractory compound with excellent properties but, unlike titanium carbide, it has found only limited industrial importance except as coating for atomic-fuel particles (thoria and urania) for nuclear-fission power plants.[31] This lack of applications may be due to its high price and difficulty in obtaining it free of impurities.

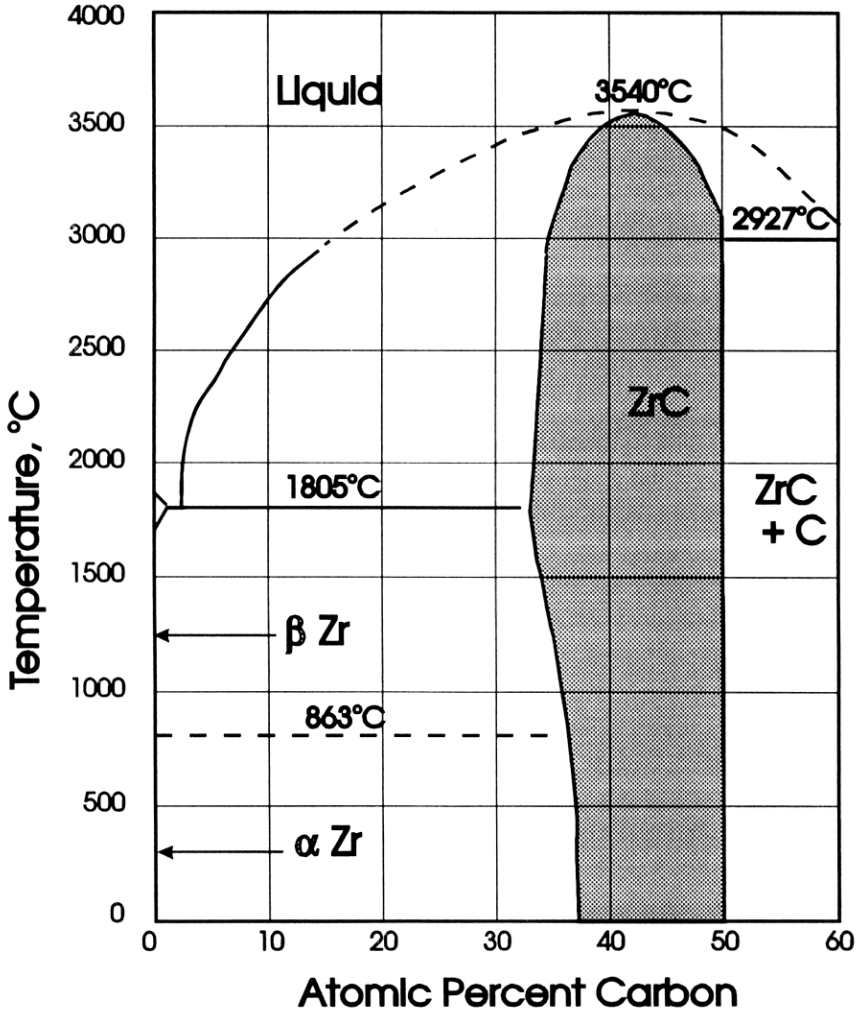


Figure 4.10: Carbon–zirconium phase diagram.

8.0 CHARACTERISTICS AND PROPERTIES OF HAFNIUM CARBIDE

8.1 Summary of Properties

The characteristics and properties of hafnium carbide are summarized in Table 4.9.

Table 4.9: Characteristics and Properties of Hafnium Carbide.
Note: Test temperature is 20°C unless otherwise stated.

Structure: cubic close packed (fcc B1, NaCl)
Lattice Parameter: 0.4636 nm
Space Group: *Fm3m*
Pearson Symbol: cF8
Composition: $HfC_{0.60}$ to $HfC_{0.99}$
Molecular Weight: 190.50 g/mol
Color: silver gray
X-ray Density: 12.67 g/cm^3

Melting Point: 3928°C (melts without decomposition)
Debye Temperature: 436 K
Specific Heat(C_p): 37.4 J/mole·K
Heat of Formation, -ΔH, at 298 K (kJ/g-atom metal): 209.6[5]
Entropy at 298.15 K (S°): 39.48 KJ/mol
Thermal Conductivity: 20.0 W/m·°C (see Fig. 4.2)
Thermal Expansion: 6.6 (× 10^{-6}/°C) (see Fig.4.4)

Electrical Resistivity: 37–45 μΩ·cm
Superconductive Transition Temperature: < 1.2K
Hall Constant: - 12.4 × 10^{-4} cm·A·s
Magnetic Susceptibility: -23 × 10^{-6} emu/mol

Vickers Hardness: 26.1 GPa
Modulus of Elasticity: 350–510 GPa
Shear Modulus: 193 GPa
Bulk Modulus: 241 GPa
Poisson's Ratio: 0.18

Table 4.9: (Cont'd)

Oxidation Resistance: Oxidizes in air at 500°C
Chemical Resistance: Not as chemically resistant as TiC. Chemical resistance similar to that of ZrC.

Isomorphism: Like TiC and ZrC, HfC forms solid solutions with oxygen and nitrogen which have a wide range of composition. HfC forms solid solutions with the other monocarbides of Group IV and V, particularly NbC and the solution HfC-NbC is used as coating for tools.[6]

8.2 Phase Diagram

The phase diagram of the Hf-C system is shown in Fig. 4.11.[27][28]

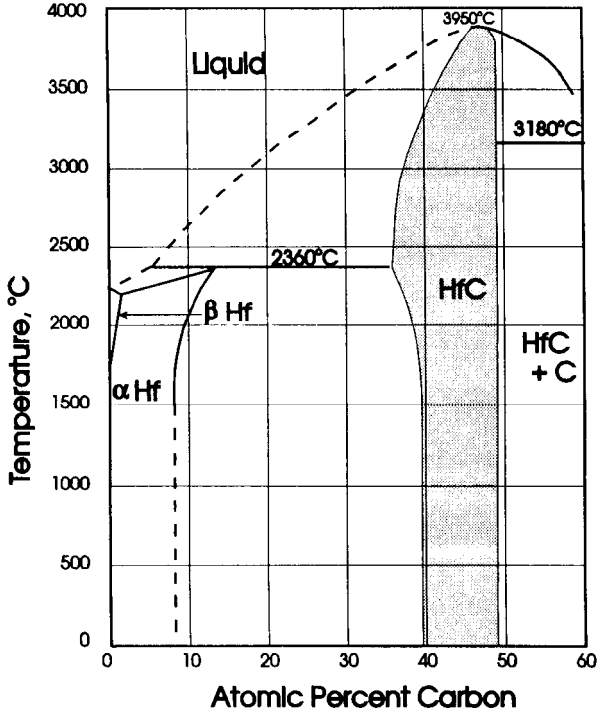


Figure 4.11: Carbon–hafnium phase diagram.

8.3 Summary of Fabrication Processes

Hafnium carbide powder is prepared by the reaction of HfO_2 with carbon at 1800–2200°C in hydrogen; by the carburization of hafnium sponge; by the carburization of hafnium hydride at 1600–1700°C, or by plasma CVD. Hafnium carbide coatings are deposited by CVD, evaporation or sputtering (see Chs. 14 and 15).

8.4 Summary of Applications and Industrial Importance

Hafnium carbide is, with tantalum carbide, the most refractory compound available. In spite of its excellent properties, it has only limited industrial importance, possibly because of its high cost (see Ch. 16). Some experimental applications are as follows:

- Oxidation resistant coatings for carbon-carbon composites (co-deposited with SiC)[33]
- Production of whiskers (with nickel catalyst)[34][35]
- Coating for superalloys[36]
- Coating on cemented carbides[6]

REFERENCES

1. Holleck, H., Material Selection for Hard Coatings, *J. Vac. Sci. Technol.*, A4 (6) (Nov/Dec. 1986)
2. Pierson, H. O., *Handbook of Chemical Vapor Deposition,* Noyes Publication, Park Ridge, NJ (1992)
3. Kosolapova, T. Ya., *Carbides*, Plenum Press, New York (1971)
4. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
5. Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)
6. Tulhoff, H., Carbides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
7. Pierson, H. O., Á Survey of the Chemical Vapor Deposition of Refractory Transition Metal Borides, in *Chemical Vapor Deposited Coatings*, American Ceramic Society, pp. 27–45 (1981)

8. Storms, E. K., *The Refractory Metal Carbides*, Academic Press, New York (1967)
9. Perecherla, A., and Williams, W. S., Room-Temperature Thermal Conductivity of Cemented Transition-Metal Carbides, *J. Amer. Ceram. Soc.*, 71(12):1130–1133 (1988)
10. Williams, W. S., High-Temperature Thermal Conductivity of Transition Metal Carbides and Nitrides, *J. Am. Ceramic Soc.*, 49(3):156–159 (1966)
11. Bethin, J. and Williams, W. S., Ambipolar Diffusion contribution to High-Temperature Thermal Conductivity of Titanium Carbide, *J. Am. Ceramic Soc.*, 60(9-10):424–427 (1977)
12. Frandsen, M. V. and Williams, W. S., Thermal Conductivity and Electrical Resistivity of Cemented Transition-Metal Carbides at Low Temperatures, *J. Am. Ceramic Soc.*, (74)6:1411–1416 (1991)
13. *Engineering Property Data on Selected Ceramics, Vol. 2, Carbides*, MCIC HB-07-2, Battelle Institute, Columbus, OH (1987)
14. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)
15. Storms, E. K., Phases Relationships and Electrical Properties of Refractory Carbides and Nitrides, in *Solid State Chemistry*, Vol 10 (L. E. Roberts, ed.), University Park Press, Baltimore (1972)
16. Ishizawa, Y., and Tanaka T., Fermi Surface Properties and Bonding Nature of TiB^2 and WC, in *Science of Hard Materials*, Institute of Physics Conf. Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
17. Sundgren, J. E., et. al., TiN Atomic Arrangement, Electronic Structure and Recent Results on Crystal Growth and Physical Properties of Epitaxial Layer, in *Physics and Chemistry of Protective Coatings*, American Inst. of Physics Conf. Proc., No. 149 (1986)
18. Sarin, V. K., *Cemented Carbide Cutting Tools*, in *Advances in Powder Technology*, (G, Y. Chin. ed.), ASM Materials Science Seminar, ASM, Metals Park, OH (1981)
19. Bunshah, R. F., *Mechanical Properties of Refractory Compounds Films*, in *Physics and Chemistry of Protective Coatings*, American Inst. of Physics Conf. Proc., No. 149 (1986)
20. Das, G., Masdiyasni, K. S., and Lipsitt, H. A., Mechanical Properties of Polycrystalline TiC, *J. Amer. Ceramic Soc.*, 65(2):104–110 (1982)
21. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials, Institute of Physics Conf.*, Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
22. Callister, W. D., *Materials Science and Engineering. An Introduction*, John Wiley & Sons (1991)

23. Benesovsky, F., Kiefer, R., and Ettmayer, P., *Nitrides*, in *Kirk-Othmer's Encyclopedia of Chemical Technology,* 4th. Ed., Vol. 15, VCH (1993)

24. Rudy, E., *Compendium of Phase Diagrams,* Air-Force Materials Laboratory Report, AFML TR 65-2, Part V (June 1969)

25. Lowther, J. E., Molecular Orbital Studies of Refractory Metal Carbides, in *Institute of Physics Conf.,* Series No. 75, Ch. 1, Adam Hilger Ltd., London (1986)

26. Hintermann, H. E., Tribological and Protective Coatings by Chemical Vapor Deposition, *Thin solid Films*, 84:215-243 (1981)

27. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)

28. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. Edition, ASM International, Metals Park, OH (1990)

29. Boving, H. J., and Hintermann, H. E., Properties and Performance of Chemical Vapor Deposited TiC-Coated Ball Bearing Components, *Thin Solid Films*, 153:253–266 (1987)

30. *Abstracts of Phase I Awards*, No. 80, SBIR, US Department of Commerce (1993)

31. Mullendore, A. W., Whitley, J. B., and Mattox, D. M., Thermal Fatigue Testing of Coatings for Fusion Reactor Applications, *Thin Solid Films*, 83:79–85 (1981)

32. Ogawa, T., Ikawa, K., High Temperature Heating Experiments on Unirradiated ZrC-Coated Fuel Particles, *J. Nucl. Mater.*, 99(1):85–93 (July 1981)

33. Pierson, H. O., Sheek, J., and Tuffias, R., *Overcoating of Carbon-Carbon Composites,* WRDC-TR-4045, Wright-Patterson AFB, OH (Aug. 1989)

34. Lackey, W., Hanigofsky, J., and Freeman, G., Experimental Whisker Growth and Thermodynamic Study of the Hafnium-Carbon System for Chemical Vapor Deposition Applications, *J. Amer. Ceram. Soc.*, 73(6):1593–1598 (1990)

35. Futamoto, M., Yuito, I., and Kawabe, U., Hafnium Carbide and Nitride Whisker Growth by Chemical Vapor Deposition, *J. Cryst. Growth*, 61(1):69–74 (Jan. Feb. 1983)

36. Hakim, M., Chemical Vapor Deposition of Hafnium Nitride and Hafnium Carbide on Tungsten Wires, *Proc. 5th Int. Conf. on CVD* (J. Blocher, et. al., eds.), pp. 634–649, Electrochem. Soc., Pennington, NJ (1975)

5

Carbides of Group V: Vanadium, Niobium and Tantalum Carbides

1.0 GENERAL CHARACTERISTICS OF GROUP V CARBIDES

This chapter is a review of the characteristics and properties of the interstitial carbides formed by the metals of Group V: vanadium, niobium, and tantalum. These three carbides have similar atomic bonding, composition, and crystallography as shown in Ch. 3. These common points can be summarized as follows:

- Both metal-to-metal and metal-to-carbon bonds are strong
- Unlike the carbides of Group IV, they have two compositions: a subcarbide M_2C with carbon atoms in half the octahedral sites, and a monocarbide MC with carbon atoms in all octahedral sites (at stoichiometry)
- They have two crystalline structures: hcp (M_2C) and ccp (MC) with a fcc B1 symmetry (NaCl)

These carbides also have similar properties and characteristics. Only the monocarbide phases are of industrial importance. TaC is produced on a relatively large scale while the importance of VC and NbC is still limited. Their fabrication processes and applications are summarized in Sections 6, 7, and 8 and reviewed in more detail in Chs. 14, 15, and 16.

2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP V CARBIDES

In this section and the next three, the properties and characteristics of the interstitial carbides of Group V are reviewed and compared with those of the parent metals and their nitrides and borides. The values given are those for compositions as close to stoichiometry as possible.[1]-[7] The properties in most cases are similar to those of the Group IV carbides and the remarks stated in Ch. 4 also apply here.

2.1 Density and Melting Point

Density and melting point are shown in Table 5.1.

Table 5.1: Density and Melting Point of Group V Interstitial Carbides and Other Refractory Compounds

Material	Density (g/cm^3)	Melting Point °C
VC	5.65	2830
V_2C	5.75	2187
NbC	7.79	3600
Nb_2C	7.85	3080
TaC	14.5	3950
Ta_2C	14.8	3330
V	6.11	1890
Nb	8.56	2468
Ta	16.6	2996
VN	6.0	2177
NbN	7.3	near 2400
TaN	14.3	3093
VB_2	5.10	2100
NbB_2	7.21	3050
TaB_2	12.60	3200

As could be expected, the density increases considerably with the increasing atomic number of the metal. The melting point of the carbides is higher in all cases than that of the other materials.

2.2 Thermal Properties

The thermal properties are shown in Table 5.2.[8]

Table 5.2: Thermal Properties of Group V Interstitial of Monocarbides and Other Refractory Materials

Material	Specific Heat at 298 K (J/mole·K)	Thermal Conductivity at 20°C (W/m·K)	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
VC	32.3	38.9	7.2
NbC	36.8	14.2	6.6
TaC	36.4	22.1	6.3
V	24.75	30.7	8.0
Nb	24.43	53.7	7.3
Ta	25.33	57.5	6.5
VN	38.00	11.3	8.7
NbN	39.01	3.8	10.1
TaN	40.60	8.78	8.0
VB_2			7.6
NbB_2		16.7	8.0
TaB_2		10.9	8.2

Thermodynamic Functions.[5] Like the carbides of Group IV, the high-temperature enthalpy data for the Group V carbides is provided by the equation: $H^o_T - H^o_{298.15K} = A + BT + CT^2 + DT^3 + (E/T)$. The values of A, B, C, D, and E are given in Table 5.3.

Table 5.3: Thermodynamic Values of Group V Carbides

	VC*	NbC**	TaC**
A	-3.0347×10^{3}	-4.0918×10^{3}	-3.7468×10^{3}
B	$+7.8928T$	$+10.8561T$	$+10.1132T$
C	$+2.4967\times10^{-3}T^{2}$	$+9.1724\times10^{-4}T^{2}$	$-1.2668\times10^{-3}T^{2}$
D	$-3.3282\times10^{-7}T^{3}$	$-5.2003\times10^{-8}T^{3}$	$-8.0868\times10^{-8}T^{3}$
E	$+1.3964\times10^{5}/T$	$+2.3105\times10^{5}/T$	$+1.8517\times10^{5}/T$

* from 298–2500 K, in cal/mole.± 1%

** from 298–3000 K, in cal/mole.± 0.3%

Specific Heat. The specific heat (C_p) of the Group V carbides as a function of temperature is shown in Fig. 5.1 and is similar to that of Group IV carbides.[9] Other thermal functions are detailed in Ref. 5.

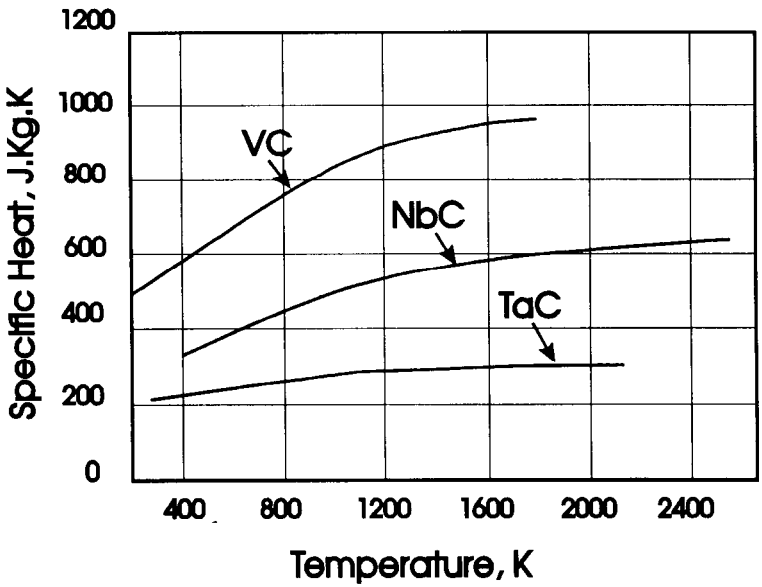


Figure 5.1: Specific heats of Group V carbides as a function of temperature.

Thermal Conductivity. The thermal conductivity (k) of Group V carbides is relatively high and similar to that of the Group IV, showing the metallic character of these compounds (for discussion, see Sec. 2.4 of Ch. 4). It is slightly lower than that of the host metals. It increases with increasing temperature as shown in Fig. 5.2 (only values for NbC are available).[9]

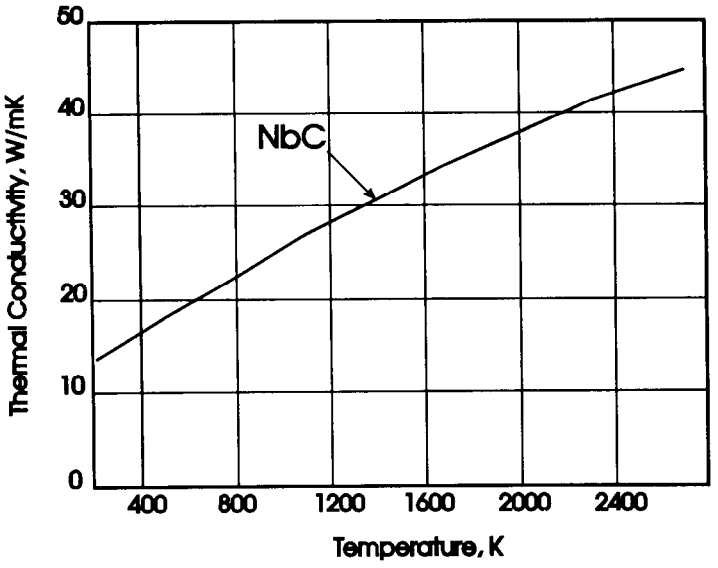


Figure 5.2: Thermal conductivity of niobium carbide as a function of temperature.

Thermal Expansion. Like the carbides of Group IV, the Group V carbides have a low thermal expansion (for discussion see Ch. 4, Sec. 2.5). As shown in Table 5.4, the higher the bond energy, the lower the expansion. The thermal expansion as a function of temperature is shown in Fig. 5.3,[9] and like that of the other interstitial carbides, it increases slightly with increasing temperature.

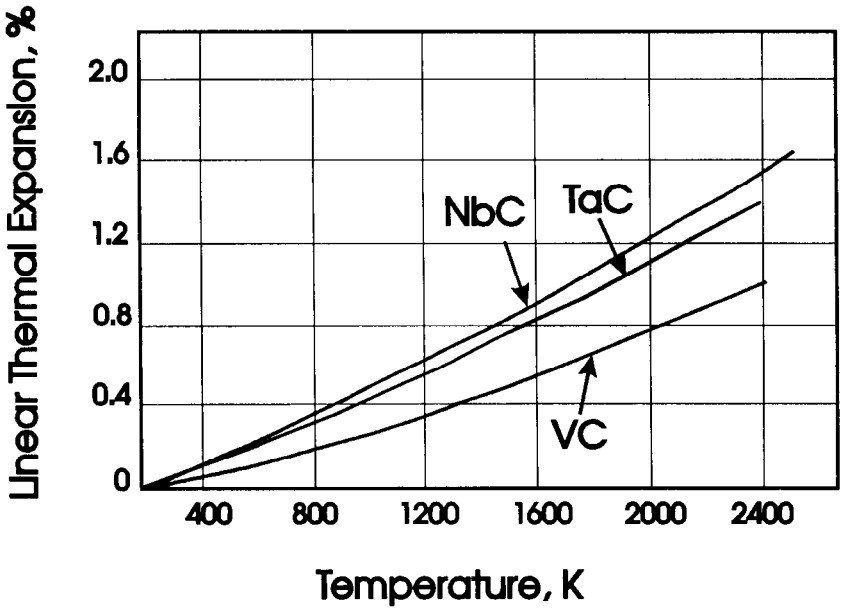


Figure 5.3: Linear thermal expansions of Group V carbides as a function of temperature.

Table 5.4: Bond energy and Thermal Expansion of Group V Carbides

Carbide	Bond Energy E_o, eV	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
VC	14.63	7.2
NbC	16.62	6.6
TaC	16.92	6.3

3.0 ELECTRICAL PROPERTIES OF GROUP V CARBIDES

Like the other interstitial carbides, the Group V carbides are electrical conductors (see Ch. 4, Sec. 3.1). Their electrical properties are shown in Table 5.5.[5][6][10]

Table 5.5: Electrical Properties of Group V Interstitial Carbides and Other Refractory Compounds

Compound	Electrical Resistivity at 20°C ($\mu\Omega$·cm)	Hall Constant at 20°C 10^{-4} $cm^3/A{\cdot}s$	Magnetic Susceptibility 10^{-6} emu/mol
VC	60	- 0.48	+ 35
NbC	35	- 1.3	+ 20
TaC	25	- 1.1	+ 12
V	24–26		
Nb	12.5	+ 0.9	
Ta	12.4	+ 1.0	
VN	85		
NbN	58–78	- 0.52	+ 31
TaN	135–250		
VB_2	13		
NbB_2	12		
TaB_2	14		

The electrical resistivity of the carbides is only slightly higher than that of the host metals, reflecting the metallic character of these compounds and their strong metal-to-metal bond. The nitrides and especially the borides have lower resistivity. The Hall constant is negative, like that of the Group IV carbides (see Sec. 3.2 of Ch. 4).

4.0 MECHANICAL PROPERTIES OF GROUP V CARBIDES

The mechanical properties of Group V carbides are summarized in Table 5.6. The values are average values reported in the recent literature[1][5][6][9][11] (see Sec. 4.1 of Ch. 4).

Table 5.6: Mechanical Properties of Group IV Interstitial Carbides and Other Refractory Compounds at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)	Shear Modulus (GPa)	Transverse Rupture Strength (MPa)
VC	27.2	430		
NbC	19.6	338–580	214	300–400
TaC	16.7	285–560	214	350–400
VN	14.2	357		
NbN	13.3	493		
TaN	11.0			
VB_2	20.9	261		
NbB_2	23.2			
TaB_2	22.6	248		

The fracture mechanism and the ductile-brittle transition are similar to those of the Group IV carbides (see Sec. 4, Ch. 4).

Hardness. Table 5.6 shows that carbides are the hardest, followed by the borides and the nitrides. The Group V carbides have higher hardness than those of Group VI but are not quite as hard as those of Group IV (see Ch. 4, Sec. 4.4 and Ch. 6, Sec. 4.0). This reflects the intermediate strength of M-C bonds found in these carbides.

Hardness varies with composition as shown in Fig. 4.5 of Ch. 4 (see comments in Ch. 4, Sec. 4.4). Maximum hardness occurs with a carbon to metal ratio of about 0.8. It decreases with temperature as shown in Fig. 4.6 (Ch. 4).

5.0 CHEMICAL PROPERTIES OF GROUP V CARBIDES

5.1 Mutual Solubilities

The existence of ternary carbides and nitrides was discussed in Ch. 4, Sec. 5.0. As shown in Fig. 4.7 (Ch. 4), VC, NbC, and TaC have complete mutual solubility and variable solubility with the carbides of Group IV. With the partial exception of VC, they are also mutually soluble with the nitrides of Groups IV and V (see Fig. 4.8).[12]

5.2 Chemical Properties

The Group V carbides are chemically stable and have a chemical resistance similar to that of the Group IV carbides.[3]

6.0 CHARACTERISTICS AND PROPERTIES OF VANADIUM CARBIDE

6.1 Summary of Properties

The properties of vanadium carbide as summarized in Table 5.7.

Table 5.7: Characteristics and Properties of Vanadium Carbide.

Note: 1. When phase is not indicated, value reported is for VC.
2. Test temperature is 20°C unless otherwise stated.

Phases: V_2C, VC

Structure and Lattice Parameter (nm):

αV_2C (low temperature phase):

orthorhombic, $a = 0.2873$, $b = 1.0250$, $c = 0.4572$

βV_2C (high temperature phase):

hexagonal, $a = 0.290$, $c = 0.4587$

VC: fcc B1 (NaCl), $a = 0.4159$

Table 5.7: *(Cont'd)*

Space Group and Pearson Symbol:	
	αV_2C: Pbcn, oP12
	βV_2C: $P6_{23}/mmc(b)$, hP3
	VC: Fm3m, 3F8
Composition:	$VC_{0.73}$ to $VC_{0.99}$
Molecular Weight:	V_2C: 113.89 g/mol
	VC: 62.953 g/mol
Color:	gray
X-ray Density:	V_2C: 5.75 g/cm^3
	VC: 5.65 g/cm^3
Melting Point:	2830°C
Debye Temperature:	V_2C 490 K
	$VC_{0.88}$ 659 K
Specific Heat (C_p):	32.3 J/mol·K (see Fig. 5.1)
Heat of Formation:	($-\Delta H_f$) at 298 K (kJ/g-atom metal)[5]
	V_2C 69.0
	VC 102.6

Thermal Conductivity (K): 38.9 W/m·°C at 20°C

Thermal Expansion: 7.3×10^{-6}/°C at 20°C (see Fig. 5.3)

Electrical Resistivity: 60 μΩ·cm

Superconductive Transition Temperature: < 1.2K

Hall Constant: -0.48×10^{-4}cm^3/A·s

Magnetic Susceptibility: $+ 26.2 \times 10^{-6}$ emu/mol

Vickers Hardness: 27.2 GPa

Modulus of Elasticity: 430 GPa

Shear Modulus: 157 GPa

Bulk Modulus: 390 GPa

Poisson's Ratio: 0.22

Oxidation Resistance: Oxidizes in air at 800°C

Chemical Resistance: Resistant to cold acids, except HNO_3. Easily dissolved by hot oxidizing acids. VC can be heated in hydrogen to its melting point without decomposition.

Isomorphism. VC, VN, and VO have isotypical structures and form solid solutions where nitrogen or oxygen can substitute for carbon over a wide range of homogeneity. These solutions may be considered as V(C,N,O) mixed crystals. VC forms solid solutions with the other monocarbides of Group V and TiC, and with TiN, NbN, and TaN.[13]

6.2 Phase Diagram

The V-C phase diagram is shown in Fig. 5.4.[14,15] At high temperature, only the VC and VC_2 phases are found. These phases react peritectictally at ≈1320°C to form the V_4C_{3-x} phase. More complicated phases are formed at lower temperature.

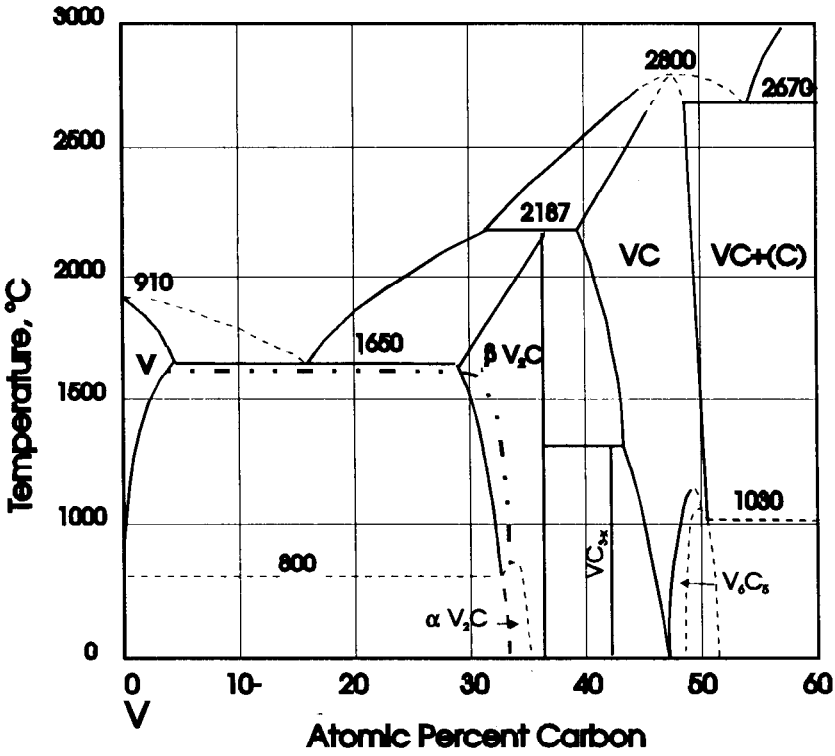


Figure 5.4: Carbon–vanadium phase diagram.

6.3 Summary of Fabrication Processes

VC powder is prepared by the reaction of vanadium oxide or ammonium vanadate with carbon at 1500–1700°C in hydrogen followed by a vacuum heat treatment. The reaction of vanadium metal with carbon under vacuum is also used. VC coatings are deposited by CVD, evaporation or sputtering (see Chapters 14 and 15).

6.4 Summary of Applications and Industrial Importance

The monocarbide VC is the only phase produced industrially but its use is limited. The following is a summary of its applications in production or development (see Ch. 16).

- Grain-growth inhibitor in WC-cobalt hard metals
- In steel alloys where it forms during melting

7.0 CHARACTERISTICS AND PROPERTIES OF NIOBIUM CARBIDE

7.1 Summary of Properties

The properties of niobium carbide are summarized in Table 5.8.

Isomorphism. NbC, NbN, and NbO have isotypical structures and form solid solutions where nitrogen or oxygen can substitute for carbon over a wide range of homogeneity. These solutions may be considered as Nb(C,N,O) mixed crystals. NbC forms solid solutions with the carbides of Group IV and the other monocarbides of Group V, and with the nitrides of Group IV and V.[13]

7.2 Phase Diagram

The C-Nb phase diagram is shown in Fig. 5.5.[14,15] Nb_2C has two phases: γNb_2C, a disordered hexagonal phase which transforms above 2500°C into βNb_2C and an ordered hexagonal phase.

Table 5.8: Characteristics and Properties of Niobium Carbide.

Note: 1. When phase is not indicated, value reported is for NbC.
2. Test temperature is 20°C unless otherwise stated.

Phases: Nb_2C, NbC

Structure and Lattice Parameter (nm):
Nb_2C hexagonal, a = 0.3122, c = 0.4964
NbC ccp, a = 0.44691

Space Group and Pearson Symbol.
Nb_2C C3m, hP3
NbC Fm3m, cF8

Composition: $NbC_{0.70}$ to $NbC_{0.99}$

Molecular Weight: Nb_2C 197.82 g/mol
NbC 104.92 g/mol

Color: gray sometimes with a lavender tint

X-ray Density : Nb_2C 7.79 g/cm^3
NbC 7.85 g/cm^3

Melting Point: Nb_2C 3080°C (decomposes)
NbC 3600°C (melts without decomposition)

Debye Temperature: Nb_2C 662 K
NbC 546 K

Specific Heat (C_p): 36.8 J/mole-K (see Fig. 5.1)

Heat of Formation ($-\Delta H_f$) at 298 K (kJ/g-atom metal)[5]
Nb_2C 97.5
NbC 140.6

Thermal Conductivity: 14.2 W/m·°C at 20°C (see Fig. 5.2)

Thermal Expansion: 6.6×10^{-6}/°C at 20°C (see Fig. 5.3)

Electrical Resistivity: 35 μΩ·cm

Superconductive Transition Temperature: 6 K

Hall Constant: -1.3×10^{-4}cm^3/A·s

Magnetic Susceptibility: $+15.3 \times 10^{-6}$ emu/mol

Vickers Hardness: 19.65 GPa

Table 5.8: *(Cont'd)*

Modulus of Elasticity: 338-580 GPa

Shear Modulus: 214 GPa

Bulk Modulus: 296 GPa

Poisson's Ratio: 0.21

Transverse Rupture Strength: 300-400 MPa

Oxidation Resistance: oxidizes in air at 800°C

Chemical Resistance: Reacts with nitrogen and ammonia at high temperature to form NbN. Less chemically resistant than TaC. Dissolved by hot oxidizing acids.

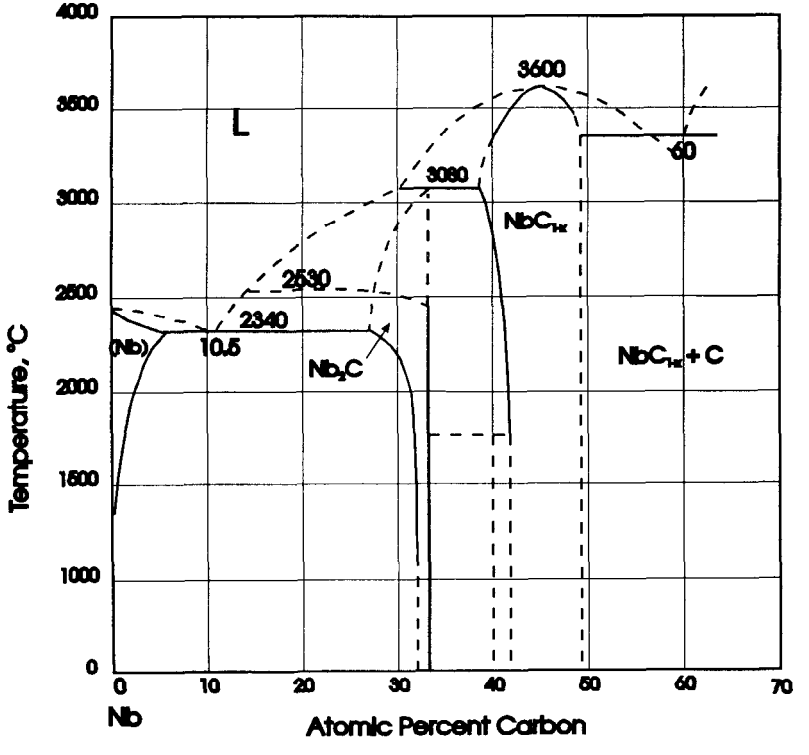


Figure 5.5: Carbon–niobium phase diagram.

7.3 Summary of Fabrication Processes

NbC powder is prepared by the reaction of niobium oxide with carbon at 1700°C in hydrogen. The reaction of niobium metal or niobium hydride with carbon under vacuum is also used. NbC coatings are deposited by CVD, reactive evaporation, or sputtering (see Chs. 14 and 15).

7.4 Summary of Applications and Industrial Importance

The monocarbide NbC is the only phase found industrially but its use is limited. It is found mostly in combination with TaC in 10, 20, or 50 wt% NbC. The following is a summary of its applications in production or development (see Ch. 16).

- In special grades of cemented carbides in combination with alumina
- With TaC to improve the properties of cemented carbides

8.0 CHARACTERISTICS AND PROPERTIES OF TANTALUM CARBIDE

8.1 Summary of Properties

The properties of tantalum carbide are summarized in Table 5.9.

Table 5.9: Characteristics and Properties of Tantalum Carbide.

Note: 1. When phase is not indicated, value reported is for TaC.
2. Test temperature is 20°C, unless otherwise stated.

Phases. Ta_2C, TaC

Structure, Lattice Parameter (nm).

Ta_2C Orthorhombic, a = 0.2873, b = 1.0250, c = 0.4572

TaC ccp, a = 0.4455

Space Group and Pearson Symbol.

Ta_2C	P3m1, hP3
TaC	Fm3m, 3F8

Table 5.9: *(Cont'd)*

Composition:	$TaC_{0.73}$ to $TaC_{0.99}$	
Molecular Weight:	Ta_2C	373.91 g/mol
	TaC	192.96 g/mol
Color:	brown, gold	
X-ray Density:	Ta_2C	14.8 g/cm^3
	TaC	14.5 g/cm^3
Melting Point:	Ta_2C	3330°C (decomposes)
	TaC	3950°C (melts without decomposing)
Debye Temperature:	Ta_2C	378 K
	TaC	489 K

Specific Heat (C_p): 36.4 J/mole·K (see Fig. 5.1)

Heat of Formation: ($-\Delta H_f$) at 298 K (kJ/g-atom metal)[5]

Ta_2C	104.2
TaC	142.7

Thermal Conductivity: 22.1 W/m·°C at 20°C

Thermal Expansion: 6.3×10^{-6}/°C at 20°C (see Fig. 5.3)

Electrical Resistivity: 25 μΩ·cm

Superconductive Transition Temperature: 10.3K

Hall Constant: -1.1×10^{-4}cm^3/A·s

Magnetic Susceptibility: $+9.3 \times 10^{-6}$ emu/mol

Vickers Hardness: 16.7 GPa

Modulus of Elasticity: 285-560 GPa

Shear Modulus: 214 GPa

Bulk Modulus: 414 GPa

Poisson's Ratio: 0.24

Transverse Rupture Strength: 350–400 MPa

Oxidation Resistance: Oxidizes rapidly in air at 800°C

Chemical Resistance: TaC is one of the most chemically stable carbides. Decarburizes when heated in hydrogen at very high temperatures (3000°C). Does not react with nitrogen up to 2700°C. Reacts at high temperature with Nb, Ta, and Mo. Stable in nonoxidizing acids, but is attacked easily by HNO_3 and HF and by melts of oxidizing salts.

Isomorphism. TaC forms solid solutions with the carbides of Group IV and the other monocarbides of Group V and with the mononitrides of these two groups.

8.2 Phase Diagram

The C-Ta phase diagram is shown in Fig. 5.6.[14][15]

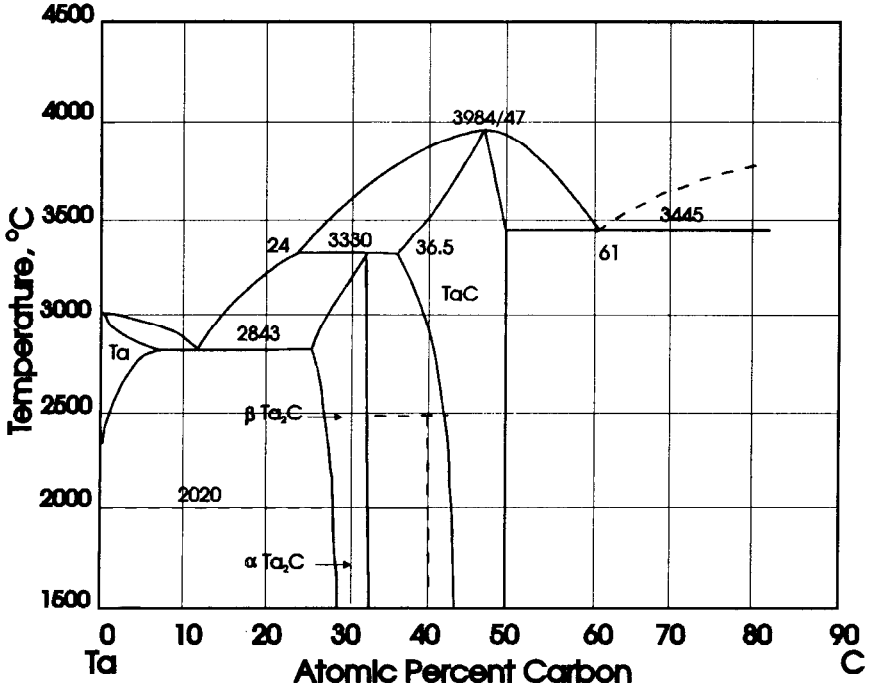


Figure 5.6: Carbon–tantalum phase diagram.

8.3 Summary of Fabrication Processes

TaC powder is prepared by the reaction of Ta_2O_3 with carbon at 1700°C in hydrogen usually in two steps, by the direct carburization of tantalum sponge, or by the reaction of tantalum hydride with carbon. TaC coatings are deposited by CVD, reactive evaporation and sputtering (see Chs. 14 and 15).

8.4 Summary of Applications and Industrial Importance

Tantalum carbide is produced industrially in appreciable quantity with a world production estimated at 500 tons annually (1994). The following is a summary of applications of tantalum carbide in production or development. More details are given in Ch. 16.

- In combination with WC-Co cemented carbides (up to 2 wt%) to inhibit WC grain growth
- With WC-Co cutting tools to improve cutting characteristics (up to 15 wt%)
- With WC-Co cutting tools to improve shock resistance, high-temperature hardness, cratering, and wear and oxidation resistance

REFERENCES

1. Holleck, H., Material Selection for Hard Coatings, *J. Vac. Sci. Technol. A*, 4(6) (Nov/Dec. 1986)
2. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
3. Kosolapova, T. Ya., *Carbides*, Plenum Press, New York (1971)
4. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
5. Toth, L. E., *Transition Metal Carbides and Nitrides*, Academic Press, New York (1971)
6. Tulhoff, H., Carbides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
7. Storms, E. K., *The Refractory Metal Carbides*, Academic Press, New York (1967)

8. Perecherla, A., and Williams, W. S., Room-Temperture Thermal Conductivity of Cemented Transition-Metal Carbides, *J. Amer. Ceram. Soc.*, 71(12):1130–1133 (1988)
9. *Engineering Property Data on Selected Ceramics, Vol. 2, Carbides,* MCIC HB-07-2, Battelle Institute, Columbus, OH (1987)
10. Storms, E. K., Phases Relationships and Electrical Properties of Refractory Carbides and Nitrides, in *Solid State Chemistry*, Vol 10 (L. E. Roberts, ed.), University Park Press, Baltimore (1972)
11. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
12. Lowther, J. E., Molecular Orbital Studies of Refractory Metal Carbides, in *Institute of Physics Conf. Series No. 75,* Ch. 1, Adam Hilger Ltd., London (1986)
13. Rudy, E., *Compendium of Phase Diagrams,* Air-Force Materials Laboratory Report, AFML TR 65-2, Part V (June 1969)
14. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)
15. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. ed., ASM International, Metals Park, OH (1990)

6

Carbides of Group VI: Chromium, Molybdenum, and Tungsten Carbides

1.0 GENERAL CHARACTERISTICS OF GROUP VI CARBIDES

1.1 Common Features of Group VI Carbides

This chapter is a review of the characteristics and properties of the interstitial carbides formed by the metals of Group VI: chromium, molybdenum, and tungsten. These three carbide systems have similar atomic bonding, composition, and crystallography. Their properties and characteristics are also similar.

They have a more complex composition and crystallography than the carbides of Groups IV and V. As shown in Ch. 3, their structural characteristics can be summarized as follows:

- They have several compositions:[1]

  $Cr_{23}C_6$ Mo_2C W_2C
  Cr_7C_3 Mo_3C_2 WC
  Cr_3C_2 MoC_{1-x}

- They have two major crystalline structures: hexagonal and orthorhombic

- The monocarbide form is retained in MoC and WC but, unlike the carbon atoms of the monocarbides of Group IV and V which occupy octahedral sites (B1 structure), the carbon atoms in MoC and WC occupy the more spacious trigonal prismatic sites (hexagonal structure)[2][3]
- The metal-to-metal bonds are strong and the metal-to-carbon bonds are weak

The carbides of Group VI are important industrial materials, particularly tungsten carbide and chromium carbide. Their fabrication processes and applications are summarized in Secs. 6, 7, and 8 and reviewed in more detail in Chs. 14, 15, and 16.

1.2 Refractory Characteristics

A criterion of this book is that only those carbides and nitrides having a melting point above 1800°C and good chemical resistance are considered. Chromium carbide is a marginal case as mentioned in Ch. 3, Sec. 4.4.[1][4] Its cubic form, $Cr_{23}C_6$, decomposes on melting at approximately 1500°C and cannot be considered refractory. The hexagonal form, Cr_7C_3, melts without decomposition at 1755°C but, because of its industrial importance, it is considered here. Only the orthorhombic form, Cr_3C_2, with a melting point of 1810°C, truly (if barely) meets the refractory criteria.

2.0 PHYSICAL AND THERMAL PROPERTIES OF GROUP VI CARBIDES

In this section and the next three, the properties and characteristics of the major phases of interstitial carbides of Group VI, i.e., Cr^3C_2, Mo_2C, and WC, are reviewed and compared with those of the parent metals and their borides. The nitrides of Group VI are not included since they are not considered refractory (see Ch. 9). The values given are those for composition as close to stoichiometry as possible.[5]–[8] The properties in most cases are similar to those of the Groups IV and V carbides and the statements in Ch. 4 also apply here.

2.1 Density and Melting Point

Density and melting point are shown in Table 6.1.

Table 6.1: Density and Melting Point of Group VI Interstitial Carbides and Other Refractory Compounds

Material	Density (g/cm^3)	Melting Point °C
Cr_3C^2	6.68	1810
Mo_2C	9.06	2520
WC	15.8	2870
Cr	7.20	1865
Mo	10.22	2620
W	19.3	3410
CrB_2	5.20	2170
Mo_2B_5	7.48	2100
W_2B_5	13.1	2600

As could be expected, the density increases considerably with the increasing atomic number of the metal. Unlike the carbides of Groups IV and V, the carbides of Group VI have melting points that are lower than those of their respective host metals but are relatively close to those of the borides (see Sec. 6.3 of Ch. 3).

2.2 Thermal Properties

The thermal properties are shown in Table 6.2,[9][10]

Thermodynamic Functions.[5] Like the carbides of Groups IV and V, the high-temperature enthalpy data for the Group VI carbides is provided by the equation: $H°_T - H°_{298.15K} = A + BT + CT^2 + DT^3 + (E/T)$. The values of A, B, C, D, and E for Cr_3C_2, Mo_2C, and WC are given in Table 6.3.

Table 6.2: Thermal Properties of Group VI Interstitial Carbides and Other Refractory Materials

Material	Specific Heat at 298 K (J/mole·K)	Thermal Conductivity at 20°C (W/m·K)	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
Cr_3C_2	32.7	19	10.4
Mo_2C	30.3	21.5	7.9
WC	39.8	63	a 5.2, c 7.3
Cr	23.29	91	6.0
Mo	24.23	138	5.0
W	23.90	173	4.5
CrB_2		20.5	10.5
Mo_2B_5			8.6
W_2B_5			7.8

Table 6.3: (after Ref. 1) Thermodynamic Values of Group VI Carbides.

	Cr_3C_2	Mo_2C	WC
A	-3.6074×10^{3}	-2.9502×10^{3}	-2.7595×10^{3}
B	$+9.4443T$	$+9.0920T$	$+8.5025T$
C	$+1.1635\times10^{-4}T^{2}$	$+1.0471\times10^{-3}T^{2}$	$+2.0550\times10^{-3}T^{2}$
D	$+2.8241\times10^{-8}T^{3}$	$-9.9403\times10^{-8}T^{3}$	$-2.4625\times10^{-7}T^{3}$
E	$+2.0496\times10^{5}/T$	$+1.3333\times10^{5}/T$	$+144249\times10^{5}/T$

from 298–1600 K, in cal/mole ± 0.5 %

Specific Heat. The specific heat (C_p) of the Group VI carbides increases essentially linearly with increasing temperature. Figure 6.1 shows this relationship for WC.[9]

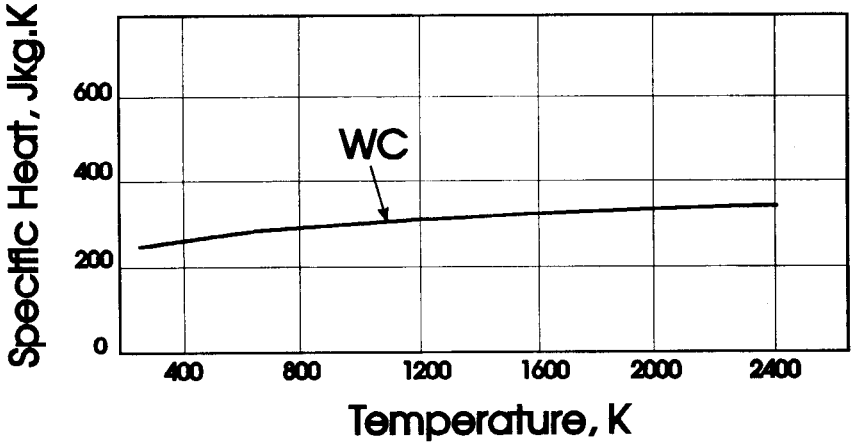


Figure 6.1: Specific heat of tungsten carbide as a function of temperature.[9]

Thermal Conductivity. Like the other interstitial carbides, the carbides of Group VI are good thermal conductors, thus reflecting their metallic character. This is especially true of WC which has the highest thermal conductivity of any of the transition-metal carbides and can be considered as an excellent thermal conductor (for discussion, see Sec. 2.2 of Ch. 4).[10][11]

Thermal Expansion. Like the carbides of Groups IV and V, the Group VI carbides have a relatively low thermal expansion which varies with temperature as shown in Fig. 6.2.[9] For discussion see Ch. 4, Sec. 2.4.

3.0 ELECTRICAL PROPERTIES OF GROUP VI CARBIDES

Like the carbides of Groups IV and V, the Group V carbides are electrical conductors (see Ch. 4, Sec. 3.1). The electrical properties of the Group VI carbides are shown in Table 6.4.[5–7][12] These materials can be considered as good electrical conductors even though their electrical resistivity

is higher than that of the host metals. WC has the lowest resistivity of any of the interstitial carbides (and, as mentioned above, the highest thermal conductivity).[10] It can qualify as the most metallic of these carbides.

The Hall constant is negative (see Sec. 3.2 of Ch. 4).

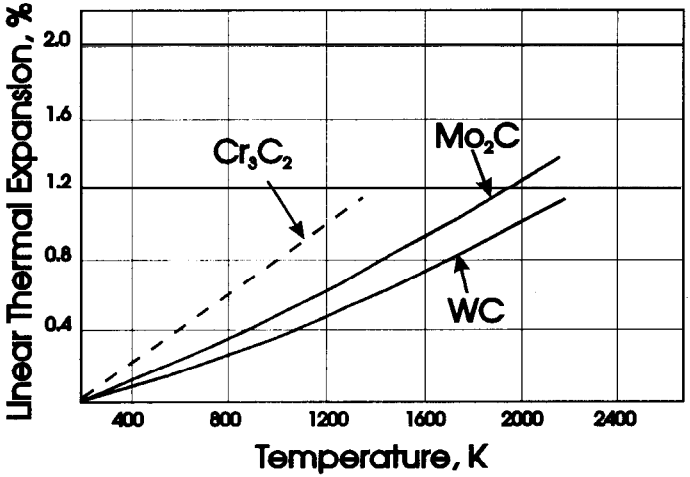


Figure 6.2: Linear thermal conductivities of Group VI carbides as a function of temperature.[9]

Table 6.4: Electrical Properties of Group VI Interstitial Carbides and Other Refractory Compounds

Compound	Electrical Resistivity at 20°C ($\mu\Omega$·cm)	Hall Constant at 20°C 10^{-4} $cm^3/A·s$	Magnetic Susceptibility 10^{-6} emu/mol
Cr_3C_2	75	-0.47	
Mo_2C	71	-0.85	
WC	22	-21.8	+10.0
Cr	12.9		
Mo	5.2		
W	5.65		
CrB_2	18		
Mo_2B^5	18		
W_2B_5	19		

4.0 MECHANICAL PROPERTIES OF GROUP VI CARBIDES

The mechanical properties of Group VI carbides are summarized in Table 6.5. The values are average values reported in the recent literature[1][3][5]-[7] (see Sec. 4.1 of Ch. 4).

Table 6.5: Mechanical Properties of Group VI Interstitial Carbides and Borides at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)	Shear Modulus (GPa)	Transverse Rupture Strength (MPa)
Cr_3C_2	10–18	344–400		49
Mo_2C	15.5–24.5	535		
WC	22 (0001)	620–720	262	550
CrB_2	20.5			
Mo_2B_5	23.0			
W_2B_5	26.1			

The fracture mechanism and the ductile-brittle transition are similar to those of the carbides of Groups IV and V (see Sec. 4, Ch. 4). The high strength of WC should be noted.

Hardness. Table 6.5 shows that carbides of Group VI are not as hard as the carbides of Groups IV and V (see Ch. 4, Table 4.6 and Ch. 5, Table 5.6). This may reflect the lower strength of their M-C bonds. The hardness decreases with temperature as shown in Fig. 4.6 (Ch. 4). Alone among the refractory carbides, WC retains its hardness up to approximately 800°C and, above 400°C, it is the hardest carbide.

5.0 CHEMICAL PROPERTIES OF GROUP VI CARBIDES

5.1 Mutual Solubilities

The existence of ternary carbides and nitrides was discussed in Ch. 4, Sec. 5.0. As shown in Fig. 4.7 (Ch. 4), the carbides of Group VI, Cr_3C_2, Mo_2C, and WC, with their hexagonal or orthorhombic structure, cannot readily accommodate the cubic structure of the Groups IV and V carbides in solid solution. However the reverse is possible. For instance W-C and Mo-C are soluble in Ti-C and Ta-C although the solubility is limited as shown below.

W-Ti-C and W-Ta-C Systems.[3] The ternary system tungsten titanium carbide is an important material system with applications in cemented carbides for cutting tools. The solubility of WC in the TiC lattice is a function of temperature. It is 60 wt.% at 1500°C, reaches 90 wt.% at 2400°C, and is probably complete above 2600°C. WC is also soluble in TaC but to a lesser degree. In both systems, WC crystals precipitate upon cooling from sintering temperature and, as a result, these systems should be considered as mixed crystals or as a ceramic/ceramic composite.

Mo-Ti-C System. Similarly to the W-Ti-C and W-Ta-C systems, molybdenum carbide is partially soluble in TiC to form a useful material for cemented carbides. As already mentioned, the study of these ternary (and quaternary) systems is outside the scope of this book (for a general review of these systems, see Ref. 13).

5.2 Chemical Properties

The Group VI carbides are chemically stable and have a chemical resistance similar to that of the Group IV carbides.[6]

6.0 CHARACTERISTICS AND PROPERTIES OF CHROMIUM CARBIDE

6.1 Summary of Properties

The characteristics and properties of chromium carbide are summarized in Table 6.6.

6.2 Phase Diagram

The phase diagram of the C-Cr system is shown in Fig. 6.3.[14][15]

Table 6.6: Characteristics and Properties of Chromium Carbide.

Notes: 1. When phase is not indicated, value reported is for Cr_3C_2.
2. Test temperature is 20°C unless otherwise stated.

Phases: $Cr_{23}C_6$, Cr_7C_3, Cr_3C_2

Crystal Structure and Lattice Parameters (nm):

Cr_3C_2 is an intermediate carbide having carbon chains with C-C distance approximately 0.165 nm running through distorted metal lattice where the Cr atoms are at the corners of trigonal prisms and the carbon atoms in the center of the prisms (see Ch. 3, Sec. 4.4).[1][4]

Cr_7C_3: Hexagonal, a = 1.398, c = 0.4523

Cr_3C_2: Orthorhombic, a = 0.283, b = 0.554, c = 1.1470

Space Group and Pearson Symbol:

Cr_7C_3: Pnma, oP40

Cr_3C_2: Pnma, oP20

Composition: narrow range of homogeneity (approximately 39–40 at/°C)

Molecular Weight:

Cr_7C_3: 393.70 g/mol

Cr_3C_2: 180.01 g/mol

Color: gray

X-ray Density:

Cr_7C_3: 6.97 g/cm^3

Cr_3C_2: 6.74 g/cm^3

Melting Point:

Cr_7C_3: 1755°C (melts congruently)

Cr_3C_2: 1810°C (decomposes at melting temperature)

Specific Heat (C_p): 32.7 J/mole·K

Heat of Formation ($-\Delta aH_f$) at 298 K (KJ/g-atom metal):[1] 23.0

Thermal Conductivity: 19 W/m·°C at 20°C

Thermal Expansion: 10.4 x 10^{-6}/°C at 20°C (see Fig. 6.2)

Electrical Resistivity: 75 μΩ·cm

Superconductive Transition Temperature: <1.2 K

Table 6.6: *(Cont'd)*

Hall Constant: -0.47×10^{-4} $cm^3/A \cdot s$

Vickers Hardness: 10–18 GPa

Young Modulus of Elasticity: 15.5–24.5 GPa

Transverse Rupture Strength: 49 MPa

Oxidation Resistance: Generally superior to that of other interstitial carbides. Oxidation in air starts at 1000°C and a dense and strong oxide layer is formed.

Chemical Resistance: Insoluble in cold HCl; dissolves in hot oxidizing acids.

Solid Solubility: See Sec. 5.1

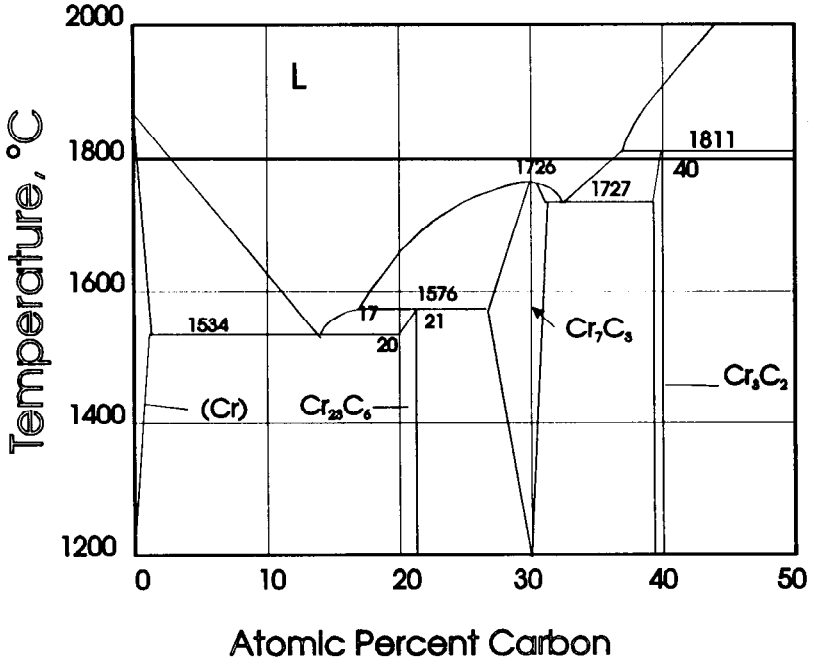


Figure 6.3: Carbon–chromium phase diagram.

6.3 Summary of Fabrication Processes

Cr_3C_2 powder is prepared by the reaction of chromium oxide (Cr_2O_3) with carbon up to 1600°C in hydrogen; if the temperature is kept below 1300°C, Cr_7C_3 is obtained. An oxygen free-carbide can be obtained by the carburization of the chromium metal. Chromium carbide coatings are deposited by CVD, reactive evaporation, and sputtering (see Chs. 14 and 15).

6.4 Summary of Applications and Industrial Importance

A partial list of applications is as follows (see also Ch. 16).

- Thermal spray powder for applications requiring high corrosion and wear resistance for tools and machine parts
- Welding electrodes for hard facing (Cr_7C_3, Cr_3C_2C eutectic) and weld-applied overlays on machine wear surfaces
- Grain growth inhibitor in W-Co cemented carbides
- Special tools for maximum chemical resistance
- Chromium carbide by thermal spray or CVD is extremely resistant to corrosion and resists atmospheric oxygen up to 900°C. It is used to coat steel and as an intermediate coating for combined corrosion and wear-resistance

7.0 CHARACTERISTICS AND PROPERTIES OF MOLYBDENUM CARBIDE

7.1 Summary of Properties

The characteristics and properties of molybdenum carbide are summarized in Table 6.7.

7.2 Phase Diagram

The phase diagram of the C-Mo system is shown in Fig. 6.4.[14][15]

Table 6.7: Characteristics and Properties of Molybdenum Carbide.

Notes: 1. When phase is not indicated, value reported is for Mo_2C.
2. Test temperature is 20°C unless otherwise stated.

Phases: Mo_2C, Mo_3C_2, MoC_{1-x}

Crystal Structure and Lattice Parameters (nm):

β-Mo_2C: hexagonal, a = 0.3007, c = 0.4729 (only stable phase at room temperature)

α-Mo_2C: orthorhombic, a = 0.4736, b = 0.6024, c = 0.5217 (stable only above 1475°C)

MoC_{1-x}: hexagonal above 1655°C and cubic above 1960°C

Space Group and Pearson Symbol:

β-Mo_2C: Pbcn, oP12

Composition: narrow range of homogeneity (33–34 mol % C)

Molecular Weight: Mo_2C 203.91 g/mol
MoC 107.96 g/mol

Color: gray

X-ray Density : β-Mo_2C 9.06 g/cm^3
MoC 9.15 g/cm^3

Melting Point: 2520°C (melts without decomposing)

Debye Temperature: β-Mo_2C: 531 K
α-Mo_2C: 473 K

Specific Heat (C_p): 30.3 J/mole·K

Heat of Formation ($-\Delta aH_f$) at 298 K (KJ/g-atom metal):[1] 23.0

Thermal Conductivity: 21.5 W/m·°C

Thermal Expansion: 7.9×10^{-6}/°C (see Fig. 6.2)

Electrical Resistivity: 71 $\mu\Omega$·cm at 20°C

Superconductive Transition Temperature: 13 K

Hall Constant: -0.85×10^{-4} cm^3/A·s at 20°C

Vickers Hardness: 15.5–24.5 GPa

Young Modulus of Elasticity: 535 GPa

Transverse Rupture Strength: 49 MPa

Table 6.7: *(Cont'd)*

Oxidation Resistance: oxidizes above 500°C

Chemical Resistance: MO_2C is attacked by HNO_3 and by boiling H_2SO_4; insoluble in cold HCl; stable in hydrogen.

Isomorphism: See Sec. 5.1

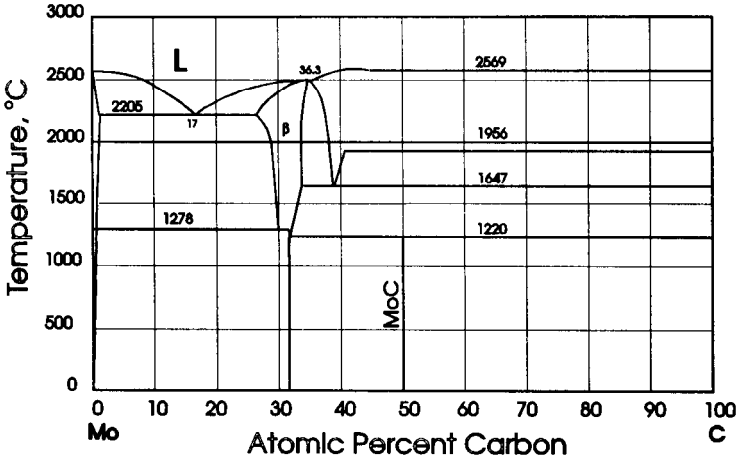


Figure 6.4: Carbon–molybdenum phase diagram.

7.3 Summary of Production Processes

The carburization of molybdenum oxide at 1500°C produces a carbide powder but the carbon content is difficult to control. A preferred process is the direct heating of the metal and carbon in the form of powders in hydrogen at approximately 1500°C (see Chs. 14 and 15).

7.4 Summary of Applications and Industrial Importance

The only phase of industrial importance is the β-Mo_2C. Industrial applications are limited to special grades of cemented carbides. Mo_2C is found in steel alloys where it is formed during melting (see Ch. 16).

8.0 CHARACTERISTICS AND PROPERTIES OF TUNGSTEN CARBIDE

8.1 Summary of Properties

The characteristics and properties of tungsten carbide are summarized in Table 6.8.

Table 6.8: Characteristics and Properties of Tungsten Carbide.

Notes: 1. When phase is not indicated, value reported is for WC.
2. Test temperature is 20°C unless otherwise stated.

Phases:	W_2C (subcarbide) WC (also called α-WC) β-WC_{1-x} (unstable, forming only above 1530°C)
Crystal Structure and Lattice Parameters (nm):[16][17]	W_2C: hexagonal, a 0.30008, c 0.47357 WC: hexagonal, a 0.2907, c 0.2837 Crystal structure shown in Fig. 3.9
Space Group and Pearson Symbol:	W_2C: P3m1, hP3 WC: P6m2, hP2
Composition:	Narrow range of homogeneity, α-$WC_{0.98}$-$WC_{1.00}$
Molecular Weight:	W_2C: 379.71 g/mol WC: 195.86 g/mol
Color:	gray
X-ray Density:	W_2C: 17.2 g/cm^3 WC: 15.8 g/cm^3
Melting Point:	W_2C: 2730°C WC: 2870°C WC decomposes by melting incongruently. WC has a large stability domain but reacts with W_2C or W. W_2C starts to decompose at 1300C (W + hexagonal WC).

Table 6.8: *(Cont'd)*

Debye Temperature: 493 K

Specific Heat (C_p): 39.8 J/mole·K

Heat of Formation ($-\Delta aH_f$) at 298 K (KJ/g-atom metal:[1] 37.7

Thermal Conductivity: 63 W/m·°C (see Fig. 6.2)

Thermal Expansion: a 5.2, c 7.3

Electrical Resistivity: 17–22 μΩ·cm

Superconductive Transition Temperature: 10.0 K

Hall Constant: -21.8×10^{-4} $cm^3/A{\cdot}s$ at 20°C

Magnetic Susceptibility: $+10 \times 10^{-6}$ emu/mol

Vickers Hardness: 22 GPa

Young's Modulus of Elasticity: 620–720 GPa

Shear Modulus: 262 GPa

Poisson's Ratio: 0.18

Transverse Rupture Strength: 550 MPa

Oxidation Resistance: Oxidation in air starts at 500–600°C.

Chemical Resistance: Resistant to acids and not attacked at room temperature by mixtures of HF and HNO_3 but attacked by these acids at elevated temperature. Attacked by chlorine above 400°C. Attacked by fluorine at room temperature. Stable in dry hydrogen to melting point. W_2C is less stable than WC; it reacts with Murakami's reagent while WC does not.

Isomorphism: See Sec. 5.1. The eutectic WC_2-WC is prepared by fusion (known as fused or cast tungsten carbide).

8.2 Phase Diagram

The phase diagram of the C-W system is shown in Fig. 6.5.[14][15]

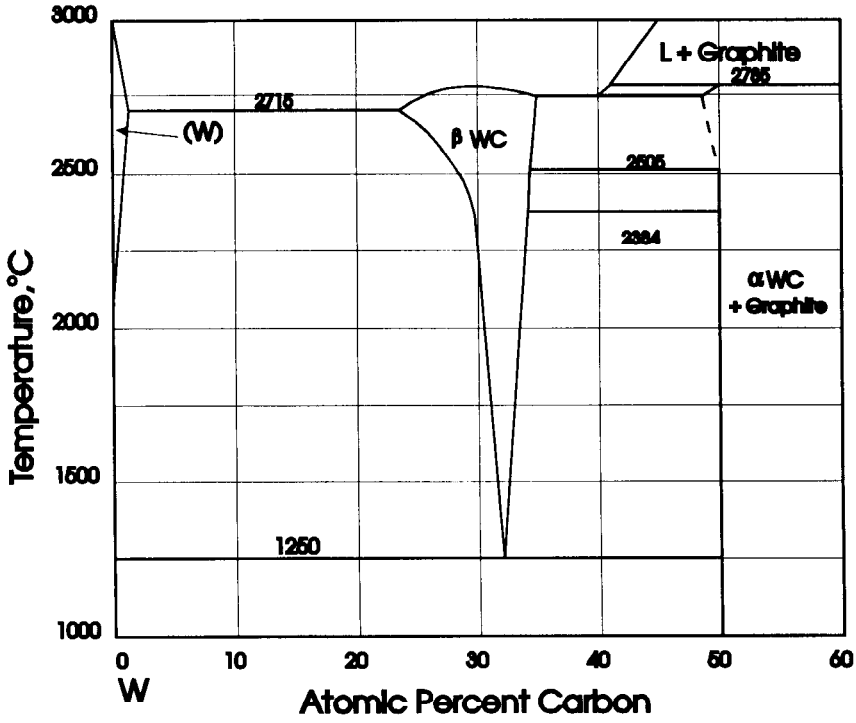


Figure 6.5: Carbon–tungsten phase diagram.

8.3 Summary of Production Processes

Tungsten carbide is made by the direct carburization of tungsten metal with carbon such as lamp black or graphite at 1400–2000°C in hydrogen or vacuum. Grain size control is critical and is usually determined by the processing parameters. Other starter materials are tungsten oxide, tungstic acid, and ammonium paratungstate.

Tungsten-carbide composites (and composites of the other interstitial carbides as well) are known in the industry as *cemented carbides* or *hard metals*, a term somewhat misleading since they are not metals. These cemented carbides are sintered with a metallic binder which is generally cobalt and less often nickel. Many combinations are possible.

Coatings of tungsten carbide are deposited by thermal and plasma CVD. Very fine submicron powder is now produced by CVD and sol-gel for potential use in high-quality cemented carbides (see Chs. 14 and 15).

8.4 Summary of Applications and Industrial Importance

Tungsten carbide is a major industrial material with a yearly world production estimated at 20,000 tons. Its largest use is in cemented carbides for cutting tools (see Ch. 16).[3][17] A partial list of applications is as follows:

- Cutting and drilling tools
- Oil-field and mining drilling tools
- Drawing and extrusion dies
- Balls for ball mills and ball-point pens
- Rolls, nozzles, sealing rings

REFERENCES

1. Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)
2. Oyama, S. T., Crystal Structure and Chemical Reactivity of Transition Metal Carbides and Nitrides, *J. Solid State Chem.*, 96:442–445 (1992)
3. Tulhoff, H., Carbides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
4. Morniroli, J. P., and Gantois M., Etude Microstructural du Carbure M_7C_3, *J. Applied Crystallography,* 16:1–10 (983)
5. Holleck, H., Material Selection for Hard Coatings, *J. Vac. Sci. Technol. A, 4(6)* (Nov/Dec. 1986)
6. Kosolapova, T. Ya., *Carbides*, Plenum Press, New York (1971)
7. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
8. Pierson, H. O., A Survey of the Chemical Vapor Deposition of Refractory Transition Metal Borides, in *Chemical Vapor Deposited Coatings*, American Ceramic Society, pp. 27–45 (1981)
9. *Engineering Property Data on Selected Ceramics, Vol. 2, Carbides,* MCIC HB-07-2, Battelle Institute, Columbus, OH (1987)

10. Frandsen, M. V., and Williams, W. S., Thermal Conductivity and Electrical Resistivity of Cemented Transition-Metal Carbides at Low Temperatures, *J. Am. Ceramic Soc.*, 74(6):1411–1416 (1991).
11. Perecherla, A., and Williams, W. S., Room-Temperture Thermal Conductivity of Cemented Transition-Metal Carbides, *J. Amer. Ceram. Soc.*, 71(12):1130–1133 (1988)
12. Storms, E. K., Phases Relationships and Electrical Properties of Refractory Carbides and Nitrides, in *Solid State Chemistry*, Vol 10 (L. E. Roberts, Ed.), University Park Press, Baltimore (1972)
13. Rudy, E., *Compendium of Phase Diagrams,* Air-Force Materials Laboratory Report, AFML TR 65-2, Part V (June 1969)
14. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)
15. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. Edition, ASM International, Metals Park, OH (1990)
16. Ishizawa, I., and Tanaka T., Fermi Surface Properties and Bonding Nature of TiB_2 and WC, in *Institute of Physics Conf. Series,* No. 75, Ch. 1, Adam Hilger Ltd., London (1986)
17. Lowther, J. E., Molecular Orbital Studies of Refractory Metal Carbides, in *Institute of Physics Conf. Series,* No. 75, Ch.. 1, Adam Hilger Ltd., London (1986)
18. Sarin, V. K., Cemented Carbide Cutting Tools, in *Advances in Powder Technology*, (G, Y. Chin ed.), ASM Materials Science Seminar, ASM, Metals Park, OH (1981)

7

Covalent Carbides: Structure and Composition

1.0 GENERAL CHARACTERISTICS OF COVALENT CARBIDES

As mentioned in Ch. 2, the refractory carbides include two structurally different types: *(a)* the interstitial carbides of the transition metals of Group IV, V, and VI (reviewed in Ch. 3, 4, 5, and 6), and *(b)* two covalent carbides: boron carbide and silicon carbide. The structural characteristics of these two carbides are reviewed in this chapter and their properties and general characteristics in the following chapter.

The two covalent carbides have these general features:

- They fully meet the refractory criteria of high melting point and thermal and chemical stability
- They are nonmetallic compounds
- Their electronic bonding is essentially covalent
- They have low density
- Their elemental constituents have low atomic weight
- They have useful semiconductor properties
- They are extremely hard and strong materials which exhibit typical ceramic characteristics

- They are both important industrial materials with many current and potential applications

2.0 ATOMIC STRUCTURE OF CARBON, BORON, AND SILICON

The atomic and crystalline structures of covalent carbides are less complex and generally better understood and characterized than those of interstitial carbides. Bonding is essentially covalent where the carbon atoms bond to the silicon or boron atoms by sharing a pair of electrons and, like all covalent bonds, these atoms form definite bond angles. The bonding is achieved by the hybridization of the valence electrons of the respective atoms.

2.1 Electronic Configuration

In the Periodic Table of the Elements, carbon (with an atomic number of six) follows boron (with an atomic number of five) and is just above silicon in the column of Group IVb (see Table 2.1 of Ch. 2). Table 7.1 shows the electronic configuration, the electronegativity, and the atomic radius of these three elements.[1][2]

Table 7.1: Electronic Configuration of Carbon, Boron, and Silicon

		Shell							
Element	Z	1*s*	2*s*	2*p*	3*s*	3*p*	Electronic Structure	Electro-Negativity	Atomic Radius (nm)*
Boron	5	2	2	1			[He]$2s^2 2p^1$	2.0	0.088
Carbon	6	2	2	2			[He]$2s^2 2p^2$	2.5	0.077
Silicon	14	2	2	6	2	2	[Ne]$3s^2 3p^2$	1.8	0.117

* In the tetrahedral configuration (sp^3)

As shown in this table, carbon, boron, and silicon have comparable electronic structure. They also have some of the smallest atoms. Silicon and boron are similar elements which can be considered borderline cases between metals and nonmetals. They also have lower electronegativity than carbon and, by convention, their compounds with carbon can be called carbides (see Sec. 2.0 of Ch. 2). The differences between the atomic structure, electronegativity, and atomic radius of these three elements are not as significant as those between carbon and the transition metals (see Ch. 3, Table 3.8).

2.2 Hybridized States

Carbon Hybridization. The hybridization of the carbon atom from the ground state to the hybrid sp^3 (or tetragonal) orbital state was described in Ch. 3, Secs. 2.2 and 2.3. It was shown that this hybridization accounts for the tetrahedral symmetry and the valence state of four with four $2sp^3$ orbitals arranged in a regular tetrahedron with equal angles to each other of 109° 28'. The diamond structure is formed when carbon atoms are bonded to each other in the sp^3 configuration (see Fig. 2.1 of Ch. 2).[3]

Silicon Hybridization. Hybridization of the silicon atom occurs in a manner similar to the tetragonal hybridization of the carbon atom to form a configuration of four $3sp^3$ orbitals also arranged in a regular tetrahedron.[1]

Boron Hybridization. As shown in Table 7.1, the boron atom has only one valence electron in the ground state ($2p^1$). Yet boron is never monovalent but always trivalent as the atom is hybridized.[1][2] However, unlike the tetragonal hybridization of carbon and silicon, the boron hybridization is trigonal (sp^2). It occurs as follows:

$$1s^2 2s^2 2p^1 \rightarrow 1s^2\ (sp^2)^3$$

The $2s^2$ electrons are uncoupled and one is promoted to the $2p_y$ orbital to form three equivalent sp^2 hybrid orbitals with three axes located in the same plane, each directed to the corners of an equilateral triangle and separated by the same angle of 120°. The covalent radius is not well defined and is estimated to be 0.085–0.090 nm. Since boron has four orbitals available for bonding and only three electrons, it is an electron-pair acceptor and it tends to form multi-center bonds.

3.0 STRUCTURE AND COMPOSITION OF SILICON CARBIDE

3.1 The Carbon-Silicon Crystal Unit Cell

Silicon carbide is a relatively simple substance in the sense that its structure and properties are essentially isotropic. In the basic unit cell, each atom of one element is surrounded by a tetrahedron of four atoms of the other element. Each element shares pairs of electrons with the other (the four $2sp^3$ orbitals of carbon with the four $3sp^3$ orbitals of silicon), A schematic representation of the SiC crystal is shown in Fig. 7.1.

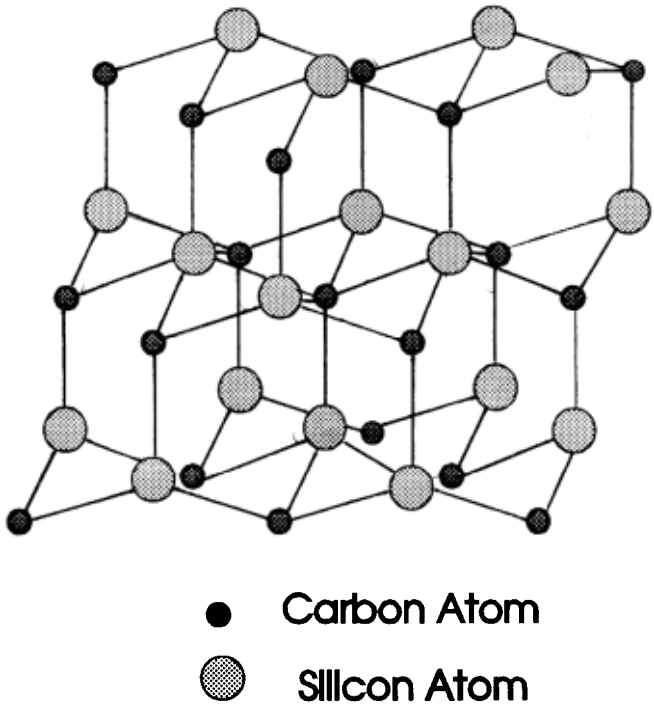


Figure 7.1: Schematic representation of the β–SiC structure.

Each SiC unit cell has eight atoms located as follows: 1/8 × 8 (silicon) at the corners, 1/2 × 6 (silicon) at the faces and 4 (carbon) inside the unit cube as illustrated in Fig. 7.2[4] (for the sake of clarity, only the silicon atoms are shown). In such a structure, each atom has a coordination number of four.

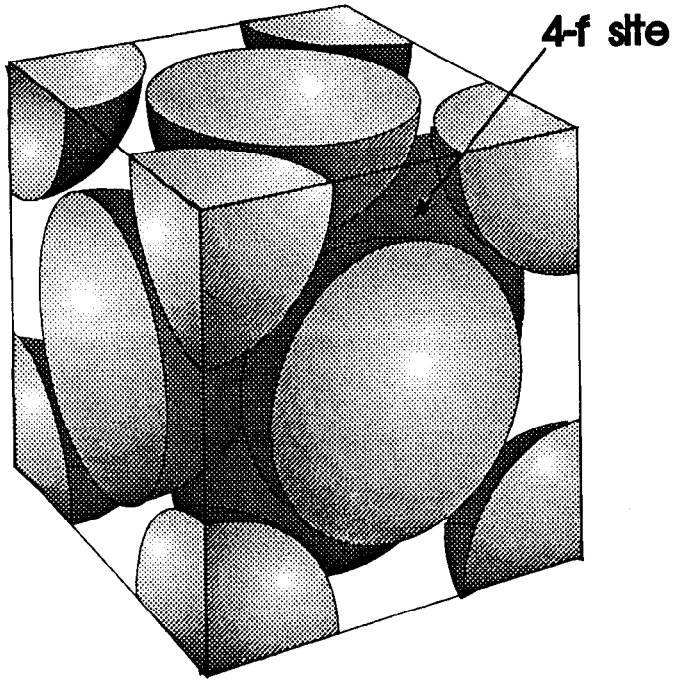


Figure 7.2: Schematic representation of the silicon–carbide unit cell (for clarity only silicon atoms are shown).

3.2 Covalent and Ionic Bonding

The bonding in silicon carbide is essentially covalent. These covalent bonds are strong since both atoms are small, the bond length is short, and four of the six electrons of carbon and four of the fourteen electrons of silicon form bonds. The average bond energy is estimated at 300 kJ/mol.[2]

The bonding in silicon carbide is also ionic. As mentioned in Ch. 2, an ionic bond results from the transfer of valence electrons between two

different atoms which causes the formation of a positive and a negative ion and consequently an electrostatic attraction between these ions of unlike charges.

As shown by Kisly,[6] the difference between *(a)* the atomic spacing of SiC and the sum of the covalent radii of carbon and silicon and *(b)* the atomic spacing and the sum of their ionic radii shows that the bonding is mainly covalent but that a certain degree of ionicity is retained. The calculated covalent bond energy E_o is 9.42 eV and the ionic bond energy E_p is 1.41 eV.[6]

3.3 Beta Silicon Carbide

Silicon carbide occurs in two slightly different crystal structures: the cubic βSiC, and a large number of hexagonal rhombohedral varieties known collectively as αSiC.[7][8] The single cubic form, βSiC, is obtained when the carbide is synthesized below 2100°C. It is a face-centered cubic (fcc) structure of the zincblende type shown in Fig. 7.1. Zincblende is a mineral of zinc sulfide also known as sphalerite. In this illustration, the zincblende structure is represented with the cube diagonals vertical and appears as series of identical (although translated) puckered sheets of atoms with an AA layer sequence.[1] Another view of the βSiC crystal is shown in Fig. 7.2 (the carbon atoms, all located in the 4*f* sites, are omitted for clarity] The βSiC structure has no polytype (see Table 7.3 for crystal structure data).

The layer sequence of the {111} plane is ABCABCABC which means that every third layer is identical (Fig. 7.3).[9] This gives a Ramsdell notation of 3C-SiC where the numeral 3 refers to the number of layers of carbon atoms and silicon atoms necessary to produce a unit cell and C indicates cubic symmetry.[10] It is analogous to the diamond structure and is also the structure of cubic boron nitride (see Ch. 12).

3.4 Alpha Silicon Carbide and Polytypes

Alpha SiC is the high temperature form of SiC. Unlike βSiC which is a single compound, αSiC has a large number of polytypes, approximately 250 having been identified so far.[11][12] These polytypes have either a rhombohedral or a hexagonal structure. Polytypes, unlike polymorphs, are the same thermodynamic phase, are formed under the same conditions of temperature and pressure, and have similar properties and structure. Their close-packed layers ({0001} for hexagonal) are identical but have a

different stacking sequence. They have essentially the same lattice constant in two dimensions but a different one in the third.[13]

The major polytypes of αSiC are listed in Table 7.2. Of these, the most common is 6H-SiC whose stacking structure is shown in Fig. 7.4.

Table 7.2: The Common Polytypes of αSiC

Polytypes	Structure	Layer Unit Cell	Sequence
C (βSiC)	Cubic	1	ABCABCABC
2H (αSiC)	Hexagonal	2	ABABAB
4H -	Hexagonal	4	ABACABAC
6H -	Hexagonal	6	ABCACBABCACBA
15R -	Rhombohedral	15	ABDACBCABACABCBA

The 2H polytype has the structure of wurtzite, a mineral of zinc sulfide, shown in Fig. 7.5.[14] It is considered a metastable modification which undergoes solid-state transformation to the 3C and 6H polytypes above 1400°C.

3.5 Summary of Structural Data

The structural data for silicon carbide is summarized in Table 7.3.[8]

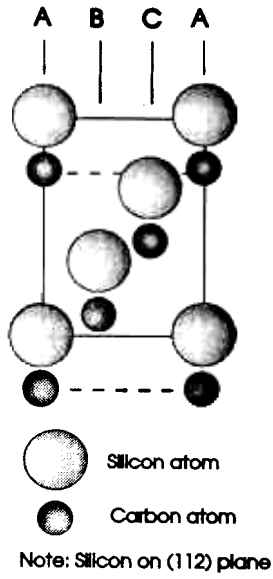


Figure 7.3: Layer sequence ABCABC of the βSiC structure along the (112) plane.

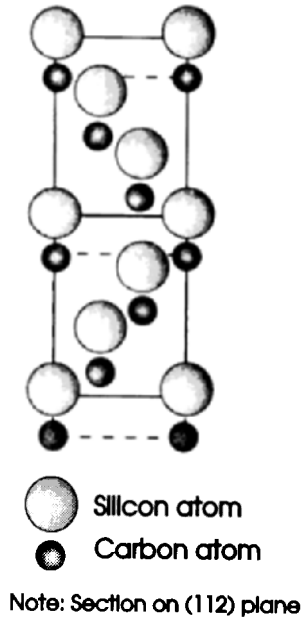


Figure 7.4: Layer sequence of the 6H αSiC structure along the (112) plane.

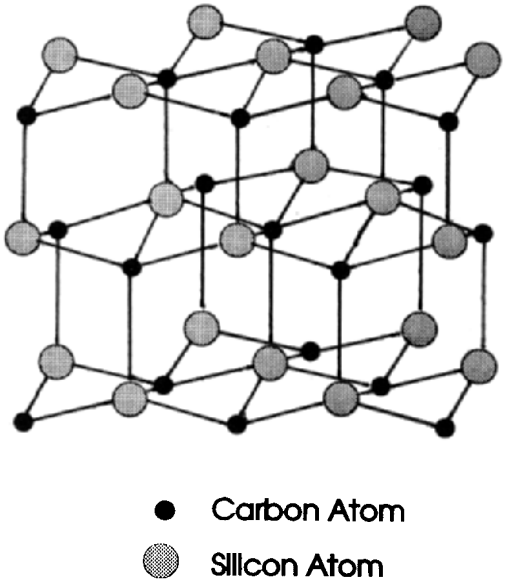


Figure 7.5: Schematic representation of the α–SiC structure (2H).

Table 7.3: Silicon Carbide Structural Data at 298 K

Polytypes	Density (g/cm^3)	Lattice a_o (nm)	Parameters c_o (nm)	Space Group
C (βSiC)	3.214	0.43596	f43m	
2H (αSiC)	3.214	0.30763	0.50480	C6mc
4H -	3.235	0.3076	1.0046	
6H -	3.211	0.3080	1.5117	
15R -	3.274	0.3073	3.730	R3m

It should be noted that the hexagonal cell parameter a_o of a αSiC polytype remains essentially constant while its c_o varies as $c_o = n \times 0.2518$ nm (with slight differences), where n is the number of double layers of SiC in the hexagonal cell.[13]

3.6 Structural Correlation

As could be expected, the density, lattice parameters, and bond strength of βSiC are in between those of silicon and diamond (the sp^3 form of carbon) as shown in Table 7.4.[2][5]

Table 7.4: Structural Correlation Between SiC, Si, and C

Material	Density (g/cm^3)	Lattice a_o (nm)	Bond Energy kJ/mol
βSiC	3.210	0.43596	300
Si	2.329	0.5431	226
C (diamond)	3.515	0.3567	356

3.7 Phase Diagram

The phase diagram of carbon-silicon is shown in Fig. 7.6.[15][16] This diagram does not attempt to distinguish between αSiC and βSiC. βSiC is thought to be more stable than αSiC at any temperature below a peritectic reaction temperature of 2545 ± 40°C.

Some studies have determined that a transformation of βSiC to αSiC apparently takes place above 2100°C but the reverse transformation is also possible in nitrogen and at high pressure (30–40 atm).[13] The study of this transformation is still incomplete and more investigation in this field is necessary.

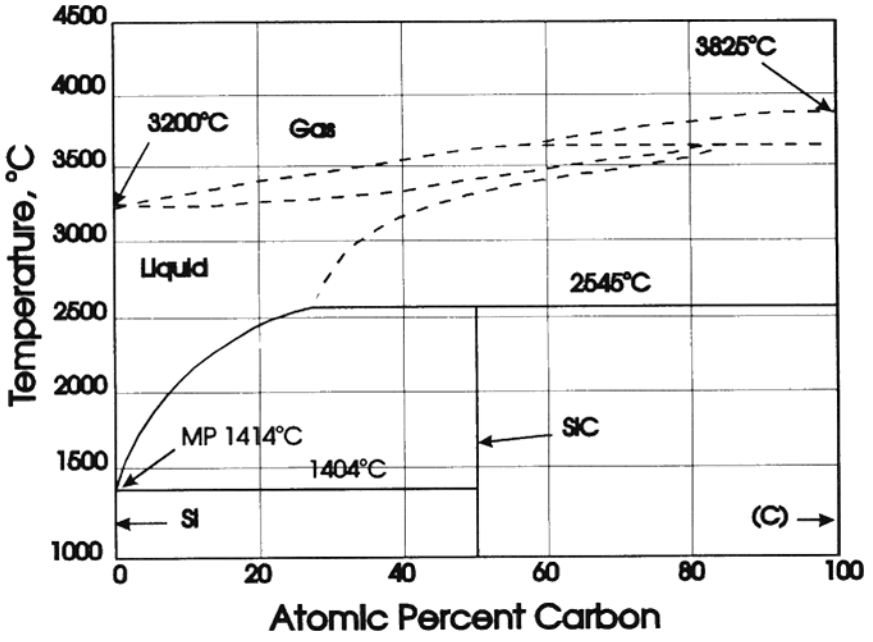


Figure 7.6: Carbon–silicon phase diagram.

4.0 STRUCTURE AND COMPOSITION OF BORON CARBIDE

4.1 The Boron Icosahedron

The basic boron structural element is the icosahedron, i.e., a polyhedron having twenty faces, twelve equivalent vertices and I_{2h} symmetry, forming a cage of twelve atoms shown in Fig. 7.7.[2] To form a boron crystal, these icosahedra combine in a rhombohedral configuration, i.e., a geometrical pattern with axes of equal length and equal axial angles (but not 90°) (Fig. 7.8).

The centers of these icosahedra are located on each of the corners of the rhombohedron as shown in Fig. 7.9 for boron carbide.

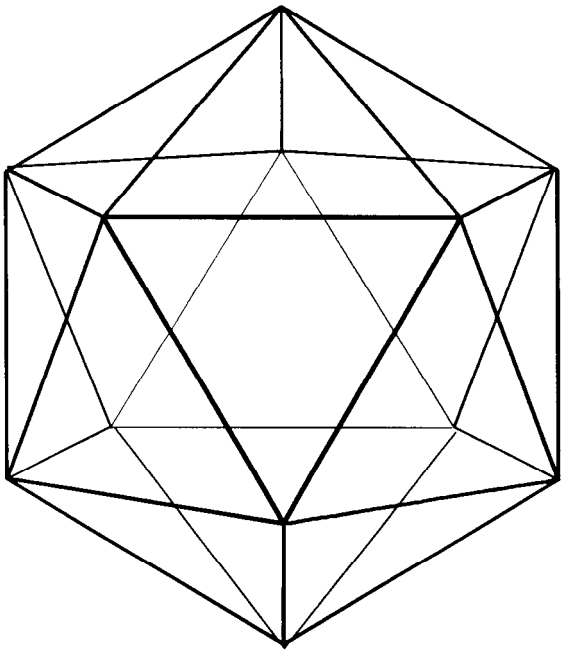


Figure 7.7: Schematic representation of the icosahedron.

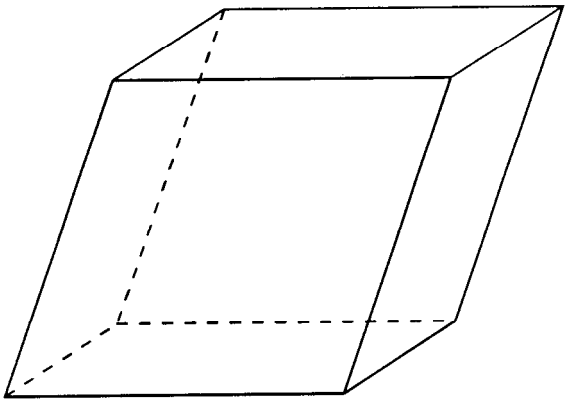


Figure 7.8: Schematic of the rhombohedron.

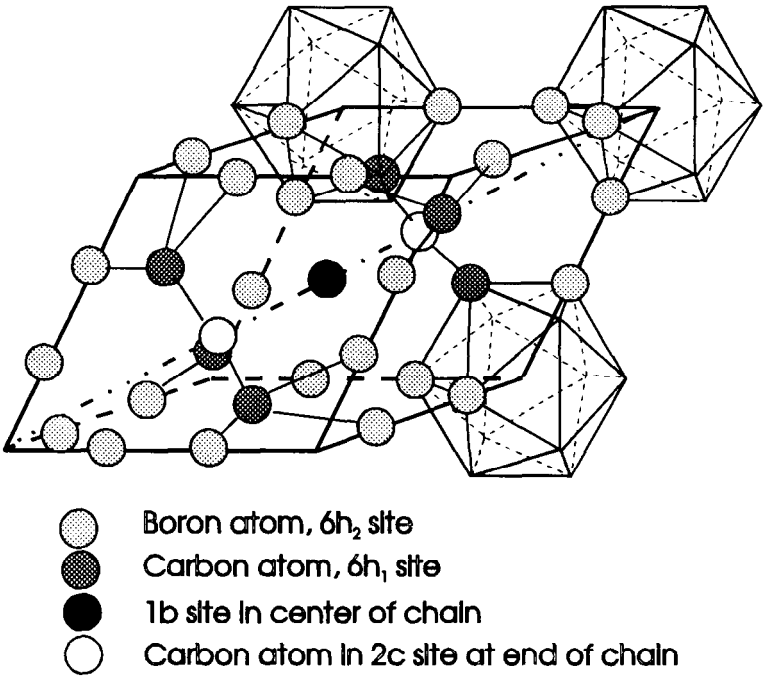


Figure 7.9: Schematic representation of the boron carbide structure.

4.2 The Structure of Boron Carbide

Boron carbide has an unusual structure which has been the subject of much controversy and apparently is yet to be completely clarified.[17]–[20] It can be described as a slightly distorted boron crystal structure as described above where the boron icosahedra are linked directly and also by a chain of three atoms located on the principal body diagonal of the rhombohedron, as shown in Fig. 7.9.[18] The 12 atoms of the icosahedra and these three atoms form a 15-atom unit cell. Another view of the structure is shown in Fig. 7.10.[9]

The carbon atoms can be positioned in the three-atoms chain and as part of the icosahedra. Because of their tetragonal (sp^3) hybridization, they occupy both ends of the chain while the center atom is boron (CBC chain), although singly ionized carbon atoms have occasionally been detected in the center position. They can also be incorporated in the icosahedron, although

due to bonding constraints, only to a maximum number of two.[21] The boron icosahedron is deficient in electrons and requires two additional electrons in order to acquire a thermodynamically favorable closed-shell structure. These electrons are provided by a substitutional carbon atom (see Fig. 7.11).[20]

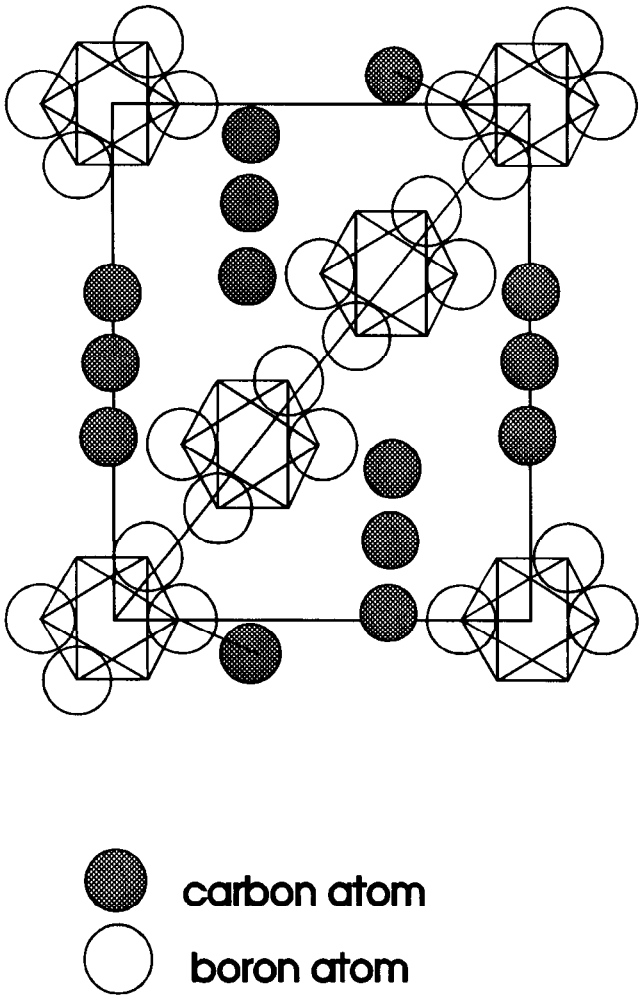


Figure 7.10: Structure of boron carbide along the (112) elevation.

4.3 Composition

Several structures are possible:

- $(B_{11}C)CBC$ with one carbon atom in the icosahedra (equivalent to B_4C)
- $(B_{12})CBC$ with no carbon atom in the icosahedra (equivalent to $B_{13}C_2$)
- Higher boron compositions by boron atom substitution within the chain or interstitially

The combination of these various structures within a given boron carbide compound gives an overall composition from about 7.7 to 20.5 at % carbon. Each composition has slightly different lattice constants as determined by powder x-ray diffraction (see Table 7.6). Such a composition dependence provides a fast and reliable method of determining the composition.[21]

Thus, boron carbide, unlike SiC, has a wide range of composition and the formula B_4C usually found in the literature should not be construed to represent an exact composition. Also in many cases, the composition of a boron carbide material is not fixed as localized phases having different composition may be found.[19]

4.4 The Boron-Carbon Bond

The bonds between the carbon atoms and boron atoms as well as between the boron atoms themselves in the icosahedra are essentially covalent. But like silicon carbide (Sec. 3.3), the bonding of boron carbide is also partially ionic.[6] The difference between the atomic spacing of SiC and the sum of the covalent radii of carbon and silicon on one hand and the sum of the ionic radii on the other hand show that the bonding, although mainly covalent, includes a certain degree of ionicity. The calculated covalent bond energy E_o is 9.42 eV and the ionic bond energy E_p is 1.41 eV.

4.5 Summary of Structural Data for Boron Carbide

The structural data for boron carbide is summarized in Table 7.5.[20][21]

Table 7.5: Boron Carbide Structural Data at 298 K

Formula: $(B^{11}C)CBC$

Density (g/cm^3): 2.52

Lattice Parameters (nm) (referenced to the hexagonal structure):

$a^o = 0.55991$

$c^o = 1.20740$

Unit Cell Volume (nm^3): 3.27809

Space Group: R3m

Variations in the lattice parameters and unit cell volume as a function of carbon concentration are given in Table 7.6.[21] Both lattice parameters decrease with decreasing carbon content.

Table 7.6: Lattice Parameters and Unit Cell Volume of Boron Carbide as a Function of Carbon Content (referenced to the hexagonal structure)

Carbon Content (at%)	Lattice Parameters (nm) *a*	*c*	Unit Cell Volume (nm^3)
20.2	0.55991	1.20740	3.27809
19.2	0.5995	1.20707	3.27763
19.6	0.56030	1.20802	3.28440
18.7	0.56032	1.20909	3.28745
16.0	0.56152	1.21411	3.31525
12.3	0.56286	1.21748	3.34039
9.3	0.56438	1.21750	3.35851
8.1	0.56440	1.21731	3.35818

4.6 Phase Diagram

The boron-carbon phase diagram is shown in Fig. 7.11.[15][16]

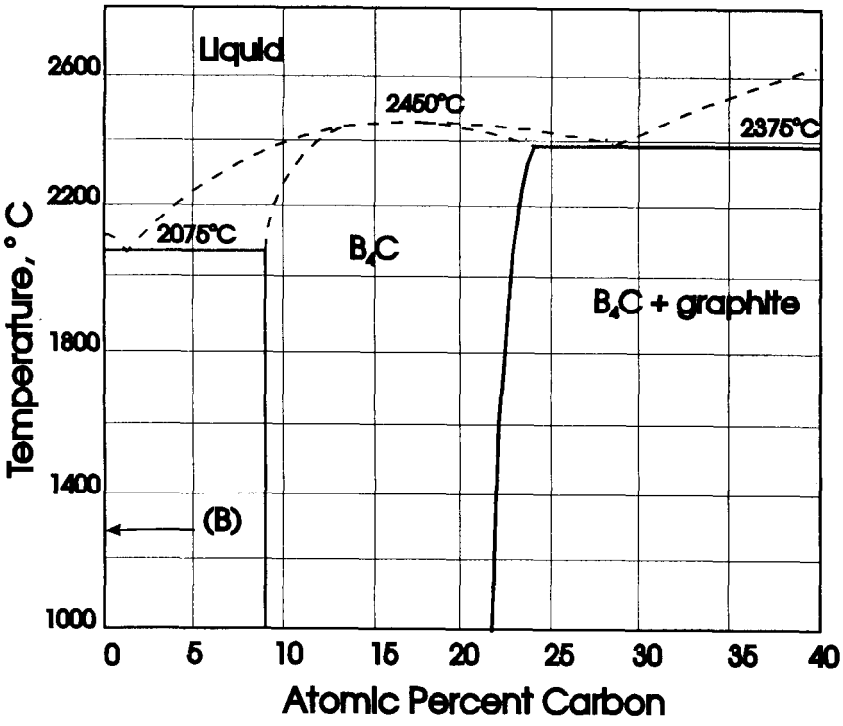


Figure 7.11: Boron–carbon phase diagram

REFERENCES

1. Evans, *An Introduction to Crystal Chemistry,* 2d. ed., Cambridge University Press, Cambridge UK (1979)
2. Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry*, Interscience Publishers, New York (1972)
3. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)
4. Van Vlack, L. H., *Elements of Materials Science & Engineering*, 4th Ed., Addison-Wesley, Reading, MA (1980)
5. Zulehner, W. et. al., Silicon, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., Vol. A23, VCH (1985)
6. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
7. Srinivasan, M., The Silicon Carbide Family of Structural Ceramics, in *Treatise on Materials Science and Technology,* Vol. 29 (J. B. Wachtman, Jr., ed.), Academic Press, Boston (1989)
8. *Silicon Carbide*, (R. C. Marshall, et al, eds.), Univ. of South Carolina Press, Columbia, SC (1973)
9. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
10. Ramsdell,. L. S., Studies on Silicon Carbide, *American Mineralogist,* 32(64) (1947)
11. Kern, R. S., et. al., Solid Solutions of AlN and SiC Grown by Plasma-assisted Gas-Source Molecular Beam Epitaxy, *J. Mater. Res.*, 8(7):1477–1480 (July 1993)
12. Fisher, G. R., and Barnes, P., Toward a Unified View of Polytypism in Silicon Carbide, *Philosophical Magazine,* B61:217–236 (1990)
13. Pandey, D., and Krishna, P., Polytypism in Close-Packed Structures, in *Current Topics in Materials Science* (E. Kaldis, ed.), pp. 415–491, North Holland Pub. Co., Amsterdam (1982)
14. Adams, D. M., *Inorganic Solids*, John Wiley & Sons, New York (1981)
15. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)
16. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. ed., ASM International, Metals Park, OH (1990)
17. Schwetz, K. A., and Lipp, A., Boron Carbide, Boron Nitride, and Metal Borides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A4, VCH (1985)

18. Alexander, M. N., Nuclear Magnetic Resonance Studies of the Structure of Boron Carbides, in *Boron Rich Solids*, Am. Inst. of Physics Conf. Proc. 140, New York (1986)
19. Madden, H. H., Nelson, G. C., and Wallace, W. O., Auger Electron Spectroscopy of Boron Carbide, in *Boron Rich Solids,* Am. Inst. of Physics Conf. Proc. 140, New York (1986)
20. Larson, A. C., Comment Concerning the Crystal Structure of B_4C, in *Boron Rich Solids,* Am. Inst. of Physics Conf. Proc. 140, New York (1986)
21. Aselage, T. L., and Tissot, R. G., Lattice Constants of Boron Carbide, *J. Am. Ceramic Soc.,* 75(8):2207–2212 (1992)

8

Characteristics and Properties of Silicon Carbide and Boron Carbide

1.0 INTRODUCTION

In the previous chapter, the structure and composition of the two covalent carbides, i.e., silicon carbide and boron carbide, were reviewed. This chapter is an assessment of the properties and a summary of the fabrication processes and applications of these two compounds.

Silicon carbide and boron carbide to a lesser degree are important industrial materials which are produced on a large scale in the form of powders, molded shapes, and thin films.

2.0 CHARACTERISTICS AND PROPERTIES OF SILICON CARBIDE

2.1 Historical Background and Present Status

Silicon carbide was first synthesized in 1891 by Acheson by passing an electric current through a mixture of carbon powder and clay. The material was originally thought to be a mixture of carbon and corundum (aluminum oxide) and trademarked *Carborundum* (CARBOncoRUNDUM).

Acheson soon determined that it was actually silicon carbide. The product was an immediate commercial success as an abrasive.[1][2]

The Acheson process is still the major production process. In the US, over 115,000 metric tons of silicon carbide were produced in 1994 with a value estimated at $40 million, much of which was for abrasives and metallurgical uses.[3]

2.2 Summary of Properties

The characteristics and properties of silicon carbide are summarized in Table 8.1[4]–[10] and reviewed in more detail in Secs. 4–8. Values quoted are for hot-pressed material and are an average of the values reported in the literature.

Table 8.1: Summary of Characteristics and Properties of Silicon Carbide.

Notes: (a) When structure is not indicated, values reported are for βSiC.
(b) Test temperature is 20°C unless otherwise stated.

Composition: SiC (very narrow range)

Molecular Weight (g/mol): 40.097

Color: colorless to yellow if pure, brown if doped with boron, nitrogen or aluminum

X-ray Density (g/cm3): αSiC(6H) 3.211
βSiC 3.214

Melting Point: 2545°C at 1 atm. (decomposes)
2830°C at 35 atm.
(decomposes to Si, Si_2C, Si_2, and SiC_3)
(see Sec. 4.2)

Specific Heat (J/mol·K) (see Fig. 8.1):
αSiC 27.69
βSiC 28.63

Heat of Formation (-ΔH) (kJ/mol·K at 298.15 K):
αSiC - 25.73 ± 0.63
βSiC - 28.03 ± 2

Thermal Conductivity (W/m·°C) (see Fig. 8.2):
αSiC 41.0
βSiC 25.5

Table 8.1: *(Cont'd)*

Thermal Expansion ($\times 10^{-6}$/°C) (see Fig. 8.3):		
	αSiC	5.12
	βSiC	3.8
Dielectric Constant @ 300 K:		
	αSiC (6H)	9.66–10.03
	βSiC	9.72
Electrical Resistivity (Ω·cm):		
	αSiC	0.0015 to 10^3
	βSiC	10^{-2} to 10^6
Debye Temperature:	αSiC	1200 K
	βSiC	1430 K
Energy Gap (eV):	αSiC (6H)	2.86
	βSiC	2.6
Exiton Energy Gap (eV) @ 4.2 K:		
	αSiC (4H)	3.265
	αSiC (6H)	3.023
	βSiC	2.39

Superconductive Transition Temperature: 5 K

Refractive Index βSiC, *n*, (Na) 2.48:

2.7104 @ 467 μm	2.6916 @ 498 μm
2.6823 @ 515 μm	2.6600 @ 568 μm
2.6525 @ 589 μm	2.6446 @ 616 μm
2.6264 @ 691 μm	

Vickers Hardness (GPa): 24.5–28.2 (varies with crystal face)

Modulus of Elasticity (GPa): 475 @ 293K
441 @ 1773K

Shear Modulus (GPa): 192

Bulk Modulus (GPa): 96.6

Elastic Constants (dynes/cm^2):

αSiC C11 5.0, C12 0.92, C33 5.64, C44 1.68, C66 2.04
βSiC C11 2.89, C12 2.34, C44 0.544

Poisson Ratio: 0.142

Flexural Strength (MPa): 350–600 (see Fig. 8.4)

Oxidation Resistance: excellent due to the formation of a layer of SiO_2

Chemical Resistance: essentially inert at room temperature

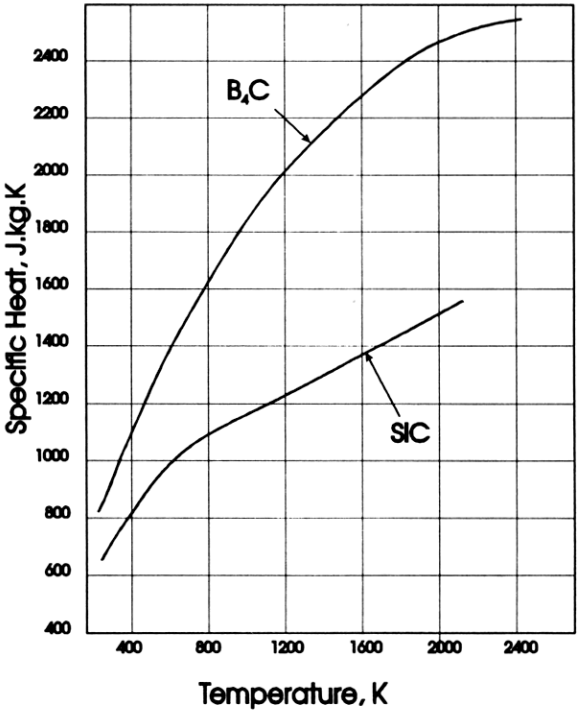


Figure 8.1: Specific heats of the covalent carbides as a function of temperature.

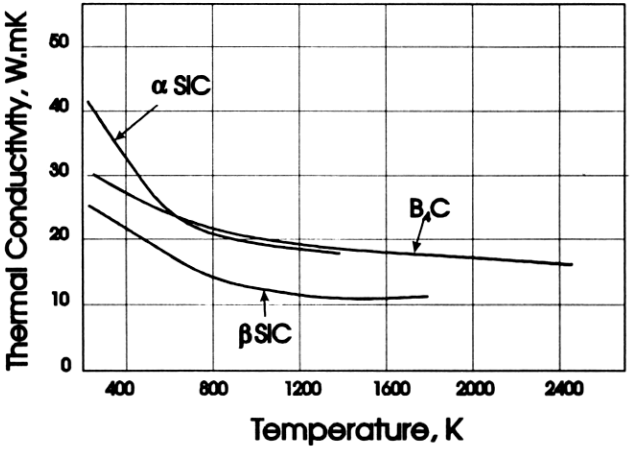


Figure 8.2: Linear thermal expansions of the covalent carbides as a function of temperature.

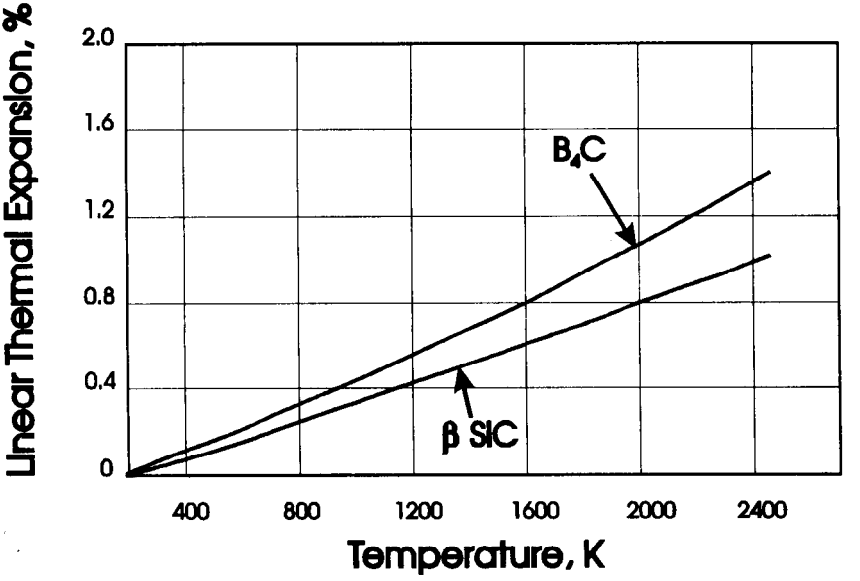


Figure 8.3: Linear thermal conductivities of the covalent carbides as a function of temperature.[15][16]

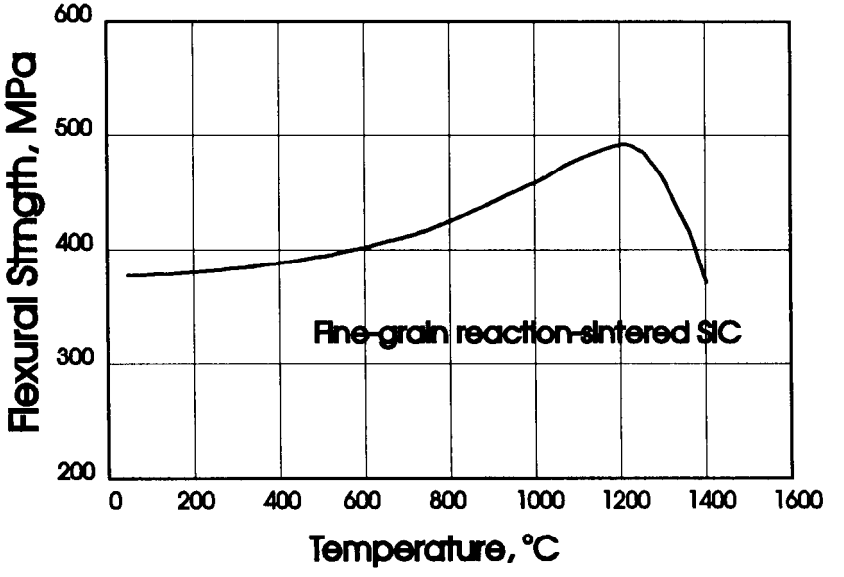


Figure 8.4: Flexural strength of silicon carbide as a function of temperature.

3.0 CHARACTERISTICS AND PROPERTIES OF BORON CARBIDE

3.1 Historical Background and Present Status

Boron carbide was first produced and identified at the end of the nineteenth century and for many years remained a laboratory curiosity. The structure and composition were tentatively determined in 1934.[11] It was not until the end of World War II that the first major applications were developed particularly in the nuclear industry. Production was estimated to reach $40 million in 1994.[12]

3.2 Summary of Properties

The characteristics and properties of boron carbide are summarized in Table 8.2 (for structural data, see Table 7.5 of Ch. 7). They are reviewed in more detail in Secs. 4–8. The material has outstanding hardness and excellent nuclear properties (see Sec. 7.0).

Table 8.2: Summary of Characteristics and Properties of Boron Carbide.
Note: Test temperature is 20°C unless otherwise stated.

Composition: $(B_{11}C)CBC$
Molecular Weight (g/mol): 55.26
Color: black (pure crystal is transparent and colorless)
X-ray Density (g/cm^3): 2.52
Melting Point: ≈2400°C (does not decompose)
Specific Heat (J/mole·K): 50.88 (see Fig. 8.1)
Heat of Formation (-ΔH) (kJ/mol·K at 298.15 K): 57.8 ± 11.3
Thermal Conductivity (W/m·°C): 30 (see Fig. 8.2)
Thermal Expansion (10^{-6}/°C): 4.3 (see Fig. 8.3)
Electrical Resistivity (Ω·cm): 0.1–10 (Fig. 8.5)
Seebeck Coefficient (μV/K): 200–300 @ 1250 (Fig. 8.6)

Vickers Hardness (GPa): 27.4–34.3

Modulus of Elasticity (GPa): 290–450

Shear Modulus (GPa): 165–200

Bulk Modulus (GPa): 190–250

Poisson's Ratio: 0.18

Flexural Strength (MPa): 323–430

Compressive Strength (MPa): 2750

Oxidation Resistance: in air up to 600°C. Formation of a film of B_2O_3 retards oxidation.

Chemical Resistance: generally excellent. Reacts with halogens at high temperature.

Absorption Cross Sec. for Thermal Neutrons (barn): 755 (see Sec. 7.0)

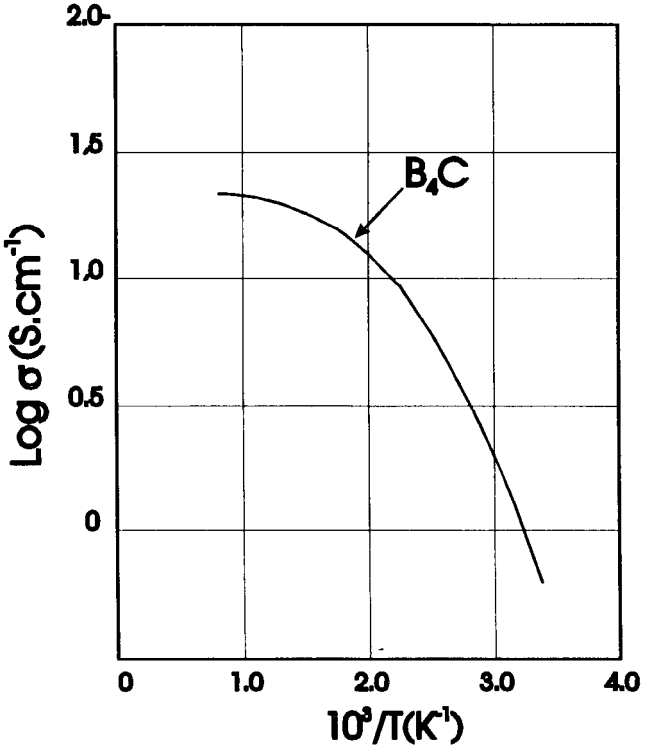


Figure 8.5: Electrical conductivity of boron carbide as a function of temperature.[23]

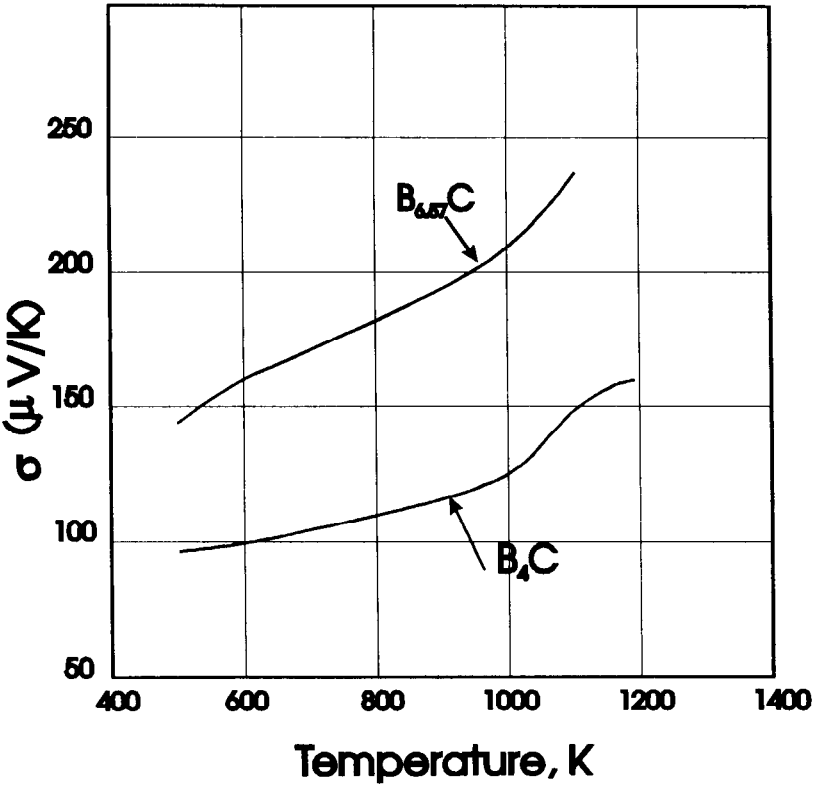


Figure 8.6: Seebeck coefficient of boron carbide as a function of temperature.

4.0 PHYSICAL AND THERMAL PROPERTIES OF THE COVALENT CARBIDES

4.1 Discussion and Comparison

In this section and the next three, the properties and characteristics of the covalent carbides are reviewed and compared whenever appropriate with those of the parent elements and of the refractory compounds of titanium. For comparison with other carbides, nitrides, or borides, see the appropriate tables in Chs. 4–6. Reported property values often vary considerably and the values given here are a general average.

4.2 Physical Properties

Physical properties are shown in Table 8.3.

Table 8.3: Density and Melting Point of Covalent Carbides and Other Refractory Compounds.

Material	Density (g/cm^3)	Melting Point °C
βSiC	3.214	2545 (decomposes)
αSiC(6H)	3.211	-
B_4C	2.52	2450
Si	2.329	1414
βB	2.35	2050
C (graphite)	2.26	3730 (sublimes)
C (diamond)	3.51	~1000 (graphitizes)
TiC	4.91	3067
TiN	5.40	2950
TiB_2	4.52	2980

Both covalent carbides have high melting points which are slightly lower than the titanium compounds but higher than silicon and boron. Under most conditions, the thermal decomposition of SiC may occur well below its intrinsic melting point[13] and decomposition can become significant at approximately 1700°C (see Sec. 3.7 and Fig. 7.8 of Ch. 7). The density of SiC is closer to that of diamond than it is to graphite, which can be expected since SiC has the structure of diamond.

Boron carbide does not appear to decompose up to its melting point. It vaporizes by the preferential loss of gaseous boron.[14]

4.3 Thermal Properties

The thermal properties of the covalent carbides are shown in Table 8.4.[15][16]

Table 8.4: Thermal Properties of Covalent Carbides and Other Refractory Materials at 20°C

Material	Specific Heat (J/mole·K)	Specific Heat (J/g·K)	Thermal Conductivity (W/m,K)	Thermal Expansion (× 10^{-6}/°C)
αSiC	27.69	0.691	41.0	5.12
βSiC	28.63	0.714	43–145	3.8
B_4C	50.88	0.921	20–35	4.3
Si	18.58	0.405	150	2.6
B(β)	11.16	1.032	60	4.8
C(diamond)	6.19	0.515	600–2100	0.8
TiC	33.8	0.563	21.0	7.4
TiN	33.74	0.545	19.2? 29.1	9.3 9.4
TiB_2	44.29	0.744	24.3	6.6

Specific Heat. The specific heat (C_p) of the covalent carbides as a function of temperature is shown in Fig. 8.1.[10] On a weight basis (J/g·K), the specific heat of silicon carbide and particularly boron carbide is higher than that of the other refractory carbides and nitrides listed in Table 8.2

Thermal Conductivity. The thermal conductivity or k (i.e., the time rate of transfer of heat by conduction) of covalent carbides, unlike that of the interstitial carbides, decreases with increasing temperature as shown in Fig. 8.2.[10] It is highly dependent on the method of formation which is reflected by the large spread in values. The thermal conductivity of silicon carbide

(particularly αSiC) is high yet considerably lower than that of the best conductors such as Type II diamond (2000 W/m·K), silver (420 W/m·K), copper (385 W/m·K), beryllium oxide (260 W/m·K), and aluminum nitride (220 W/m·K).[17]

Thermal Expansion. As shown in Fig. 8.3, thermal expansion of the covalent carbides is low and increases with increasing temperature but this increase is not entirely linear and is slightly more rapid at high temperature.[10] For discussion of thermal expansion, see Sec. 2.5 of Ch. 4.

5.0 ELECTRICAL AND SEMICONDUCTOR PROPERTIES

5.1 Electrical Properties

For discussion of electrical conductivity, see Sec. 3.1 of Ch. 4. As opposed to the transition metal carbides, the covalent carbides are considered electrical insulators since they have no metallic bonding and their electrons are strongly bonded to the nucleus and are not free to move.

Silicon carbide has self-heating and beta-emitting glow characteristics and as such is a standard material for heating elements (see Ch. 15). The anisotropy of the electrical conductivity of boron carbide is low, between 70 and 700 K.[18]

5.2 Semiconductor Properties

In a semiconductor material, the forbidden-energy gap is such that electrons in usable quantities are able to jump across it from the filled valence band to the empty conduction band.[19] The three elements that form the covalent carbides, i.e., boron, silicon, and carbon (in the form of doped diamond) are semiconductors and one would expect to find semiconductor properties in their compounds.

This is indeed the case and the semiconductor properties of βSiC have long been recognized but it is only recently, with the development of high-quality thin film techniques, that it is possible to consider it as a practical semiconductor material. βSiC is an indirect bandgap semiconductor with properties that promise significant improvements over existing materials in high power, high-frequency devices as shown in Table 8.5.

Table 8.5: Semiconductor Properties of βSiC and Other Materials

Property and Unit	Silicon	GaAs	βSiC	Diamond
Bandgap at 300K (eV)	1.12	1.43	2.35	5.45
Thermal Conductivity at RT (W/cm·K)	1.5	0.5	5	20
Saturated Drift Velocity (em/sec)	1.0×10^7	2.0×10^7	2.5×10^7	2.7×10^7
Drift Mobility, Electrons (em/V·sec)	1500	8500	1385	1800
Drift Mobility, Holes (em/V·sec)	450	400	100	1200
Breakdown Electric Field (V/cm)	3×10^5	4×10^5	5×10^6	1×10^7
Dielectric constant	11.8	12.8	9.7	5.5
Max. Junction Temperature (°C)	≈250	≈300	≈1000	≈1000

The table shows that βSiC is potentially more effective than silicon or gallium arsenide particularly in microwave and millimeter-wave devices and in high-voltage power devices (see Ch. 16).[20]

Boron carbide is a p-type semiconductor with a bandgap varying from 2.5 eV at the center of the Brillouin zone to about 1 eV at the zone boundary in the direction of the (111) wave vector.[21] It is considered a degenerate semiconductor with charge carriers (holes) of low mobility (< 1 cm/V sec) forming small polarons and moving through the material by phonon-assisted hopping.[22]

5.3 Boron Carbide as a Thermoelectric Material

Boron carbide is characterized by a relatively wide gap in its forbidden band, a low thermal conductivity, and a high thermoelectric power. These properties make it a potentially useful material for high-temperature thermoelectric energy conversion.[23] Electrical conductivity and Seebeck coefficient as a function of temperature and composition are shown in Figs. 8.5 and 8.6.

6.0 MECHANICAL PROPERTIES

6.1 Property Variables

For a discussion of mechanical properties and variables see Sec. 4.1 of Ch. 4. The mechanical properties of the covalent carbides often show a large spread in the reported values mostly due to differences in the fabrication processes. In addition, the following factors influence mechanical testing[6][24]:

- Density and porosity
- Presence of impurities
- Grain size and morphology
- Grain orientation
- Structural defects (vacancies, dislocations)
- Testing methods (3 points vs. points, Weibull statistics etc.)

6.2 Summary of Mechanical Properties

The mechanical properties of the covalent carbides are summarized in Table 8.6. The values are average values reported in the recent literature.[1][7][17][25]

6.3 Strength

Covalent carbides are strong materials especially at high temperature. However, like the transition-metal carbides and most other ceramics, they are intrinsically brittle (for discussion, see Sec. 4.3 of Ch. 4). Silicon

carbide retains its strength at high temperature up to 1200°C as shown in Fig. 8.6. This is also true for boron carbide but to a lesser degree.[6]

The covalent carbides, like the transition-metal carbides, have the ability to deform plastically above the ductile-to-brittle transition temperature. Below that temperature, the carbides fail in a brittle manner while above they show ductile behavior and undergo plastic deformation

Table 8.6: Mechanical Properties of Covalent Carbides and Other Refractory Compounds at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)	Shear Modulus (GPa)	Flexural Strength (MPa)
βSiC	24.5–28.2	475	192	350–600
B_4C	up to 48	290–450	165–200	323–430
B	25.3	up to 480		
C (diamond)	up to 100	910–1250		
TiC	28–35	410–510	186	240–390
TiN	18–21	250		
TiB_2	33	575	400	

Hot-isostatic pressing and high firing temperature (2100°C) significantly increase the strength of boron carbide. Flexural strength as high as 429 MPa and Young's modulus as high as 433 GPa are observed.[26][27]

6.4 Hardness

It is significant that two of the hardest materials contain boron (cubic boron nitride and boron carbide), boron itself being a very hard material.[26]

Boron carbide is the hardest material after diamond and cubic boron nitride, and it maintains its hardness to 1800°C.[21] For discussion on hardness, see Sec. 4.4 of Ch. 4.

7.0 NUCLEAR PROPERTIES

Boron is an important material for nuclear applications due to its high neutron absorption cross section (760 barn at neutron velocity of 2200 m/sec). The cross section of the B^{10} isotope is considerably higher (3840 barn).[24] In addition, boron does not have decay products with long half-life and high-energy secondary radioactive materials. However, pure boron is extremely brittle and difficult to produce in shapes such as control rods. Boron carbide is usually the material of choice since it provides a high concentration of boron atoms in a strong and refractory form and is relatively easy to mold (see Ch. 16).

8.0 SUMMARY OF FABRICATION PROCESSES

The fabrication processes for silicon carbide and boron carbide are also reviewed in Chs. 14 and 15.

8.1 Silicon Carbide

The Acheson process mentioned above is a carbothermic reduction now produced by electrochemical reaction of high purity silica sand and carbon in an electric furnace. The general reaction is:

$$SiO_2 + 3C \rightarrow SiC + 2CO\ (g)$$

The addition of sawdust increases the porosity of the charge and facilitates gas circulation. Chlorine is added to reduce impurities.[4] Alpha SiC is produced above 2100°C and βSiC at 1500–1600°C. Shapes are produced by standard ceramic forming technologies, pressureless sintering, and reaction bonding; coatings are produced by CVD.[6][28]

8.2 Boron Carbide

The major boron carbide production process consists of the reduction of boric oxide (B_2O_3) with carbon (usually in the form of coke) in an electric furnace by resistance heating or arc heating at high temperature (up to 2300°C).[29][30] The material is also produced by the same reduction reaction but in the presence of magnesium and by the direct synthesis of the elements.[21] Monolithic shapes are produced by hot-isostatic pressing.[26] Boron carbide coatings are usually produced by CVD.[28][31]

9.0 SUMMARY OF APPLICATIONS AND INDUSTRIAL IMPORTANCE

The following is a summary of applications of silicon carbide and boron carbide in production or development. More details are given in the Ch. 16.

9.1 Silicon Carbide[1]–[3]

Powder

- Deoxidizer in steel production and other metallurgical processes (largest tonnage use)
- Powder abrasives, bonded abrasives, coated abrasives
- Filler in refractory cements

Shapes

- Refractory products, bricks, kiln furniture, tubes and other shapes[3]
- Electric heating elements and resistors
- Igniters for gas appliances (recrystallized SiC)
- Radiation sensors (amorphous SiC)
- Low-weight, high-strength mirrors
- High-power, high-frequency, and high-temperature semiconductor devices
- Radiation-resistant semiconductors

- Fibers and whiskers
- Matrix in ceramic composites
- Thermocouple sheath
- Lightweight armor

Coatings

- Coatings for susceptors and heating elements for epitaxial silicon deposition
- Coatings for fusion reactor applications
- Nuclear waste container coatings
- Coatings for ceramic heat exchanger tubes
- Oxidation resistant coatings for carbon-carbon composites
- Heteroepitaxial deposit on silicon
- Blue light-emitting diodes (LED)

9.2 Boron Carbide[11][28][32]–[34]

- Shielding and control of nuclear reactors pellets, shapes, and coatings
- Wear parts, sandblast nozzles, seals[25][26]
- Mortar and pestle
- High-grade abrasive and lapping powder
- High-temperature thermocouple
- Lightweight body and airborne armor
- Matrix material for ceramic composites[24]
- Coating for nozzles, dressing sticks for grinding wheels
- Lightweight body armor

REFERENCES

1. Parche, M. C., *Fact about Silicon Carbide*, The Carborundum Company, Niagara Falls, NY (1961)
2. Shaffer, P. T., *Handbook of Advanced Ceramic Materials,* Advanced Refractory Technologies Inc., Buffalo, NY (1991)
3. Ault, N. N., and Crowe, J. T., Silicon Carbide, *Ceramic Bulletin*, 70(5) (1991)
4. Divakar, R., et al., Silicon Carbide in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)
5. *Silicon Carbide*, (R. C. Marshall et al., eds.), Univ. of South Carolina Press, Columbia, SC (1973)
6. Srinivasan, M., *The Silicon Carbide Family of Structural Ceramics*, in *Treatise on Materials Science and Technology,* Vol. 29 (Wachtman, J. B., Jr., ed.), Academic Press, Boston (1989)
7. Kosolapova, T. Y., *Carbides*, Plenum Press, New York (1971)
8. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
9. *High Performance Engineered Sintered Silicon Carbide*, Technical Brochure, The Carborundum Co. (1978)
10. *Engineering Property Data on Selected Ceramics,* Vol. 2, *Carbides*, MCIC HB-07-2, Battelle Institute, Columbus, OH (1987)
11. Shaffer, P. T., *Handbook of Advanced Ceramic Materials,* Advanced Refractory Technology, Buffalo, NY (1992)
12. Boron Carbide and Boron Nitride, *Mitchell Market Reports*, Monmouth, Wales (1992)
13. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. ed., ASM International, Metals Park, OH (1990)
14. Robson, H. E., and Gilles, P. W., The High Temperature Properties of Boron Carbide and the Heat of Sublimation of Boron, *J. Phys. Chem.*, 68(5):983–989 (1964)
15. Gosset, D., Guery, M., and Kryger, B., *Thermal Properties of Some Boron-rich Compounds*, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds), Am Inst. of Physics, New York (1986)
16. Türkes, P. R., Swartz, E. T., and Pohl, R. O., Thermal Properties of Boron and Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage et al., eds.), Am Inst. of Physics, New York (1986)
17. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)

18. Werheit, H., and Rospendowski, S., Anisotropy of the Electrical Conductivity of Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds.), Am Inst. of Physics, New York (1986)
19. Van Vlack, L. H., *Elements of Materials Science and Engineering*, Addison-Wesley Publishing, Reading, MA (1980)
20. Davis, R. F., Silicon Carbide and Diamond Semiconductor Thin Films, *Am. Ceram. Soc. Bull.*, 72(6) (1993)
21. Makarenko, G. N., *Borides of the IVb Group*, in *Boron and Refractory Borides* (V. L. Matkovich, ed.), Springer-Verlag, Berlin (1977)
22. Wood, C., Transport Properties of Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds.), Am Inst. of Physics, New York (1986)
23. Koumoto, K., Thermoelectric Properties of CVD Boron Carbide, *Am. Ceram. Soc. Bull.*, 73(10):84–87 (1994)
24. Hollenberg, G. W., and Walther, G., The Elastic Modulus and Fracture of Boron Carbide, *J. Am. Ceram. Soc.* 63(11–12):610–613 (1980)
25. Bower. J. G., Elemental Boron, Preparation, Properties and Applications, in *Progress in Boron Chemistry,* (R. Brotherton and H. Steinberg, eds.), Pergamon Press, Oxford, UK (1969)
26. Schwetz, K. A., and Lipp, A., Boron Carbide, Boron Nitride, and Metal Borides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., Vol. A4, VCH (1985)
27. Tressler, R. E., High-Temperature Stability of Non-Oxide Structural Ceramics, *MRS Bull.*, 58–63 (Sept. 1993)
28. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
29. Wentorf, R. H., Jr., Refractory Boron Compounds, in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)
30. Thomson, R., The Chemistry of Metal Borides and Related Compounds, in *Progress in Boron Chemistry* (R. J. Brotherton and H. Steinberg, eds.), Pergamon Press Ltd., New York (1970)
31. Janson, U., Chemical Vapor Deposition of Boron Carbides, *Materials and Manufacturing Processes*, 6(3):481–500 (1991)
32. Tetrabor Boron Carbide, *Technical Brochure*, ESK, Munich, Germany (1992)
33. Norbide Boron Carbide, *Technical Brochure*, Norton Co., Worcester, MA (1992)
34. Baudis, U., and Fichte, R., Boron and its Alloys, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. ed., Vol. A4, VCH (1985)

9

The Refractory Nitrides

1.0 INTRODUCTION

The refractory nitrides are in many respects similar to the refractory carbides. They are hard and wear-resistant with high melting points and good chemical resistance. They are important industrial materials and have a significant number of major applications in cutting and grinding tools, wear surfaces, semiconductors, and others.

This chapter is a review of the general characteristics of the refractory nitrides and their classification. Like the refractory carbides (see Ch. 2), the refractory nitrides can be divided into two major types: the interstitial nitrides reviewed in Chs. 10 and 11 and the covalent nitrides, reviewed in Chs. 12 and 13.

2.0 GENERAL CHARACTERISTICS OF NITRIDES

2.1 Definition and Classification

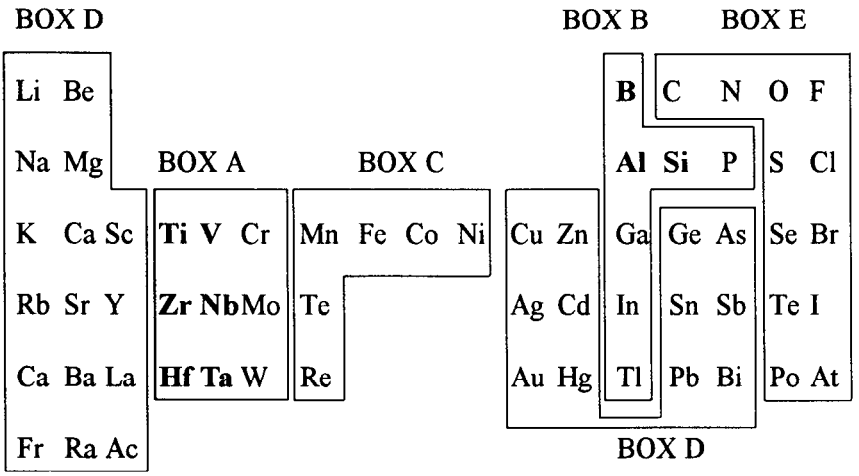
The element nitrogen forms compounds with most other elements (i.e., N_2O, NCl_3) but, by convention, the term nitride is only applied to those

compounds that nitrogen forms with elements of lower or about equal electronegativity.[1] The nitrides can be classified in five general categories, based on their electronic structure and bonding characteristics as shown in Table 9.1.[2]–[5] These categories are commonly identified as:

1. Interstitial nitrides
2. Covalent nitrides
3. Intermediate nitrides
4. Saltlike nitrides
5. Volatile (molecule forming) nitrides

Table 9.1:[2] Classification of the Elements Forming Nitrides

Note: Elements shown in bold type form refractory nitrides.



BOX A: Interstitial nitrides
BOX B: Covalent nitrides
BOX C: Intermediate nitrides
BOX D: Saltlike nitrides
BOX E: Volatile (molecule forming) nitrides

2.2 Refractory Qualifications

As stated in Ch. 1, the term *refractory*, in the context of this book, defines a material with a melting point above 1800°C and with a high degree of chemical stability.

In the five categories listed above, only some of the interstitial and covalent nitrides qualify as refractory, i.e., the nitrides of the elements of Groups IV and V and the covalent nitrides of boron, aluminum, and silicon. These elements are shown in bold type in Table 9.1. Unlike the carbides of Group VI elements, the Group VI nitrides are not refractory and consequently are not considered in any depth in this book.

Some of intermediate and saltlike nitrides have high melting points but are not chemically stable; yet they are important materials and are briefly reviewed in Secs. 5.4 and 5.3 below.

3.0 FACTORS CONTROLLING NITRIDE FORMATION

Three general and interrelated atomic characteristics play an essential part in the formation of nitrides: the difference in electronegativity between the element nitrogen and the other element forming the nitride, the size of the respective atoms, and the electronic bonding characteristics of these atoms.

3.1 Nitride Formation and Electronegativity

As shown in the partial Periodic Table of the Elements shown in Table 2.1 of Ch. 2, nitrogen has a higher electronegativity than any other of the elements with the exception of oxygen and fluorine.[1][6] As in the case of carbides, the difference in electronegativity of the respective elements plays an important part in the structure and bonding of refractory nitrides (see discussion of electronegativity in Sec. 3.1, Ch. 2).

This difference is large with the interstitial nitrides (Ti-N:1.5, V-N:1.4, Zr-N:1.6, Nb-N:1.4, Hf-N:1.7, Ta-N:1.5) but less pronounced with the covalent nitrides (B-N:1.0, Al-N:1.5, Si-N:1.2). Since nitrogen has a higher electronegativity than carbon, refractory nitrides show a greater electronegativity difference than the equivalent carbides.

3.2 Nitride Formation and Atom Size

The second factor controlling the formation of nitrides is the atomic radius of the constituent elements. The radii of these elements are listed in Table 9.2 (see discussion on atomic radius in Sec. 4.1 of Ch. 2). One should note that nitrogen is one of the smallest atoms, and smaller than carbon. Table 9.2 also shows the type of nitride formed, i.e., interstitial (IS) or covalent (C), or intermediate (IM).

Only the early transition metals (Groups IV, V, and VI) have a host lattice that is large enough for the nitrogen atom to fit readily and so form stable interstitial compounds, as shown in Table 9.1. As mentioned previously, only the nitrides of Group IV and V are considered refractory.

The importance of the atomic radius will become evident as the structure of interstitial and covalent nitrides is reviewed in Chs. 10 and 12. Generally speaking, when the difference in radii of the two elements is large, interstitial nitrides are formed (i.e., TiN); when it is small, covalent nitrides are formed (i.e., Si_3N_4).

3.3 The Electronic Bonding of Nitrides

The third factor governing the structure of nitrides is the nature of the bond between the nitrogen atom and the other element forming the compound. As mentioned in Ch. 2, the bond is the force of attraction that holds together the atoms of a molecule.[6] The bonds in refractory carbides can be ionic (saltlike nitrides), covalent (covalent nitrides), or a combination of metallic, covalent, and ionic (interstitial nitrides) (for a discussion of electronic bonding, see Ch. 2, Sec. 5.0).

4.0 GENERAL CHARACTERISTICS OF NITRIDES

The characteristics of the nitrides can be summarized as follows.

4.1 Interstitial Nitrides

The difference in electronegativity between nitrogen and the metal is large and so is the difference in atomic size so that the nitrogen atom nests readily in the interstices of the metal lattice. Like the carbide, the bonding is

mostly metallic with some covalent and ionic bond components, giving the interstitial nitrides metallic characteristics such as high electrical and thermal conductivities. In addition, these materials have high melting points and high hardness; they are chemically inert but only the nitrides of Groups IV and V fully meet the refractory criteria. They are reviewed in Chs. 10 and 11.

Table 9.2: Approximate Atomic Radius of Nitrogen and Selected Elements[7][8]

Element	Atomic Number	Atomic Radius nm	Type of Nitride
Boron	5	0.088	C
Carbon	6	0.078	
NITROGEN	**7**	**0.074**	
Oxygen	8	0.066	
Aluminum	13	0.126	C
Silicon	14	0.117	C
Titanium	22	0.1467	IS
Vanadium	23	0.1338	IS
Chromium	24	0.1267	IM
Manganese	25	0.1261	IM
Iron	26	0.1260	IM
Cobalt	27	0.1252	IM
Nickel	28	0.1244	IM
Zirconium	40	0.1597	IS
Niobium	41	0.1456	IS
Molybdenum	42	0.1386	IS
Hafnium	72	0.1585	IS
Tantalum	73	0.1457	IS
Tungsten	74	0.1394	IS

IS = Interstitial nitride
C = Covalent nitride
IM= Intermediate nitride

4.2 Covalent Nitrides

Unlike the interstitial nitrides, the covalent nitrides are not metallic compounds. The differences in electronegativity and atomic size between the nitrogen and the other element are small and their electronic bonding is essentially covalent. In this respect, they are similar to the covalent carbides. They include the nitrides of Group IIIb (B, Al, Ga, In, Tl) and those of silicon and phosphorus. Of these, only three are considered refractory: boron nitride, silicon nitride, and aluminum nitride. These are reviewed in Chs. 12 and 13.

4.3 Intermediate Nitrides

The late-transition metals (Group VII and VIII) either do not form nitrides at all, such as the precious metals, or else form nitrides with intermediate (distorted) interstitial structures. These materials decompose readily and are not chemically stable. Examples are manganese, iron, cobalt, and nickel nitrides. In this respect, they are similar to the intermediate carbides (see Ch. 2, Sec. 6.3).

4.4 Salt-Like Nitrides

The saltlike (or salinic) nitrides are composed of nitrogen and the most electropositive elements, i.e., the alkali metals, alkaline-earth metals, and the metals of Group III of the Periodic Table, including the lanthanide and actinide series. The difference in electronegativity between these elements and nitrogen is large and the atomic bonding is essentially ionic. They have the characteristics of a salt with a fixed composition.

Although some of these saltlike nitrides have high melting points (for instance, thorium nitride: 2820°C; uranium nitride: 2800°C; plutonium nitride: 2550°C; beryllium nitride: 2200°C; barium nitride: 2200°C), they are sensitive to hydrolysis and react readily with water or moisture to give ammonia and the corresponding metal oxide or hydroxide. Consequently, they do not meet the refractory requirements as interpreted here. Some of these nitrides are useful industrial materials particularly as sintering additives for the production of silicon nitride, aluminum nitride, and cubic boron nitride (see Ch. 14).

REFERENCES

1. Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry*, Interscience Publishers, New York (1972)
2. Benesovsky, F., Kiefer, R., and Ettmayer, P., Nitrides, in *Kirk-Othmer's Encyclopedia of Industrial Chemistry*, 4th. Ed., John Wiley & Sons (1993)
3. Ettmayer, P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
4. Hampshire, S., *Nitride Ceramics*, in *Materials Science and Technology*, Vol. 11, (M. V. Swain, ed.) VCH, New York (1994)
5. Haussinger, P., Leitgeb, P., and Rückborn, G., Nitrogen in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 17, VCH (1985)
6. Evans, R. C., *An Introduction to Crystal Chemistry*, Cambridge Univ. Press, Cambridge (1979)
7. Wehr, M. R., Richards, J. A., Jr. and Adair, T. W., III, *Physics of the Atom*, Addison-Wesley Publishing Co., Reading, MA (1978)
8. March, J., *Advanced Inorganic Chemistry*, John Wiley & Sons, New York (1985)

10

Interstitial Nitrides: Structure and Composition

1.0 DEFINITION AND GENERAL CHARACTERISTICS OF INTERSTITIAL NITRIDES

As mentioned in Ch. 9, the refractory nitrides consist of two structurally different types generally known as interstitial and covalent nitrides. This chapter provides a general review of the structural characteristics and composition of the interstitial nitrides and follows the outline of Ch. 3, "Interstitial Carbides: Structure and Composition." Some of these interstitial nitrides, titanium nitride in particular, are major industrial materials.

1.1 Definition

Interstitial nitrides are crystalline compounds of a host metal and nitrogen where the nitrogen atom occupies specific interstitial sites in the metal structure which is generally close packed (see Ch. 3, Sec. 1.1 for a similar definition of the interstitial carbides). This places a lower limit on the size of the metal atom in order for the nitrogen atom to fit in the available sites of the metal structure.

The metals of the nine early-transition elements, i.e., titanium, zirconium, and hafnium of Group IV, vanadium, niobium, and tantalum of Group V, and chromium, molybdenum, and tungsten of Group VI, fit the criteria of size and site availability, and form interstitial nitrides.[1]

1.2 General Characteristics

Interstitial nitrides are similar to interstitial carbides in structure and composition, and the two groups of materials closely resemble each other. The nitrides however are not as refractory. In fact, only the nitrides of Group IV and V have melting points above 1800°C. Those of Group VI, i.e., chromium, molybdenum, and tungsten nitrides, have lower melting (or decomposition) points and dissociate rapidly into N_2 and the pure element at high temperature (≈1000°C). Their chemical stability is relatively poor and they do not therefore meet the refractory criteria. They are mentioned in this chapter for reference purposes.

The interstitial nitrides have several important characteristics in common with the interstitial carbides.[1][2]

- They have a complex electronic bonding system which includes metallic, covalent, and ionic components
- They are primarily non-stoichiometric phases
- Like ceramics, they have high hardness and strength
- Like metals, they have high thermal and electrical conductivity

Much more so than the carbides, the interstitial nitrides are susceptible to the presence of even minute amounts of impurities particularly oxygen, which tend to distort the structure. Like the carbides, the interstitial nitrides allow nonmetal vacancies (i.e., nitrogen) in the lattice, but unlike the carbides, they also tolerate metal-atom vacancies. This means that, if the metal-atom vacancies are more numerous than the nitrogen-atom vacancies, the nitrogen-to-metal ratio will be >1. As a result, the structure of interstitial nitrides is sometimes difficult to identify with certainty.

Vacancy ordering has also been noted but no systematic study has been made of this phenomenon.[1][2]

2.0 ATOMIC STRUCTURE OF NITROGEN

A knowledge of the electronic structure of the nitrides is necessary to understand their mechanism of formation and their general characteristics and properties. It is thus appropriate to first review the electronic structure of nitrogen.[3]

2.1 Nucleus and Electronic Configuration of the Nitrogen Atom

Note: The concepts of quantum number, ground state, electron wave number, ground-state orbitals, and valence are briefly reviewed in Ch. 3, Sec. 2.1.

The element nitrogen has the symbol N and an atomic number (or Z number) of 7, i.e., the neutral atom has seven protons and seven neutrons in the nucleus and correspondingly seven electrons. The ground-state electronic configuration of these seven electrons is $1s^2 2s^2 2p^3$, that is, two electrons are in the K shell ($1s$) and five in the L Shell: two in the $2s$ orbital and three in the $2p$ orbital distributed among the p_x, p_y, and p_z orbital (the five valence electrons). The three $2p$ electrons are unpaired with spins parallel as shown in Fig. 10.1.

Under normal conditions, nitrogen exists as a stable diatomic molecule (N_2) formed with all three bonds from each atom pointed toward the other atom.[4] Molecular nitrogen has an extremely high heat of dissociation:[5]

$$N_2 \rightarrow 2N \quad -\Delta H_o \; 943.8 \text{ KJ/mol}$$

A photoelectron spectrum of the nitrogen molecule is shown in Fig. 10.2 and the electronic structure is shown in Fig. 10.3.[3][6] The two $2s$ orbitals of the nitrogen atoms combine to form the two orbitals indicated as 1 (bonding orbital) and 2 (antibonding orbital). The six $2p$ orbitals combine to form six orbitals. Of these six, three (marked 3, 4, and 5) are bonding orbitals. The electrons ejected from orbital 1 do not appear in the spectrum of Fig. 10.2 because the light energy used is smaller than the ionization potential of these electrons.

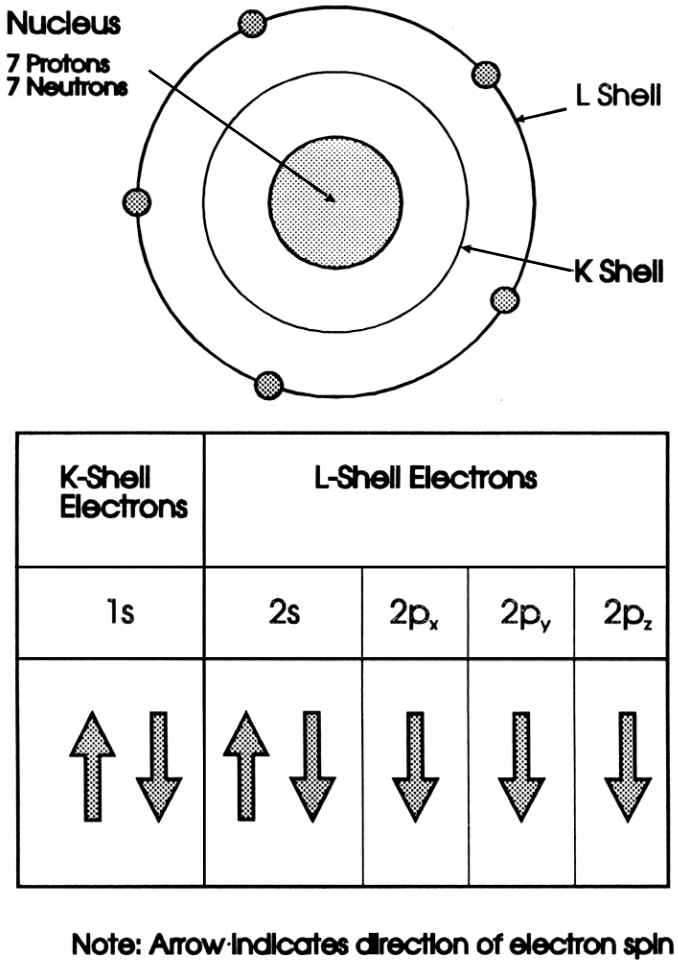


Figure 10.1: Schematic representation of the electronic configuration of the nitrogen atom.

2.2 Bonding and Hybridization

Nitrogen compounds have an electronic structure that can be visualized as a completed octet of electrons around each atom. Since nitrogen has five valence electrons, the octet is obtained by accepting or sharing three electrons from the atom bonded to nitrogen. Nitrogen accepts electrons only from the most electropositive elements (those on the left of Table 9.1 of

Ch. 9), to form the saltlike nitrides. Bonding with the transition metals occurs mostly by the sharing of electrons (covalent bonds) and by metallic bonding. Bonding with boron, aluminum, and silicon is essentially covalent (see Ch. 12).

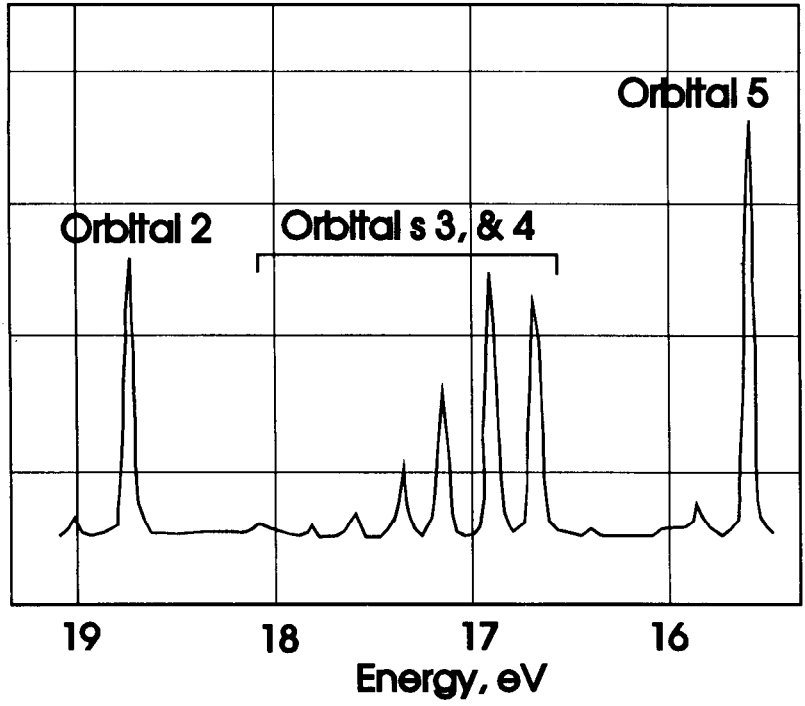


Figure 10.2: Photoelectron spectrum of the nitrogen atom.[3][6]

The ground-state configuration of the nitrogen atom does not account for the various types of bonding found in many nitrogen compounds. These bonds occur through hybridization, a concept presented in Sec. 2.0 of Ch. 3. In the nitrogen atom, the *s* and p_z orbitals can be hybridized since they belong to the same symmetry species. The hybridization results in two new levels: σ_1 which is predominately an *s* orbital with some p_z characteristic, and σ_2 which is predominately a *pz* orbital with some *s* characteristics. The net result of hybridization is to increase the bonding effect of σ_2.[3] The hybridized nitrogen atom has three unpaired orbitals, $2s$, $2p_x$, and $2p_y$, available for sp^2 bonding.

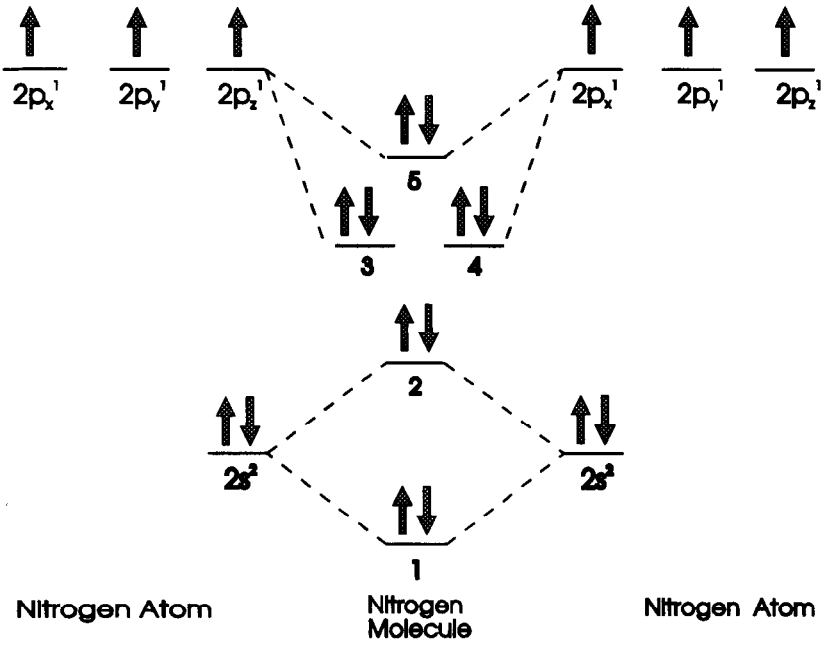


Figure 10.3: Schematic representation of the nitrogen molecule.[3][6]

3.0 ATOMIC STRUCTURE OF INTERSTITIAL NITRIDES

The electronic and crystal structures of the transition metals forming interstitial nitrides are reviewed in Ch. 3, Sections 3.0 and 4.0, and a definition of interstitial structures is given in Sec. 5.1 of the same chapter.

3.1 Atomic Radii Ratio

As mentioned in Ch. 9, Sec. 3.2, the nitrogen atom is smaller than the carbon atom and interstitial nitrides are formed more readily than the corresponding carbides (see Ch. 3). As shown in Table 10.1, the nine early

transition elements qualify as host structures for interstitial nitrides, since the ratio of the radius of the nitrogen atom to the radius of the atom of the host metal is less than 0.59. The radii ratio is smallest for the nitrides of Group IV and largest for those of Group VI.[1][4]

Table 10.1: Nitrogen/Metal Atomic Radii Ratio of Interstitial Nitrides

Group IV		Group V		Group VI	
Ti-N	0.504	V-N	0.553	Cr-N	0.584
Zr-N	0.463	Nb-N	0.508	Mo-N	0.534
Hf-N	0.467	Ta-N	0.508	W-N	0.531

Limit for interstitial formation: 0.59

3.2 Interstitial Sites

There are two types of interstitial sites in the close-packed structure of early transition metals, i.e., the tetrahedral sites and the octahedral sites. The nitrogen atoms occupy only the octahedral sites since the tetrahedral sites are too small to accommodate them. There is one octahedral site per atom of the host metal (see Ch. 3, Sec. 5.0 and Figs. 3.14, 3.15, and 3.16).

4.0 COMPOSITION AND CRYSTALLINE STRUCTURE OF INTERSTITIAL NITRIDES

4.1 Composition and Structure

The composition and structure of interstitial nitrides are listed in Table 10.2.[1][4][7][8]

Table 10.2: Known Phases and Structures of Interstitial Nitrides

Group IV	Group V	Group VI
Titanium nitride	**Vanadium nitride**	**Chromium nitride**
θ-Ti_2N (hex)	β-V_2N (hcp)	Cr_2N (hcp)
η-Ti_3N_{2-x} (r)	δ-VN_{1-x} (fcc)	δ-CrN (fcc)
ζ-Ti_4N_{3-x} (r)	δ'-$VN_{0.8}$ (hex)	CrN (orth)
δ'-$TiN_{0.5}$ (hex)		
δ-TiN_{1-x} (fcc)		
Zirconium nitride	**Niobium nitride**	**Molybdenum nitride**
Zr_3N_4 (fcc)	β-Nb_2N (hcp)	γ-MoN_{1-x} (fcc)
δ-ZrN_{1-x} (fcc)	γ-Nb_4N_{3-x} (hex)	β-Mo_2N (hex)
	η-NbN (hcp)	δ-MoN (hcp)
	δ'-NbN (hcp)	
	δ-NbN_{1-x} (fcc)	
	Nb_3N_6 (hcp)	
	Nb_4N_5 (hex)	
Hafnium nitride	**Tantalum nitride**	**Tungsten nitride**
θ-Hf_3N_{2-x} (hex)	β-Ta_2N (hcp)	W_2N (fcc)
ζ-Hf_4N_{3-x} (r)	θ-TaN (hcp)	WN (hexa)
δ-HfN_{1-x} (fcc)	η-TaN (hex)	
	δ-TaN_{1-x} (fcc)	
	Ta_5N_6 (hcp)	
	Ta_4N_5 (hex)	
	Ta_3N_5 (orth)	

fcc = face-centered cubic (close packed)
hcp = hexagonal close packed
hex = simple hexagonal
r = rhombohedral
orth = orthorhombic

4.2 Composition

As can be seen in Table 10.2, many different compositions are known and of these, the most common and important is the mononitride, usually expressed as MN_{1-x} (M = metal). This notation shows that the nitrogen content is variable and is the result of incomplete filling of the available sites. The mononitrides (with the exception of WN) have a face-centered cubic close-packed structure (fcc) where the successive layers follow the sequence ABCABC; the coordination number of the metal atom is 12 (see Sec. 4.0 of Ch. 3). A typical fcc structure, that of TiN, is shown in Fig. 10.4.[9]

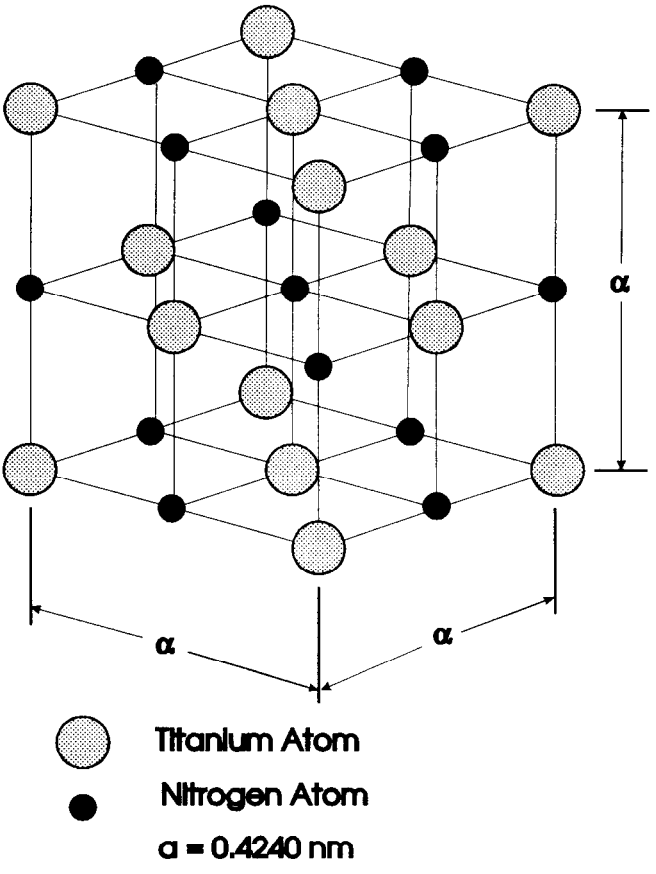


Figure 10.4: Schematic representation of the structure of the titanium–nitride crystal.

Next in importance is the M_2N composition which usually has a hexagonal close-packed structure (hcp) where the atoms of the first layer are directly over those of the third layer. It is expressed as ABAB with hexagonal symmetry and a coordination number of the metal atom of 12 (see Fig. 3.9 of Ch. 3). The hcp structure is found in the nitrides of Group V and VI but not in those of Group IV.

Another structure is the simple hexagonal structure (hex) such as that of tungsten mononitride (δWN) where the metal atom layers form a sequence of layers AA or BB. Such structures are not close-packed and do not form octahedral sites; the available interstitial sites are trigonal prisms (see Fig. 3.13 of Ch. 3). This structure cannot form if the ratio of the nitrogen/metal atomic radii is small, as is the case in the Zr-N and Hf-N systems.

Finally several compositions have rhombohedral orthorhombic structures, some of which may contain more nitrogen atoms than metal atoms.[4]

4.3 Summary of Characteristics

The characteristics of each group are summarized in Table 10.3.

4.4 Metal-to-Nitride Structural Switching

Table 10.3 indicates that the structure of a transition-metal nitride is generally different from that of the host metal. As shown in Table 3.2 of Ch. 3, most early transition metals have a bcc structure which cannot geometrically accommodate the nitrogen atoms in its interstices and, to form a nitride, the metal must switch to a close-packed structure (fcc or hcp) where the octahedral sites are large enough. The same switching situation is observed with transition-metal carbides (see Sec. 6.3 of Ch. 3).

This switch is accompanied by an increase of a few percent in the distance between the metal atoms, as shown in Table 10.4. In this table, the metal-to-metal (M-M) atomic spacings of the pure metals of Group IV and V are compared with their M-M spacings within their mononitride structures. The increase is generally more pronounced for the nitrides of Group V than for those of Group IV. This factor influences the metallic bonding as reviewed in the following section. However this increase is not as large as that of carbides (see Table 3.5 of Ch. 3).

Lattice parameters and other structural information are reported in Ch. 11.

Table 10.3: Compositional and Structural Characteristics of Transition-Metal Nitrides

Group IV Nitrides (Ti, Zr, Hf)

- Lowest nitrogen/metal atomic radii ratio
- Several compositions with mononitride being the major one and with nitrogen atoms in all octahedral sites (at stoichiometry)
- fcc structure (NaCl) of mononitrides
- The pure host metal has two structures: hcp and bcc*
- Range of melting or decomposition point: 2950–3387°C

Group V Nitrides (V, Nb, Ta)

- Intermediate nitrogen/metal atomic radii ratio
- M_2N and MN major compositions
- Nitrogen atoms occupying half the octahedral sites in M_2N
- hcp (M_2N) and fcc (MN) structures
- The pure host metal has only one structure: bcc*
- Range of melting or decomposition point: 2177–3093°C

Group VI Nitrides (Cr, Mo, W)

- Highest nitrogen/metal atomic radii ratio
- Several compositions
- fcc, hcp, and hexagonal structures
- The pure host metal has only one structure: bcc*
- Not considered refractory

* The crystalline structure of early transition metals is reviewed in Sec. 4.0 and Table 3.2 of Ch. 3.

Table 10.4: Atomic Spacing of Pure Metal and Nitride Host Metal

Nitride	M-M Spacing Pure Metal* (nm)	M-M Spacing Host Metal (nm)	Change (%)**
TiN	0.2934	0.3016	+ 2.795
ZrN	0.3194	0.322	+ 0.845
HfN	0.3170	0.3195	+ 0.789
VN	0.2676	0.3118	+ 16.52
NbN	0.2912	0.2936	+ 0.824
TaN	0.2914	0.3084	+ 5.83

* For coordination number = 12
** Change going from the pure metal to the host metal in the nitride

4.5 Density Considerations

Table 10.5 shows the density of the interstitial mononitrides (for materials closest to stoichiometry), the density of the host metals and the difference between the two in percent.[1][4][5]

The nitrides of Group IV have higher density than their host metals while the opposite occurs with the nitrides of Group V. This is related to the larger increase in M-M spacing occurring during formation of the nitride as noted in Table 10.4. The same trend is noted with the interstitial carbides (see Table 3.6 of Ch. 3).

5.0 ATOMIC BONDING OF INTERSTITIAL NITRIDES

5.1 Overall Bonding Scheme

Like the bonding of the interstitial carbides, the bonding of the interstitial nitrides is still not completely understood. Their characteristics

and properties indicate that they are more than a simple solution of nitrogen atoms within the lattice of a transition metal. Indeed the differences between nitrides and host metals are significant and indicate the presence of metal-to-nitrogen (M-N) bonds with essentially no nitrogen-to-nitrogen bonds. The overall bonding scheme is similar to that of the interstitial carbides (see Sec. 6.1 of Ch. 3) and is a combination of the three types of bonding:[10]

a) Ionic bonding resulting from a transfer of electrons from the metal to the nitrogen atom

b) Metallic bonding with a finite density of states at the Fermi-energy level E_f

c) Covalent bonding, the major type, between metal *d*-state and the nitrogen *p*-state with some metal-to-metal interaction

The electronic configuration of the interstitial mononitrides, including the band structure, the density of states, and other bonding considerations, have been the object of much research and is now relatively well defined.[10]–[13] A schematic representation of the bonding orbitals of TiN on the (100) crystallographic plane, typical of interstitial mononitrides, is shown in Fig. 10.5.[9] The nitrogen *p* orbitals and the titanium *d* orbitals form both α and π covalent bonds. The σ-bonded overlapping titanium *d* orbitals indicate a certain degree of Ti-Ti interaction. The other nitride compositions however are less well-known.

Table 10.5: Density of Mononitrides and Host Metals

Carbide		Nitride Density (g/cm^3)	Metal Density (g/cm^3)	Change (%)*
Group IV	TiN	5.39	4.54	+ 18.7
	ZrN	7.32	6.51	+ 12.4
	HfN	13.83	13.36	+ 3.5
Group V	VN	6.05	6.11	- 0.98
	NbN	8.24	8.56	- 1.6
	TaN	15.9	16.6	- 4.2

* Change in density going from the host metal to the nitride

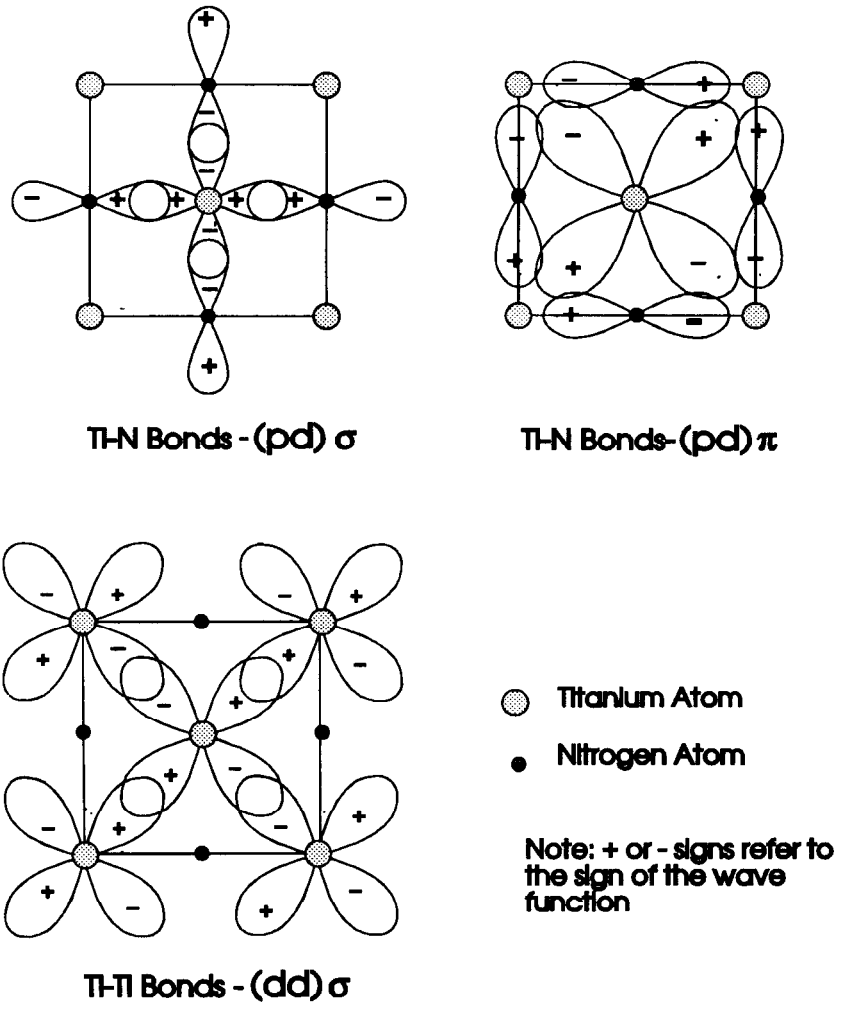


Figure 10.5: Planar view of the bonding orbitals of titanium nitride.[9]

5.2 Thermal Properties Considerations

Bond Energy and Melting Points. The comparison between the melting points of interstitial mononitrides and their host metals and the differences in the bond energy of these nitrides is shown in Table 10.6. This provides a qualitative view of the M-M and M-N bonds.[14]-[16] The

mononitrides of Groups IV and V have a higher melting point than their host metals, with the exception of VN. The differences are smaller for those of Group V. In all cases the bond energy is high and reflects the high melting point of these compounds.

Table 10.6: Bond Energy and Melting Point of Interstitial Carbides and Nitrides

		Bond Energy E_o, eV	Melting Point (°C) Compound	Metal
Group IV	TiN	13.24	2950	1660
	TiC	14.66	3067	
	ZrN	14.96	2980	1850
	ZrC	15.75	3420	
	HfN	15.98	3387	2230
	HfC	17.01	3928	
Group V	VN	12.79	2177*	1890
	VC	13.75	2830	
	NbN	14.81	near 2400*	2468
	NbC	16.32	3600	
	TaN	15.33	3093*	2996
	TaC	16.98	3950	

* decomposes

As shown in the above table, the interstitial carbides have a greater bond energy and are somewhat more refractory than the nitrides with a greater difference between their melting point and that of the host metals. These melting point considerations can be used as a qualitative gauge of the bond strength and indicate that the Group IV nitrides have a stronger M-N bond but a weaker M-M bond than the Group V nitrides (see Ch. 3, Sec. 6.3).

Heat of Formation. Figure 10.6 shows the heats of formation of the transition metal nitrides for near-stoichiometric compositions. The absolute values within each group are relatively close but those of Group V are much lower than those of Group IV.[1]

As with the interstitial carbides, it can be inferred from these considerations of the melting point and heat of formation that the nitrides of Group IV are the most stable. The nitrides of Group V (and especially those of Group VI) are less stable, a characteristic which may be related to the gradual filling of the antibonding portion of the bond which corresponds to an increase in density-of-electron states.[1][9]

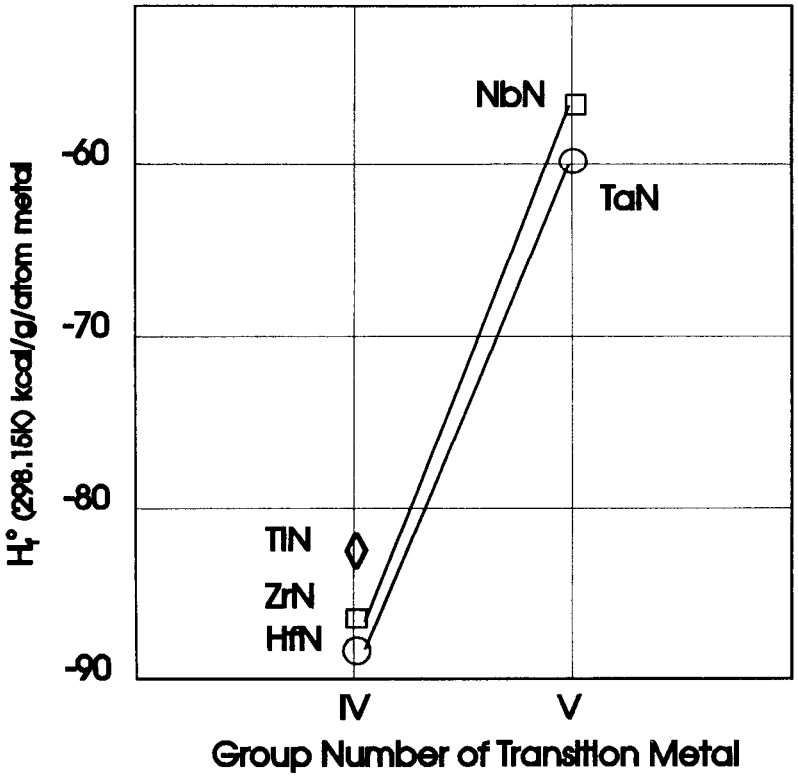


Figure 10.6: Heats of formation of the interstitial nitrides.[1]

5.3 Ionic Bonding and Electronegativity

The differences in electronegativity between nitrogen and the early transition metals are shown in Table 10.7 (see Sec. 6.4 of Ch. 3).

Table 10.7: Difference in Electronegativity Between Nitrogen and Host Metal

Group IV		Group V		Group VI	
N-Ti	1.5	N-V	1.4	N-Cr	1.4
N-Zr	1.6	N-Nb	1.3	N-Mo	1.2
N-Hf	1.7	N-Ta	1.5	N-W	1.3

The qualitative relationship between the difference in electronegativity and the ionicity of the bond was briefly reviewed in Ch. 3, Sec. 6.4.

The ionic bonding contribution in TiN indicates a charge transfer from the titanium atom to the nitrogen atom, resulting in the formation of Ti^+ and N^- ions and, correspondingly, an electrostatic interaction. This ionic bonding should be similar for the other nitrides of Group IV and lower for those of Group V and still lower for those of Group VI as the electronegativity difference decreases. Generally, in the ionic bonding contribution it is likely that the M-N bond is predominant due to the octahedral grouping of the metal atoms centered on the nitrogen atom. This grouping has six bonds to the six corners of the octahedron and, in forming the mononitrides, the valence electrons of the nitrogen atom hybridize with the *p*-state metal atom, with a likely d^2sp^3 hybridization (a common feature of the Group IV metals).

REFERENCES

1. Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)
2. Storms, E. K., Phases Relationships and Electrical Properties of Refractory Carbides and Nitrides, in *Solid State Chemistry*, Vol 10 (L. E. Roberts, ed.), University Park Press, Baltimore (1972)
3. Nitrogen Chemistry, in *Comprehensive Inorganic Chemistry* (J. C. Bailar et al, eds.), Pergamon Press, London (1971)
4. Evans, R. C., *An Introduction to Crystal Chemistry*, Cambridge Univ. Press, Cambridge (1979)
5. Haussinger, P., Leitgeb, P., and Rückborn, G., *Nitrogen* in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 17, VCH (1985)
6. March, J., *Advanced Inorganic Chemistry,* John Wiley & Sons, New York (1985)
7. Benesovsky, F., Kiefer, R., and Ettmayer, P., Nitrides, in *Kirk-Othmer's Encyclopedia of Industrial Chemistry,* 4th. Ed., John Wiley & Sons (1993)
8. Ettmayer P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
9. Sundgren, J. E., et. al., TiN_x Atomic Arrangement and Electronic Structure, *Am. Inst. of Physics Conf. Series* No. 149, New York (1986)
10. Schwarz, K., and Neckel, A., Chemical Bonding in Refractory Transition Metal Compounds, in *Science of Hard Materials* (E. A. Almond et al, eds.), Institute of Physics Conference Series No. 75, Adam Hilger Ltd., Bristol, UK (1984)
11. Calais, J. L., Band Structure of Transition Metal Compounds, *Advances in Physics*, 26(6):847–885 (1977)
12. Oyama, S. T., Crystal Structure and Chemical Reactivity of Transition Metal Carbides and Nitrides, *J. Solid State Chem.*, 96:442–445 (1992)
13. Neckel, A., Recent Investigations on the Electronic Structure of the 4th and 5th Group Transition Metal Monocarbides, Mononitrides, and Monoxides, *Int. J. of Quantum Chemistry*, Vol. XXIII, 1317–1353 (1983)
14. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
15. Galasso, F. S., *Structure and Properties of Inorganic Solids*, Pergamon Press, New York (1970)
16. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)

11

Interstitial Nitrides: Properties and General Characteristics

1.0 GENERAL PROPERTIES OF INTERSTITIAL NITRIDES

This chapter is a review of the properties and general characteristics of the interstitial nitrides formed by the metals of Group IV (titanium, zirconium, and hafnium) and Group V (vanadium, niobium, and tantalum). As mentioned in Ch. 10, these six nitrides are the only refractory transition-metal nitrides. They have similar properties and characteristics and, of the six, titanium nitride has the greatest importance from an application standpoint.

These nitrides are produced mostly in the form of coatings or powders. The fabrication processes and the applications for each nitride are summarized in Secs. 6–11 and reviewed in more detail in Chs. 14, 15, and 16.

2.0 PHYSICAL AND THERMAL PROPERTIES OF INTERSTITIAL NITRIDES

In this section and the next three, the properties of the interstitial nitrides of Group IV and V are examined and compared with those of the

parent metals and the corresponding carbides. The values given are those for composition as close to stoichiometry as possible.[1]-[11] Like the interstitial carbides, interstitial nitrides are essentially non-stoichiometric compounds which accounts in part for the variations in the property values reported in the literature. The values given here should be considered typical.

The properties of interstitial nitrides have not been studied as extensively as those of the interstitial carbides and many gaps remain, particularly in determining the effects of composition and impurities, the thermodynamic functions, and the mechanical properties.

2.1 Composition and Stoichiometry

Unlike the interstitial monocarbides, MC_x, where C is never >1, the interstitial mononitrides, MN_x, can have a composition where x >1. In substoichiometric compositions (x < 1), the sublattice of nitrogen is predominantly deficient while at hyperstoichiometric compositions (x > 1), the metal lattice is predominantly deficient. The lattice parameter is at a maximum at stoichiometry. Even at stoichiometry, a substantial fraction of both nitrogen and metal sites are usually vacant.

2.2 Density and Melting Point

The density and melting point of interstitial nitrides are shown in Table 11.1 and compared with the values for corresponding carbides and host metals.

As could be expected, the density increases considerably with the increasing atomic number of the metal. The melting point of the nitrides is lower in every case than that of the corresponding carbides but, with the exception of NbN, higher than the parent metals. At a nitrogen pressure of 1 MPa, the nitrides of Group IV melt without decomposition but those of Group V decompose (see Table 10.6, Ch. 10 for a comparison of bond energies).

Table 11.1: Density and Melting Point of Interstitial Nitrides and Other Refractory Compounds

Material	Density (g/cm^3)	Melting Point °C
TiN	5.40	2950
ZrN	7.32	2980
HfN	13.8	3387
VN	6.0	2177*
NbN	7.3	near 2400*
TaN	14.3	3093*
TiC	4.91	3067
ZrC	6.59	3420
HfC	12.67	3928
VC	5.65	2830
NbC	7.79	3600
TaC	14.5	3950
Ti	4.54	1660
Zr	6.51	1850
Hf	13.36	2230
V	6.11	1890
Nb	8.56	2468
Ta	16.6	2996

* decomposes

2.3 Thermal Properties

Thermal properties are summarized in Table 11.2.

Table 11.2: Thermal Properties of Interstitial Nitrides and Other Refractory Compounds

Compound	Specific Heat at 298K (J/mole·K)	Thermal Conductivity at 20°C (W/m·K)	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
TiN	33.74	19.2	9.35
ZrN	40.39	20.5	7.24
HfN	38.01	21.7	6.9
VN	38.00	11.29	8.7
NbN	39.01	3.76	10.1
TaN	40.60	8.78	8.0
TiC	33.8	21	7.4
ZrC	37.8	20.5	6.7
HfC	33.4	20.0	6.6
VC	32.3	24.7	7.3
NbC	36.8	14.22	6.6
TaC	36.4	22.17	6.3
Ti	25.05	21.9	8.5
Zr	26.05	22.7	
Hf	26.27	23.0	6.0
V	24.75	30.7	8.0
Nb	24.43	53.7	7.3
Ta	25.33	57.5	6.5

2.4 Thermal Conductivity

A discussion on the thermal conductivity of refractory carbides and nitrides is given in Ch. 4, Sec. 2.4. As can be seen in Table 11.2, the nitrides of Groups IV and V, like the corresponding carbides, can be considered good thermal conductors, reflecting the metallic character of

these materials.[12] However, their thermal conductivity is still considerably lower than the best conductors such as aluminum nitride (220 W/m·K) (see Ch. 13, Sec. 3.0). Their thermal conductivity generally increases slightly with increasing temperature as shown in Fig. 11.1 (reliable data not available for NbN and TaN).[5]

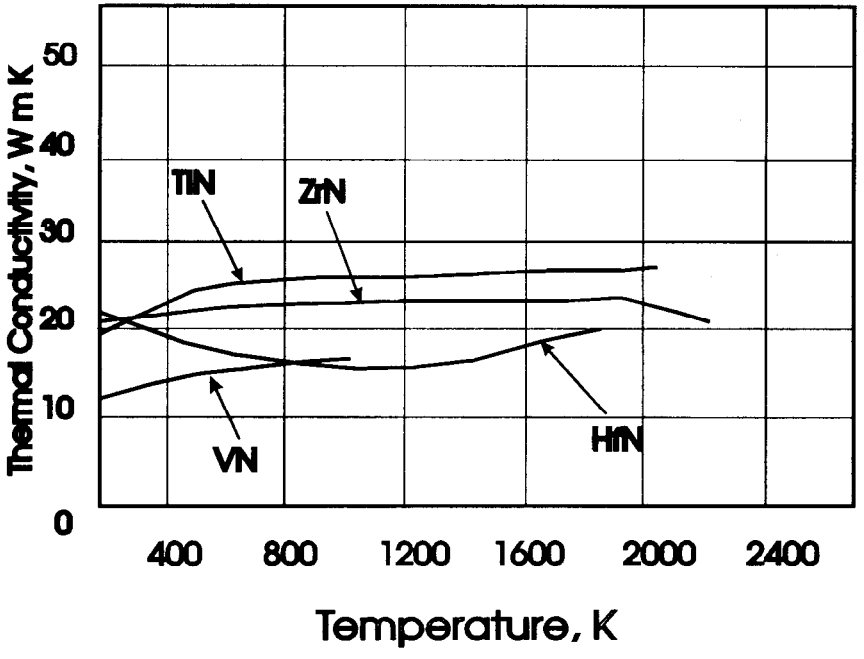


Figure 11.1: Thermal conductivities of the interstitial nitrides vs. temperature.

2.5 Thermal Expansion

The observations on thermal expansion of refractory carbides in Sec. 2.0 of Ch. 4 are applicable to the refractory nitrides. Table 11.3 shows that generally the higher the bond energy of the compound, the lower the expansion.

Table 11.3: Bond energy and Thermal Expansion of Refractory Nitrides

Nitride		Bond Energy E_o, eV	Thermal Expansion at 20°C ($\times 10^{-6}$/°C)
Group IV	TiN	12.34	9.35
	ZrN	14.96	7.24
	HfN	15.98	6.9
Group V	VN	12.79	8.7
	NbN	14.81	10.1
	TaN	15.33	8.8

As shown in Fig. 11.2, thermal expansion is essentially linear with increasing temperature (data available for Group IV nitrides only).[5]

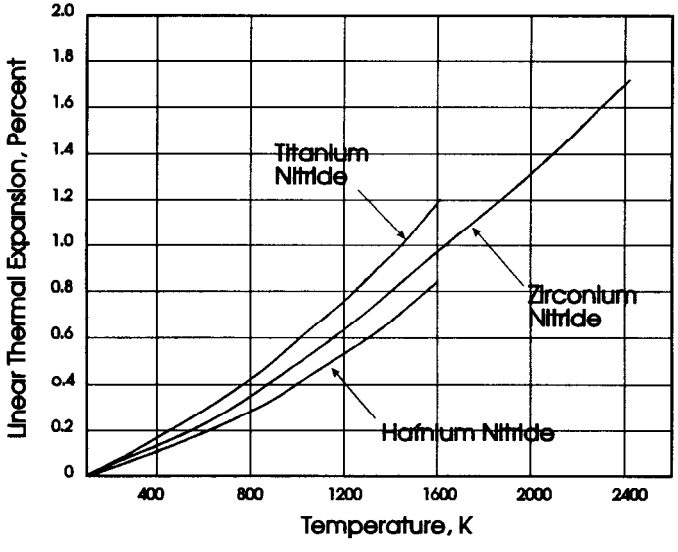


Figure 11.2: Linear thermal expansions of the interstitial nitrides vs. temperature.

3.0 ELECTRICAL PROPERTIES OF INTERSTITIAL NITRIDES

A discussion on the electrical properties of interstitial carbides and nitrides is given in Ch. 4, Sec. 3.0. The electrical properties of these materials are shown in Table 11.4.[4][10][11][13]

Table 11.4: Electrical Properties of Group IV and V Interstitial Nitrides and Carbides at 20°C.

Compound	Electrical Resistivity at 20°C ($\mu\Omega$·cm)	Hall Constant at 20°C 10^{-4} $cm^3/A{\cdot}s$	Magnetic Susceptibility* 10^{-6} emu/mol
TiN	20 ± 10	-0.7 ± 0.2	+38
ZrN	7–21	-1.3	+22
HfN	33		
VN	85		
NbN	58	-0.52	+31
TaN	135		
TiC	68	-15.0	-7.5
ZrC	43	-9.41	-30
HfC	37	-12.4	-37
VC	60	-0.48	+35
NbC	35	-1.3	+20
TaC	25	-1.1	+12

As shown in the above table, the interstitial nitrides are relatively good electrical conductors although with a resistivity slightly higher than that of the corresponding carbides and the parent metals, but still reflecting the essentially metallic character of these compounds. The electrical resistivity of TiN (and presumably of the other interstitial nitrides) increases almost linearly with temperature as shown in Fig. 11.3.[10]

Superconductivity. The interstitial nitrides are all good superconductors but their transition temperatures may be considerably affected by the presence of vacancies and impurities such as oxygen (see Secs. 6–11 for values).[13]

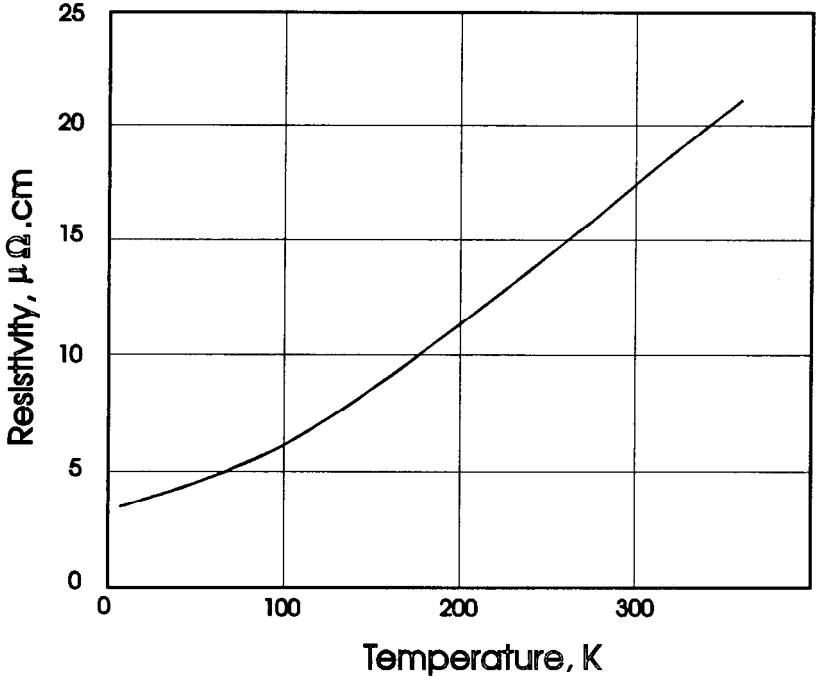


Figure 11.3: Resistivity of a single–crystal titanium nitride.

4.0 MECHANICAL PROPERTIES OF INTERSTITIAL NITRIDES

A discussion on the mechanical properties of both interstitial carbides and nitrides is given in Ch. 4, Sec. 4.0. Large spreads in the reported values are common and are related to differences in stoichiometry, impurity levels, and fabrication processes.

4.1 Summary of Mechanical Properties

The observations on failure mechanism, ductile-brittle transition, and hardness of the interstitial carbides (Ch. 4, Secs. 4.3 and 4.4) are applicable to the interstitial nitrides. These materials have a ductile-brittle transition temperature of approximately 800°C.

Little information is available on the mechanical properties of the interstitial nitrides and what has been published is summarized in Table 11.5 and compared with properties of the equivalent interstitial carbides. The values are averages reported in the recent literature.[1][4]–[7][14][15]

4.2 Hardness

As shown in Table 11.5, the hardness of the interstitial nitrides is somewhat lower than that of the corresponding carbides. The Group IV nitrides generally have higher hardnesses than those of Groups V. This reflects the greater contribution of M-N bonding found in these compounds.

Table 11.5: Mechanical Properties of Group IV and V Interstitial Nitrides and Carbides at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)
TiN	18–21	251
ZrN	15.8	397
HfN	16.3	
VN	14.2	357
NbN	13.3	493
TaN	11.0	
TiC	28–35	410–510
ZrC	25.9	350–440
HfC	26.1	350–510
VC	27.2	430
NbC	19.6	338–580
TaC	16.7	285–560

Hardness vs. Composition. Hardness varies with composition as shown in Fig. 11.4.[1][11] The hardness of the interstitial nitrides of Group IV (TiN, ZrN, and presumably HfN) reaches a maximum at stoichiometry while the maximum hardness of the nitrides of Group V (NbN, TaN, and presumably VN) occurs before stoichiometry is reached. A similar behavior is observed for the corresponding carbides (see Fig. 4.5 of Ch. 4).

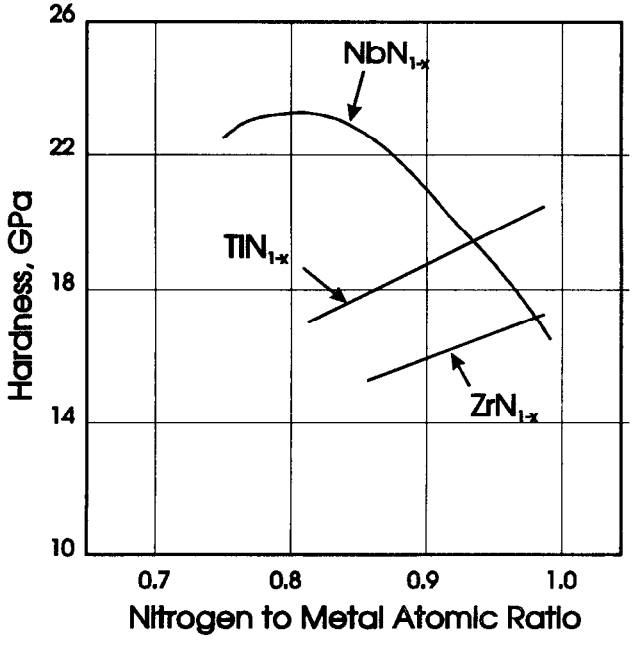


Figure 11.4: Hardnesses of the interstitial nitrides vs. nitrogen–to–metal atomic ratio.

Hardness vs. Crystal Orientation. The hardness varies depending on crystal orientation, the (111) orientation being the hardest as shown in Fig. 11.5.[10] Extremely high hardness up to 50 GPa has been reported for epitaxial superlattices of interstitial nitrides such as NbN/TiN and VN/TiN.[16]

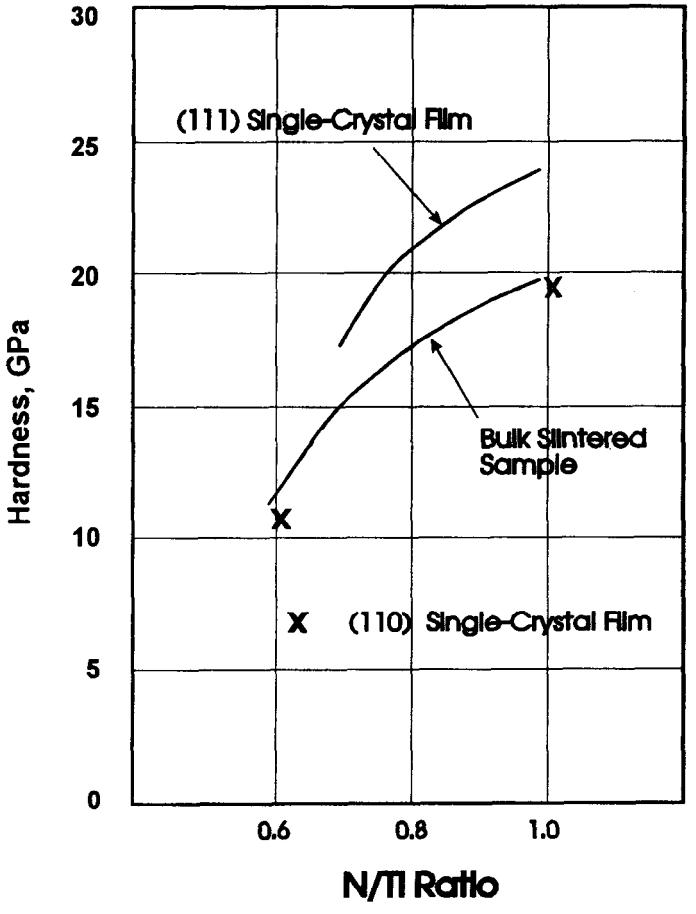


Figure 11.5: Hardnesses of single-crystal ({111} orientation) TiN and bulk-sintered TiN as a function of N/Ti ratio.

5.0 CHEMICAL PROPERTIES OF INTERSTITIAL NITRIDES

5.1 Mutual Solubilities

The existence of ternary carbides and nitrides was discussed in Ch. 4, Sec. 5.0. As shown in Fig. 11.6, TiN has complete mutual solubility with the other nitrides of Groups IV and V while mutual solubility with the

other nitrides is not as complete. With the partial exception of VN, they are also mutually soluble with the carbides of Groups IV and V (see Fig. 4.8 of Ch. 4).[6]

5.2 Chemical Properties

The interstitial nitrides are chemically stable and have a chemical resistance similar to that of the Group IV and V carbides.

	TiN	ZrN	HfN	VN	NbN	TaN
TiN		O	O	X	O	O
ZrN	O		O	X	O	?
HfN	O	O		O	O	?
VN	O	X	X		O	?
NbN	O	O	O	O		?
TaN	O	O	O	O	O	

O Completely soluble

X Insoluble or partially soluble

? Not reported

Figure 11.6: Mutual solubilities of interstitial nitrides.

6.0 TITANIUM NITRIDE: SUMMARY OF PROPERTIES

6.1 Summary of Properties

The properties of titanium nitride are summarized in Table 11.6.

Table 11.6: Characteristics and Properties of Titanium Nitride.
Note: Test temperature is 20°C unless otherwise stated.

Phase: TiN (major) (see Table 10.2 of Ch. 10)
Structure and Lattice Parameter: fcc B1 (NaCl), a = 0.424 nm
Space Group: Fm3m
Pearson Symbol: cF8
Composition: $TiN_{0.6}$ to $TiN_{1.1}$
Molecular Weight: 64.95
Color: gold
X-ray Density : 5.40 g/cm^3
Melting Point: 2950°C
Debye Temperature: 636K

Specific Heat (C_p): 33.74 J/mol·K
Heat of Formation ($-\Delta H_f$) at 298K: 338 kJ/g-atom metal
Thermal Conductivity (K): 19.2 W/m·°C (see Fig. 11.1)
Thermal Expansion: 9.35×10^{-6}/°C (see Fig. 11.2)

Electrical Resistivity: 20 ± 10 μΩ·cm
Superconductive Transition Temperature: 5.6 K
Hall Constant: $-0.7 \pm 0.2 \times 10^{-4}$cm^3/A·s
Magnetic Susceptibility: $+38 \times 10^{-6}$ emu/mol

Vickers Hardness: 18–21 GPa
Modulus of Elasticity: 251 GPa

Oxidation Resistance: Begins to oxidizes in air at approximately 800°C
Chemical Resistance: Chemically stable at room temperature. Slowly attacked by concentrated acid solution with rising temperature.

6.2 Isomorphism

Titanium nitride is completely and mutually soluble with nitrides of Groups IV and V see Fig. 11.6). It is isomorphous with TiC as carbon can substitute for nitrogen to form a binary solid solution, titanium carbonitride, Ti(CN), over a wide range of composition. The properties of TiCN are comparable to those of TiC and TiN (see Ch. 4, Sec. 6.0 and Fig. 4.8).

6.3 Phase Diagram

The Ti-N phase diagram is shown in Fig. 11.7.[17][18]

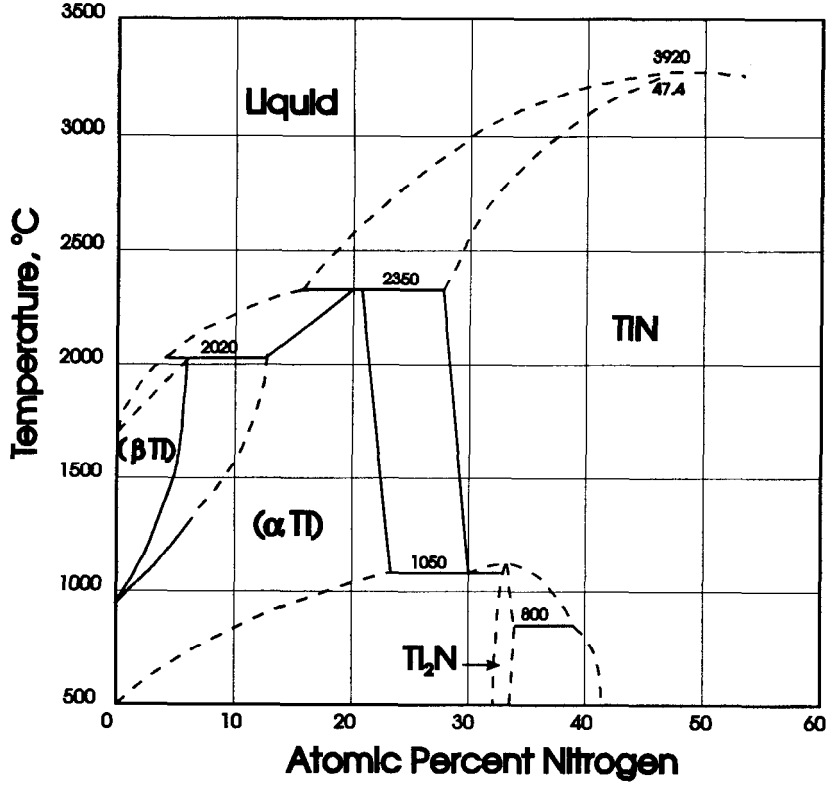


Figure 11.7: Nitrogen–titanium phase diagram.

6.4 Summary of Fabrication Processes

TiN coatings are deposited by CVD, reactive evaporation, reactive sputtering, and ion-beam-assisted deposition. They can also be obtained by thermal spray. TiN powder is produced by the nitridation of Ti metal with nitrogen or ammonia at 1200°C (see Chs. 14 and 15).

6.5 Summary of Applications and Industrial Importance

Titanium nitride offers excellent protection against abrasive wear and has good lubricating characteristics. It is chemically resistant, thermally stable and, unlike titanium carbide, is an excellent diffusion barrier. It is a major industrial material. The following is a summary of its applications in production or development. More details are given in Ch. 16.

- Wear and erosion resistant coatings on cemented carbides, either singly or in combination with TiC, TiCN and Al_2O_3
- Coatings on tool steel for twist drills
- Diffusion barriers in semiconductor devices, between Si and Al, Ti and Pt, and between Ag and Si

7.0 ZIRCONIUM NITRIDE: SUMMARY OF PROPERTIES

7.1 Summary of Properties

The properties of zirconium nitride are summarized in Table 11.7.

7.2 Isomorphism

Zirconium nitride is completely and mutually soluble with the nitrides and carbides of Groups IV and V with the exception of VN and VC (see Fig. 11.6 and Fig. 4.8 of Ch. 4).

7.3 Phase Diagram

The Zr-N phase diagram is shown in Fig. 11.8.[17][18]

Table 11.7: Characteristics and Properties of Zirconium Nitride.
Note: Test temperature is 20°C unless otherwise stated.

Phase: ZrN (major) (see Table 10.2 of Ch. 10)
Structure: fcc B1 (NaCl)
Lattice Parameter: a = 0.4567 nm
Space Group: Fm3m
Pearson Symbol: cF8
Composition: $ZrN_{0.55}$ to $ZrN_{1.0}$
Molecular Weight: 105.23
Color: pale yellow
X-ray Density : 7.32 g/cm^3
Melting Point: 2980°C
Debye Temperature: 515 K

Specific Heat (C_p): 40.39 J/mol·K
Heat of Formation ($-\Delta H_f$) at 298K: 365.4 kJ/g-atom metal
Thermal Conductivity (K): 20.5 W/m·°C (see Fig. 11.1)
Thermal Expansion: 7.4 × 10^{-6}/°C (see Fig. 11.2)

Electrical Resistivity: 7-21 μΩ·cm
Superconductive Transition Temperature: 10.7 K
Hall Constant: -1.3 × 10^{-4}cm^3/A·s
Magnetic Susceptibility: +22 × 10^{-6} emu/mol

Vickers Hardness: 15.0 GPa
Modulus of Elasticity: 397 GPa

Oxidation Resistance: Begins to oxidizes in air at approximately 800°C
Chemical Resistance: Chemically stable at room temperature. Slowly attacked by concentrated acid solution with rising temperature.

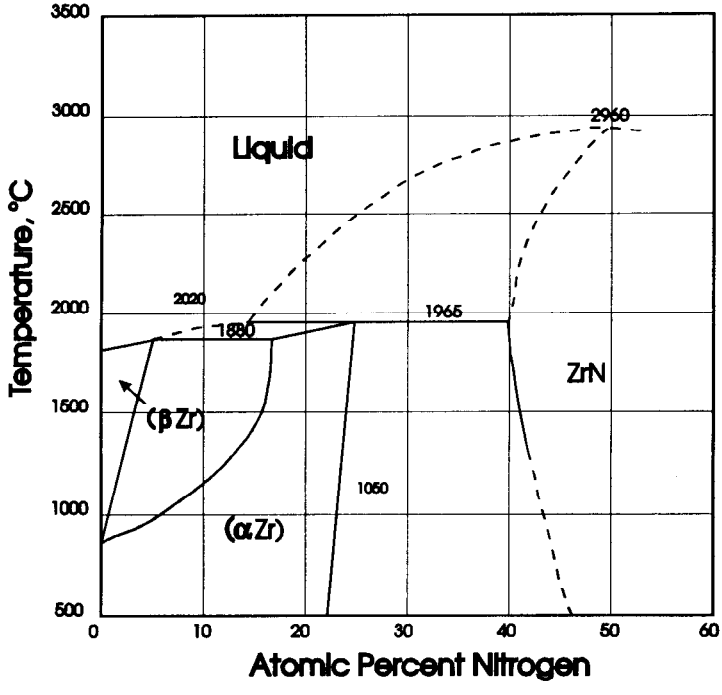


Figure 11.8: Nitrogen–zirconium phase diagram.

7.4 Summary of Fabrication Processes

Zirconium nitride is produced mostly on an experimental basis. Coatings are deposited by CVD, reactive evaporation, and reactive sputtering. They can also be obtained by thermal spray. ZrN powder is produced by the nitridation of Zr metal with nitrogen or ammonia at 1200°C (see Chs. 14 and 15).

7.5 Summary of Applications and Industrial Importance

Applications are presently limited to experimental studies.

8.0 HAFNIUM NITRIDE. SUMMARY OF PROPERTIES

8.1 Summary of Properties

The properties of hafnium nitride are summarized in Table 11.8.

Table 11.8: Characteristics and Properties of Hafnium Nitride.
Note: Test temperature is 20°C unless otherwise stated.

Phase: HfN (major) (see Table 10.2 of Ch. 10)
Structure: fcc B1 (NaCl),
Lattice Parameter: a = 0.452 nm
Space Group: Fm3m
Pearson Symbol: cF8
Composition: $HfN_{0.75}$ to $HFN_{1.12}$
Molecular Weight: 192.497
Color: greenish yellow
X-ray Density: 13.8 g/cm^3
Melting Point: 3387°C
Debye Temperature: 421 K

Specific Heat (C_p): 38 J/mol·K
Heat of Formation ($-\Delta H_f$) at 298K: 369.4 kJ/g-atom metal
Thermal Conductivity (K): 21.7 W/m·°C (see Fig. 11.1)
Thermal Expansion: 6.9×10^{-6}/°C (see Fig. 11.2)

Electrical Resistivity: 33 μΩ·cm
Superconductive Transition Temperature: 2–8.7 K (varies with composition)

Vickers Hardness: 16.3 GPa

Oxidation Resistance: Begin to oxidizes in air at approximately 800°C
Chemical Resistance: Chemically stable at room temperature. Slowly attacked by concentrated acid solution with rising temperature.

8.2 Isomorphism

Hafnium nitride is completely and mutually soluble with the nitrides and carbides of Groups IV and V with the exception of VN and VC (see Fig. 11.6 and Fig. 4.8 of Ch. 4).

8.3 Phase Diagram

The Hf-N phase diagram is shown in Fig. 11.9.[17][18]

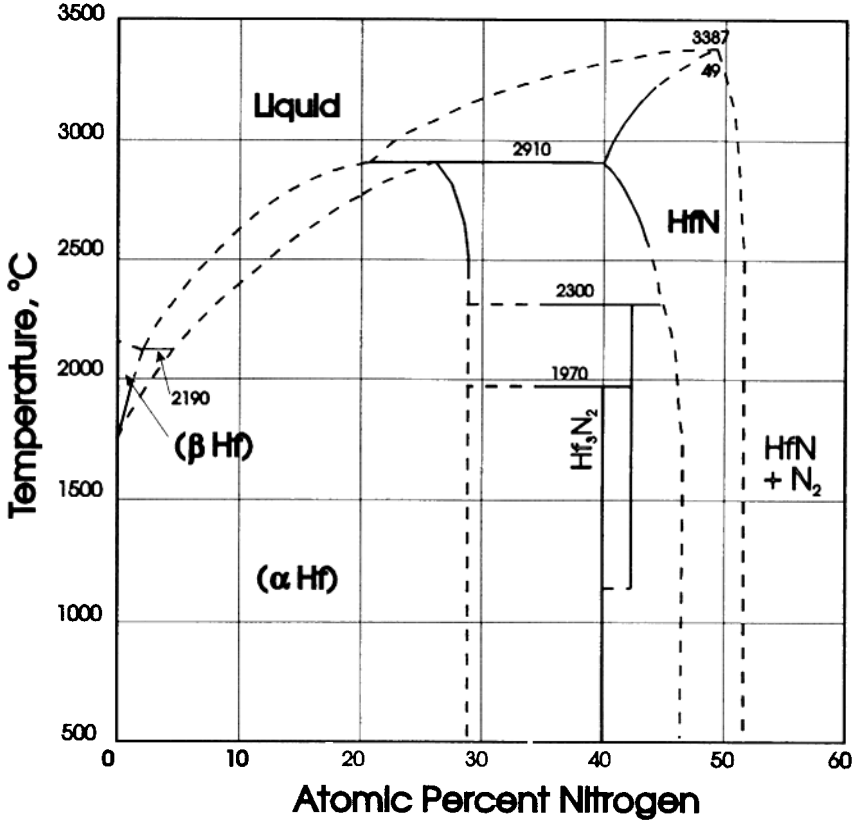


Figure 11.9: Nitrogen–hafnium phase diagram.

8.4 Summary of Fabrication Processes

HfN coatings are deposited by CVD, reactive evaporation, and reactive sputtering (see Chs. 14 and 15). HfN powder is produced by the nitridation of Hf metal with nitrogen or ammonia at 1200°C.

8.5 Summary of Applications and Industrial Importance

- Coatings for cutting tools
- Tribological and corrosion resistant coatings
- Diffusion barriers for microelectronic devices (experimental)
- Whiskers[19]
- Coatings on tungsten wires[20]

9.0 VANADIUM NITRIDE: SUMMARY OF PROPERTIES

9.1 Summary of Properties

The properties of vanadium nitride are summarized in Table 11.9.

9.2 Isomorphism

VN, VC, and VO have isotypical structures and form solid solutions where nitrogen or oxygen can substitute for carbon over a wide range of composition. These solutions may be considered as V(C,N,O) mixed crystals. VN forms solid solutions with TiN and NbN, and with TiC, NbC, and TaC (see Fig. 11.6 and Fig. 4.8 of Ch. 4).

9.3 Phase Diagram

The V-N phase diagram is shown in Fig. 11.10.[17][18]

9.4 Summary of Fabrication Processes

Vanadium nitride is produced mostly on an experimental basis. Coatings are deposited by CVD, reactive evaporation, reactive sputtering,

and ion-beam-assisted deposition. VN powder is produced by the nitridation of V metal with nitrogen or ammonia at 1200°C (see Chs. 14 and 15).

Table 11.9: Characteristics and Properties of Vanadium Nitride.

Note: Unless otherwise stated, test temperature is 20°C and quoted properties are those of the mononitride

Phases: V_2N, VN (see Table 10.2 of Ch. 10)
Structure and Lattice Parameters:
V_2N hex: a = 0.2835 nm, c = 0.4541 nm
VN fcc B1 (NaCl), a = 0.4126 nm
Space Group:
V_2N $C6_32$
VN Fm3m
Pearson Symbol:
V_2N hP9
VN cF8
Composition (VN): $VN_{0.72}$ to $VN_{1.0}$
Molecular Weight (VN): 64.95
Color: brown
X-ray Density: 6.8 g/cm^3
Melting Point: 2177°C (decomposes)
Debye Temperature: 420 K

Specific Heat (C_p): 38.0 J/mol·K
Thermal Conductivity (K): 11.29 W/m·°C
Thermal Expansion: 8.7 × 10^{-6}/°C

Electrical Resistivity: 85 μΩ·cm
Superconductive Transition Temperature: 8.2 K

Vickers Hardness: 14.2 GPa
Modulus of Elasticity: 357 GPa

Oxidation Resistance: Oxidation begins in air at approximately 800°C
Chemical Resistance: Resistant to cold acids, except HCl. Dissolved by hot oxidizing acids.

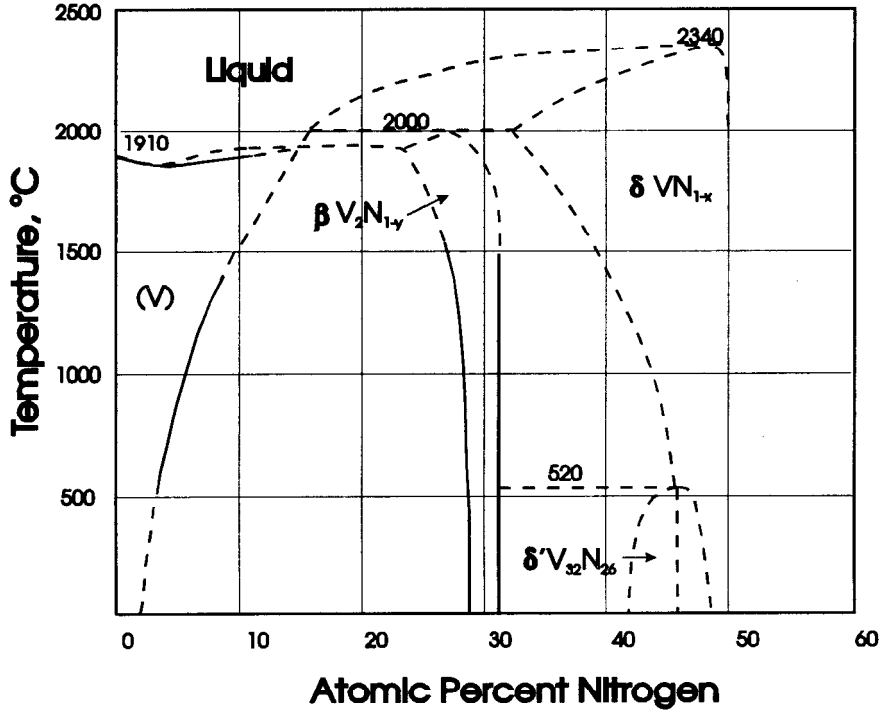


Figure 11.10: Nitrogen–vanadium phase diagram.

9.5 Summary of Applications and Industrial Importance

Applications are presently limited to experimental studies.

10.0 NIOBIUM NITRIDE: SUMMARY OF PROPERTIES

10.1 Summary of Properties

The properties of niobium nitride are summarized in Table 11.10.

Table 11.10: Characteristics and Properties of Niobium Nitride.

Note: Unless otherwise stated, test temperature is 20°C and quoted properties are those of the mononitride.

Phases: Nb_2N, Nb_4N_3, NbN (see Table 10.2 of Ch. 10)
Structure and Lattice Parameters:
Nb_2N hex: a = 0.3054 nm, c = 0.5005 nm
NbN hcp: a = 0.4395 nm, c = 0.4338 nm
Space Group:
Nb_2N P31m
NbN $P6_3/mmc$
Pearson Symbol:
Nb_2N hP9
NbN hP8
Composition (NbN): $NbN_{0.92}$ to $NbN_{1.06}$
Molecular Weight (NbN): 106.91
Color: dark gray
X-ray Density: 7.3 g/cm^3
Melting Point: near 2400°C
Debye Temperature: 307 K

Specific Heat (C_p): 39.01 J/mol.K
Heat of Formation ($-\Delta H_f$) at 298K: 236 kJ/g-atom metal
Thermal Conductivity (K): 3.76 W/m·°C
Thermal Expansion: 10.01×10^{-6}/°C

Electrical Resistivity: 58 μΩ·cm
Superconductive Transition Temperature: 16 K
Hall Constant: -0.52×10^{-4}cm^3/A·s
Magnetic Susceptibility: $+31 \times 10^{-6}$ emu/mol

Vickers Hardness: 13.3 GPa
Modulus of Elasticity: 493 GPa

Oxidation Resistance: Begins to oxidizes in air at approximately 800°C
Chemical Resistance: Chemically stable at room temperature. Slowly attacked by concentrated acid solution with rising temperature.

10.2 Isomorphism

Niobium nitride is completely and mutually soluble with the nitrides and carbides of Groups IV and V (see Fig. 11.6 and Fig. 4.8 of Ch. 4).

10.3 Phase Diagram

The Nb-N phase diagram is shown in Fig. 11.11.[17][18]

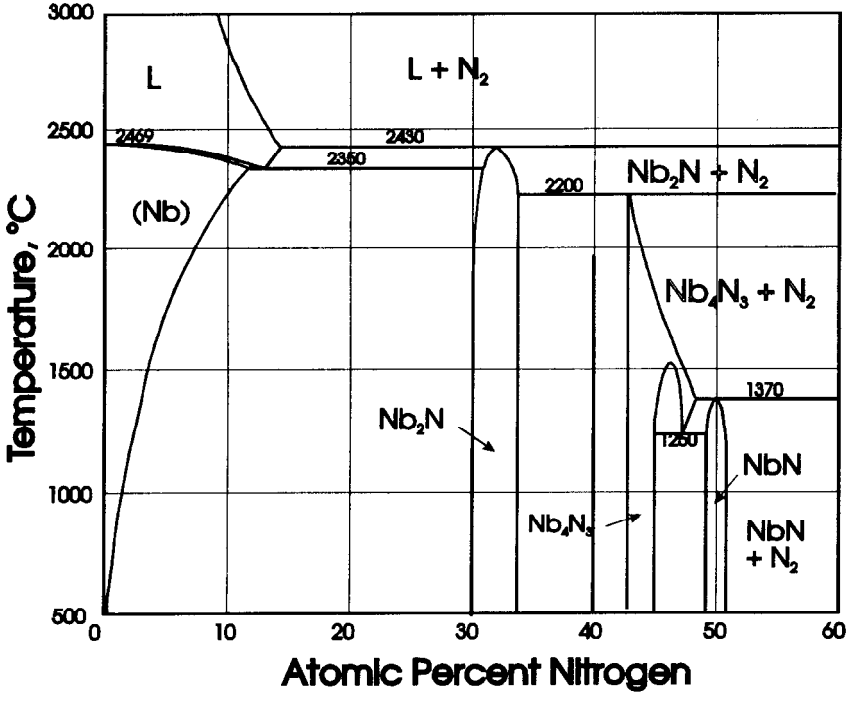


Figure 11.11: Nitrogen–niobium phase diagram.

10.4 Summary of Fabrication Processes

Niobium nitride is produced mostly on an experimental basis. Coatings are deposited by CVD, reactive evaporation, reactive sputtering, and

ion-beam-assisted deposition. NbN powder is produced by the nitridation of Nb metal with nitrogen or ammonia at 1200°C (see Chs. 14 and 15).

10.5 Summary of Applications and Industrial Importance

Applications are presently limited. A potential area is as a superconducting coating.

11.0 TANTALUM NITRIDE. SUMMARY OF PROPERTIES

11.1 Summary of Properties

The properties of tantalum nitride are summarized in Table 11.11.

11.2 Isomorphism

Tantalum nitride is completely and mutually soluble with the nitrides and carbides of Groups IV and V with the exception of VN and VC (see Fig. 11.6 and Fig. 4.8 of Ch. 4).

11.3 Phase Diagram

The Ta-N phase diagram is shown in Fig. 11.12.[17][18]

11.4 Summary of Fabrication Processes

TaN is produced mostly on an experimental basis. Coatings are deposited by CVD, reactive evaporation, reactive sputtering, and ion-beam-assisted deposition. TaN powder is produced by the nitridation of Ta metal with nitrogen or ammonia at 1200°C (see Chs. 14 and 15).

11.5 Summary of Applications and Industrial Importance

TaN is used as a decorative coating for jewelry and similar items to impart a pleasing metallic shine.

Table 11.11: Characteristics and Properties of Tantalum Nitride.
Note: Unless otherwise stated, test temperature is 20°C and quoted properties are those of the mononitride.

Phases: Ta_2N, TaN (see Table 10.2 of Ch. 10)
Structure and Lattice Parameters:
Ta_2N hcp: a = 0.5191 nm, c = 0.2906 nm
ΔTaN fcc (NaCl) a = 0.4336 nm
Space Group:
Ta_2N $P6_3/mmc$ TaN Fm3m
Pearson Symbol:
Ta_2N hP3
TaN cF8
Molecular Weight (TaN): 194.95
Color: yellowish gray
X-ray Density: 14.3 g/cm^3
Melting Point: 3093°C (only melts under high N_2 pressure)

Specific Heat (C_p): 40.60 J/mol·K
Heat of Formation ($-\Delta H_f$) at 298 K: 251 kJ/g-atom metal
Thermal Conductivity (K): 8.78 W/m·°C (see Fig. 11.1)
Thermal Expansion: 8.0×10^{-6}/°C (see Fig. 11.2)

Electrical Resistivity: 135 μΩ·cm
Superconductive Transition Temperature (Ta_2N): 1.2 K

Vickers Hardness: 11 GPa

Oxidation Resistance: Begins to oxidizes in air at approximately 800°C
Chemical Resistance: Chemically stable at room temperature. Slowly attacked by concentrated acid solution with rising temperature.

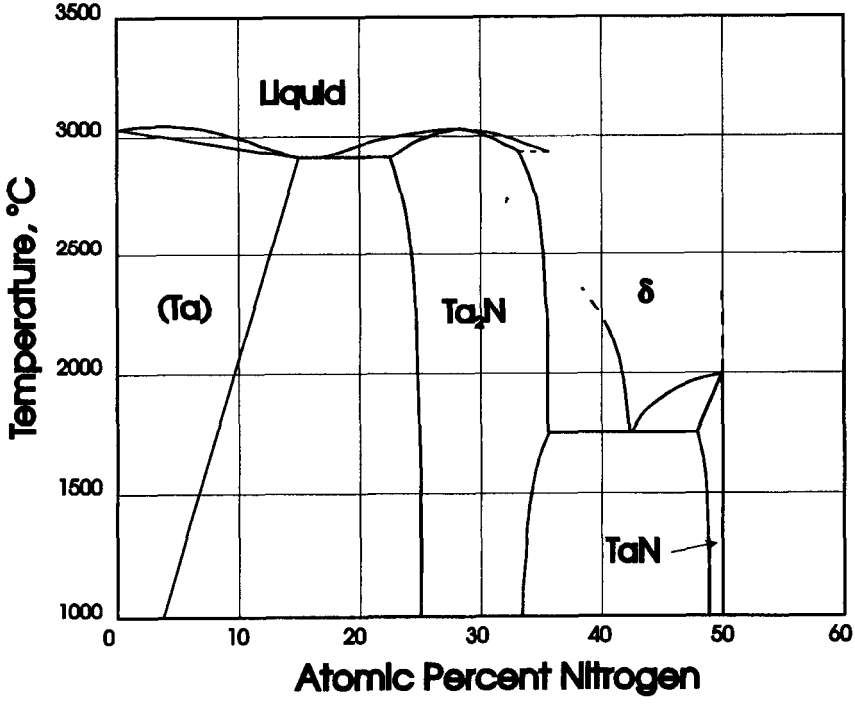


Figure 11.12: Nitrogen–tantalum phase diagram.

REFERENCES

1. Holleck, H., Material Selection for Hard Coatings, *J. Vac. Sci. Technol., A,* 4(6), Nov/Dec. 1986
2. Pierson, H. O., *Handbook of Chemical Vapor Deposition,* Noyes Publications, Park Ridge, NJ (1992)
3. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
4. Toth, L. E., *Transition Metal Carbides and Nitrides,* Academic Press, New York (1971)
5. *Engineering Property Data on Selected Ceramics, Vol. 1, Nitrides,* MCIC HB-07-1, Battelle Institute, Columbus, OH (1976)

6. Benesovsky, F., Kiefer, R., and Ettmayer, P., Nitrides, in *Kirk-Othmer's Encyclopedia of Chemical Technology,* 4th. Ed., Vol. 15, VCH (1993)
7. Ettmayer P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
8. Galasso, F. S., *Structure and Properties of Inorganic Solids*, Pergamon Press, New York (1970)
9. Hampshire, S., Nitride Ceramics, in *Materials Science and Technology,* Vol. 11 (M. V. Swain, ed.) VCH, New York (1994)
10. Sundgren, J. E., et. al., TiN Atomic Arrangement, Electronic Structure and Recent Results on Crystal Growth and Physical Properties of Epitaxial Layer, in *Physics and Chemistry of Protective Coatings,* American Inst. of Physics Conf. Proc., No.149 (1986)
11. Sundgren, J. E., Structure and Properties of TiN Coatings, *Thin Solid Films*, 120:21–44 (1985)
12. Williams, W. S., High-Temperature Thermal Conductivity of Transition Metal Carbides and Nitrides, *J. Am. Ceramic Soc.*, 49(3):156–159 (1966)
13. Storms, E. K., Phases Relationships and Electrical Properties of Refractory Carbides and Nitrides, in *Solid State Chemistry*, Vol 10 (L. E. Roberts, ed.), University Park Press, Baltimore (1972)
14. Bunshah, R. F., *Mechanical Properties of Refractory Compounds Films,* in *Physics and Chemistry of Protective Coatings,* American Inst. of Physics Conf. Proc., No.149 (1986)
15. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd. Bristol, UK (1984)
16. Studt, T., Coating Made Better than the Sum of its Components, *R&D Magazine,* 7 (Aug. 1993)
17. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)
18. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. Edition, ASM International, Metals Park, OH (1990)
19. Futamoto, M., Yuito, I., and Kawabe, U., Hafnium Carbide and Nitride Whisker Growth by Chemical Vapor Deposition, *J. Cryst. Growth*, 61(1):69–74, (Jan. Feb. 1983)
20. Hakim, M., Chemical Vapor Deposition of Hafnium Nitride and Hafnium Carbide on Tungsten Wires, *Proc. 5th Int. Conf. on CVD* (J. Blocher et al, Eds.), 634-649, Electrochem. Soc., Pennington, NJ (1975)

12

Covalent Nitrides: Composition and Structure

1.0 GENERAL CHARACTERISTICS OF COVALENT NITRIDES

As stated in Ch. 9, the refractory nitrides consist of two structurally different types: *(a)* the interstitial nitrides of the early transition metals (reviewed in Chs. 10 and 11), and *(b)* the covalent nitrides of which three are refractory: boron nitride, aluminum nitride, and silicon nitride. The composition and structure of these three nitrides are reviewed in this chapter and their properties and general characteristics in Ch. 13.

The three covalent nitrides have the following common features and are in many ways similar to the covalent carbides reviewed in Chs. 7 and 8:

- They fully meet the refractory criteria of high melting point and thermal and chemical stability
- All three have similar cubic structures (although boron nitride also has a graphite-like structure)
- Their electronic bonding is mainly covalent
- They have low density
- Their elemental constituents have low atomic weight

- They are good electrical insulators
- They are hard and strong materials and exhibit typical ceramic characteristics
- All three are produced industrially with important applications

2.0 ATOMIC STRUCTURE OF NITROGEN, BORON, ALUMINUM, AND SILICON

Like the covalent carbides, the covalent nitrides have a relatively simple crystal structure and an atomic bonding which is less complex than the interstitial nitrides. The bonding is mostly covalent by the sharing of electrons and is achieved by the hybridization of the respective electron orbitals.

2.1 Electronic Configuration

The location in the Periodic Table and the atomic number of the four elements forming the refractory covalent nitrides is as follows:

B	C	N	O	F
5	6	7	8	9
Al	Si	P	S	Cl
13	15	16	16	17

These elements are close together and have low atomic numbers (see Table 2.1 of Ch. 2). Table 12.1 shows their electronic configuration, electronegativity, and atomic radius.[1][2]

The table shows that these four elements have comparable electronic structure. Boron, silicon, and aluminum have lower electronegativity than nitrogen and, by convention, their compounds with nitrogen are called nitrides. Nitrogen has the smallest atomic radius.

Table 12.1: Electronic Configuration of Boron, Nitrogen, Silicon, and Aluminum

Element	Z	Shell 1s	2s	2p	3s	3p	Electronic Structure	Electro-negativity	Atomic Radius (nm)
Boron	5	2	2	1			$[He]2s^2 2p^1$	2.0	0.088
Nitrogen	7	2	2	3			$[He]2s^2 2p^3$	3.0	0.074
Aluminum	13	2	2	6	2	1	$[Ne]3s^2 3p^1$	1.5	0.126
Silicon	14	2	2	6	2	2	$[Ne]3s^2 3p^2$	1.8	0.117

2.2 Characteristics of the Elements Forming Covalent Nitrides

The three elements forming covalent nitrides: boron, silicon, and aluminum, have the following characteristics:[2]

- Silicon is essentially nonmetallic
- Boron can be placed between metals and nonmetals. It is a semiconductor and not a metallic conductor and, from the chemical standpoint, it is essentially a nonmetal. Its chemistry is closer to that of silicon than it is to aluminum
- Aluminum has a larger atom and is clearly more metallic than boron yet, in its compounds, it has borderline ionic and covalent characteristics[2]

Hybridizaton. The hybridization of the silicon and boron atoms is reviewed in Ch. 7, Sec. 2.2, and that of nitrogen in Ch. 10, Sec. 2.0. In the case of aluminum, promotion from its ground state $3s^2 3p^1$ to the hybrid $3s3p^2$ allows the use of all three valence electrons in bonding.[3]

3.0 COMPOSITION AND STRUCTURE OF BORON NITRIDE

3.1 Composition

Boron nitride (BN) is the only major compound known in the boron-nitrogen system although a nitrogen rich composition has recently been reported (see Sec. 3.5 below).

3.2 The Two Major Structures of Boron Nitride

Boron nitride has two major allotropes which are comparable to those of carbon: one has an hexagonal structure which is similar to graphite and the other a cubic structure which is similar to diamond (and to aluminum nitride and silicon nitride as will be reviewed below).[4] These allotropes (or polymorphs) have the same building blocks, i.e., the boron and nitrogen atoms, but their physical form, i.e., the way the building blocks are put together, is different. In other words, they have distinct crystalline forms. The similarity between boron nitride and graphite is not unexpected since they are isoelectronic, having an average of four valence electrons per atom.

The structural analogy with the carbon allotropes can be extended to the properties of the two boron-nitride allotropes. For instance, hexagonal boron nitride (h-BN) is soft and lubricious like graphite, and cubic boron nitride (c-BN), like diamond, is extremely hard.

No boron-nitrogen phase diagram is presently available but a tentative pressure-temperature diagram is shown in Fig. 12.1.[5] This diagram suggests that c-BN (with the zincblende structure) is stable below 225°C while h-BN is stable above 225°C and melts at approximately 3000°C. A second cubic structure (with the wurtzite structure) is stable only at pressures >11 GPa.

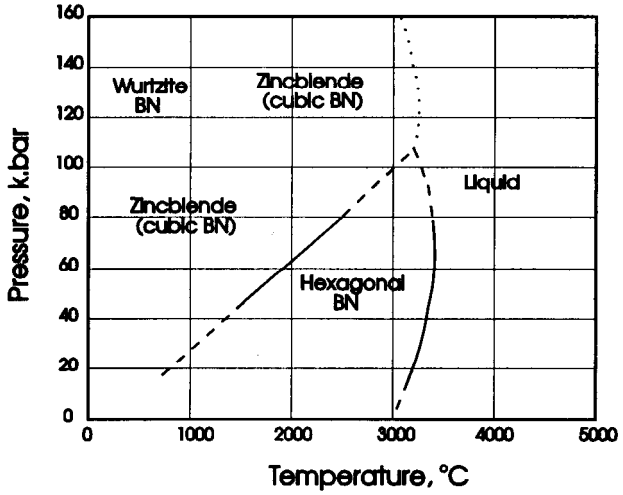


Figure 12.1: Pressure–temperature diagram of boron nitride.

3.3 Structure of Hexagonal Boron Nitride

Crystal Structure. Hexagonal boron nitride is composed of series of stacked parallel layer planes shown schematically in Fig. 12.2. In this figure, the circles showing the position of the nitrogen and boron atoms do not represent the actual size of these atoms. In fact, each atom contacts its neighbors.

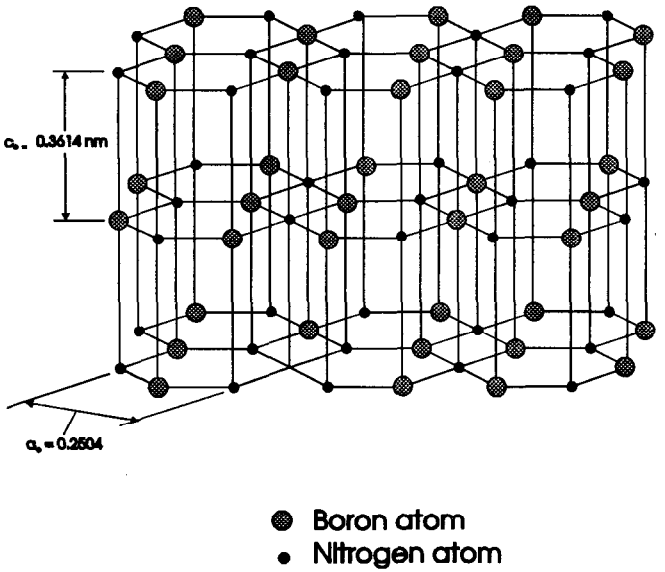


Figure 12.2: Schematic representation of the crystal structure of hexagonal boron nitride (h–BN)

Stacking. The stacking of these layer planes occurs with the hexagon immediately above each other. The boron and nitrogen atoms alternate from one layer to the other; in other words, each nitrogen atom has a boron atom directly above and below and vice versa. The stacking is thus different from graphite which has the same planar arrangement but offset planes so that only half the carbon atoms have neighbors directly above and directly below.[4]

Within the layer plane, each nitrogen atom is bonded to three boron atoms (and vice versa) with a short bond length (0.1446 nm), forming a series of continuous hexagons in what can be considered as an essentially

infinite two-dimensional array. The spacing between layer planes is relatively large (0.3615 nm) or more than twice the spacing between atoms within the layer plane. This means that hexagonal boron nitride, like graphite, should be able to accommodate intercalation elements or compounds.[6] As a result of the large anisotropy in its crystal, hexagonal boron nitride has very anisotropic properties (see Ch. 13).

Bonding. The distribution of the three bonds of each boron and nitrogen atom within the layer plane derives from the sp^2 hybridization of the respective atoms. This bonding is thus similar to the sp^2 bonding within the planes of graphite. It is a strong covalent (sigma) bond with a short bond length as mentioned above and a high bond dissociation energy (4.0 ± 0.5 eV, 385 kJ/mol).

In contrast, the bond between the planes of h-BN is very weak and even weaker than that of graphite. It is readily broken and layers can be cleaved with a knife like an onion skin. However this bond is electronically different from that in graphite. In graphite, it stems from the hybridized fourth valence electron which is paired with another delocalized electron of the adjacent plane by a weak *van der Waals bond* (pi bond). The high electrical conductivity of graphite is attributed to these delocalized electrons.

In h-BN, no free electrons are available since the corresponding p_z orbitals in the boron atom are vacant and those of the nitrogen atom are occupied by two electrons. Overlap to form pi bonds is not possible. In addition, the relatively large difference in electronegativity between nitrogen (3.0) and boron (2.0) imparts greater localization of pi electrons than in graphite. As a result, boron nitride is an electrical insulator.[1][3]

3.4 Structure of Cubic Boron Nitride

The structure of cubic boron nitride is of the zincblende (or sphalerite) type which is similar to that of diamond and β-SiC and is characterized by extreme hardness and excellent chemical resistance. It is shown in Fig. 12.3. Note the similarity with Fig. 7.1 of Ch. 7. This structure is relatively simple in the sense that it is essentially isotropic, in contrast with the pronounced anisotropy of hexagonal boron nitride. It can be visualized as a stacking of puckered infinite {111} layers or as two face-centered interpenetrating cubic sublattices, one consisting entirely of boron atoms and the other entirely of nitrogen atoms.[7]

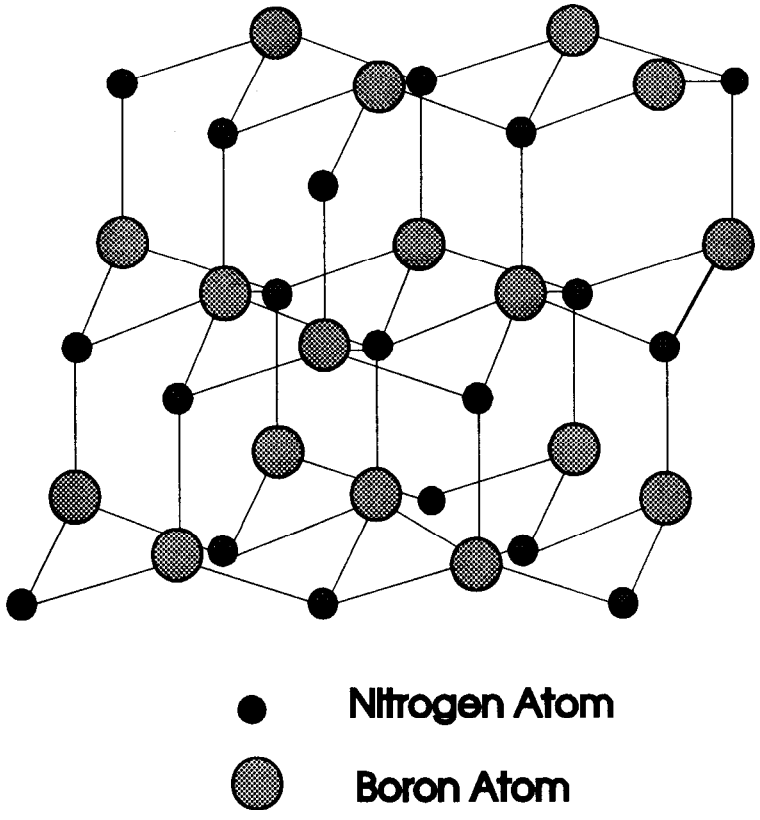


Figure 12.3: Schematic representation of the crystal structure of cubic boron nitride (c–BN).

Bonding. Each boron atom is bonded to four nitrogen atoms in a fourfold coordinated tetrahedral (sp^3) arrangement with a short bond length (0.158 nm). The bonding is essentially covalent although some degree of ionic bonding has been reported (see Ch. 2, Sec. 5.0). As derived by Kisly,[8] the difference between *(a)* the atomic spacing of c-BN and the sum of the covalent radii of nitrogen and boron and *(b)* that atomic spacing and the sum of their ionic radii, shows that the bonding is mainly covalent but that a sizeable degree of ionicity is retained. The calculated covalent bond energy, E_o, is 13.33 eV and the ionic bond energy, E_p, is 3.12 eV (see Ch. 7, Sec. 3.2 for analogy with covalent carbides).

Density of Cubic Boron Nitride. The c-BN structure, with its tetrahedral bonding, is isotropic and, except on the (111) plane, is more compact than that of h-BN (with its sp^2 anisotropic structure and wide interlayer spacing). Consequently c-BN has higher theoretical density than h-BN (3.43 g/cm^3 vs. 2.34 g/cm^3). It should be pointed out that the diamond-like structure of cubic boron nitride is similar to those of the other two refractory covalent nitrides, i.e., aluminum nitride and silicon nitride, as well as silicon carbide (see Ch. 7, Sec. 3.0).

3.5 Other Boron Nitride Structures

Polycrystalline boron nitride films with a structure similar to rhombohedral boron carbide and a ratio of boron to nitrogen of 3:1 were produced by hot-filament CVD. This work indicates the possible existence of other boron nitride structures.[9]

3.6 Summary of Structural Data of Boron Nitride

The structural data of boron nitride is summarized in Table 12.2.

Table 12.2: Boron Nitride Structural Data at 298 K

	h-BN	c-BN
Theoretical Density (g/cm^3)	2.34	3.43
Unit Cell Dimensions		
a_o (nm)	0.2504	0.661
c_o (nm)	0.3615	
B-N Bond Length (nm)	0.1446	0.158
Space Group	F43m	
Pearson Symbol	h**	cF8

4.0 COMPOSITION AND STRUCTURE OF ALUMINUM NITRIDE

4.1 Composition

Aluminum nitride (AlN) is the only major compound known in the aluminum-nitrogen system (a nitrogen rich phase, AlN_9 is also reported). It is formed by the reaction of NH_3 and AlH_3 and may be a stable phase of the condensed Al-N system.[5]

4.2 Structure

The structure of aluminum nitride is normally hexagonal close-packed (hcp) of the wurtzite (2H) type (hP4) and is shown in Fig. 12.4. The difference between this structure and the zincblende structure of cubic boron nitride shown in Fig. 12.3 should be noted (the so-called *chair form* vs the *boat form*).

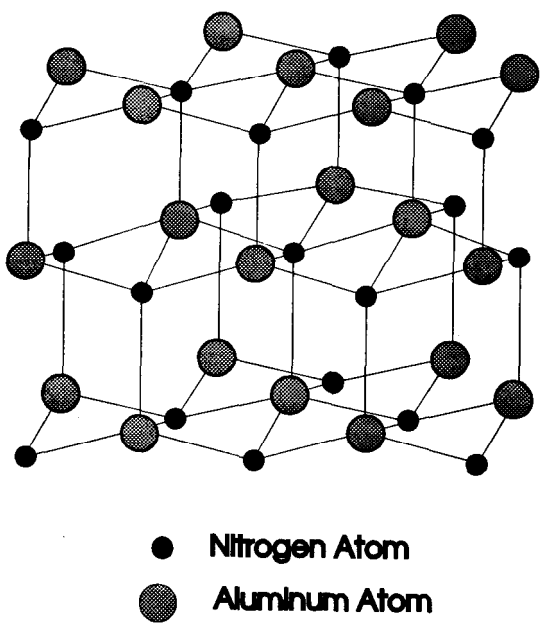


Figure 12.4: Schematic representation of the crystal structure of aluminum nitride.

The lattice parameters of AlN are: a_o = 0.3114 nm and c_o = 0.4986 nm. This structure is similar to that of α-SiC (2H) described in Sec. 3.4 and shown in Fig. 7.5 of Ch. 7. It is essentially isotropic and, like that of c-BN, it can be visualized as a stacking of puckered infinite {111} layers or as two face-centered interpenetrating cubic sublattices, one consisting entirely of aluminum atoms and the other entirely of nitrogen atoms.

The less frequent and closely related zincblende cubic structure (cF8) has also been reported (similar to the structure of c-BN shown in Fig. 12.3). The common wurtzite structure is transformed into the zincblende structure at elevated pressure.[5] Also recently reported is a cubic (NaCl) phase with a calculated lattice constant of 0.3982 nm which is formed at high pressure (16 GPa).[11]

4.3 Bonding

Each aluminum atom is bonded to four nitrogen atoms in a fourfold coordinated tetrahedral (sp^3) arrangement. As discussed in Sec. 3.3 above, the bonding is mainly covalent but a large degree of ionicity is retained. The calculated covalent bond energy E_o is 9.42 eV and the ionic bond energy E_p is 4.09 eV.[8]

4.4 Summary of Structural Data of Aluminum Nitride

The structural data for aluminum nitride is summarized in Table 12.3.

Table 12.3: Aluminum Nitride Structural Data at 298K

Theoretical Density (g/cm^3)		3.16
Unit Cell Dimensions (nm)		
	a_o	0.3114
	c_o	0.3896
Space Group		F43m
Pearson Symbol		hP4

5.0 COMPOSITION AND STRUCTURE OF SILICON NITRIDE

5.1 Composition

The major composition of silicon nitride is Si_3N_4. Other compositions such as Si_2N_3, SiN, and Si_3N have been reported but remain unconfirmed.[5]

5.2 Structure

Silicon (Si_3N_4) nitride has two crystallographic forms, both hexagonal: α-Si_3N_4 with a 28-atom unit cell, and β-Si_3N_4 with a 14-atom unit cell. These two forms differ in the stacking order of the SiN_4 tetrahedral layers. The β form has an ABAB stacking order with a phenacite-type structure (Be_2SiO_4). In the α form, the AB stacking is followed by its mirror image with an ABCD,ABCD pattern. This explains why its elementary cell is twice as large as the α cell. Other structural data are summarized in Table 12.4.

The basal plane common to both forms is illustrated in Fig. 12.5.[13] It can be described as comprising six puckered rings, each containing four silicon and four nitrogen atoms, joined as shown in the figure to form a puckered layer. These layers form the AB stacking of β-Si_3N_4 and the ABCD stacking of α-Si_3N_4.[12][13]

The exact relationship between the two crystallographic forms is still a subject of debate. The α form may be a metastable modification of the β form or a high-temperature stable phase with a slightly different stoichiometry and chemical composition.[5] Oxygen may stabilize the α form but it does not appear to be necessary for its formation. The transformation from α-Si_3N_4 to β-Si_3N_4 has never been observed experimentally, putting in doubt the polymorph nature of the forms.

Both forms can exchange silicon and nitrogen atoms for foreign atoms without significant structural changes. Notably, silicon can be replaced by aluminum and nitrogen by oxygen to form stable and hard quaternary compounds known as *sialons*.[12] The addition of oxygen forms silicon oxynitride. Thus, an essentially amorphous silicon oxynitride with the formula Si_2N_2O has been obtained by the nitridation of high-purity silica in ammonia at 1120°C.[14]

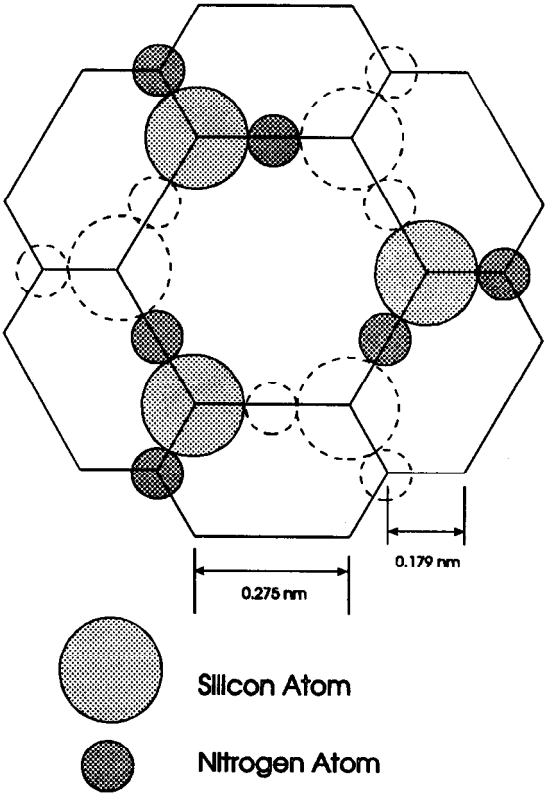


Figure 12.5: Basal plane common to α– and β–silicon nitride.

5.3 Bonding

The bonding in silicon nitride is mostly covalent. These covalent bonds are strong since both atoms are small and the bond length is short (0.179 nm). As discussed in Sec. 3.3 above, the bonding also maintains a large degree of ionicity. The calculated covalent bond energy E_o is 10.87 eV and the ionic bond energy E_p is 3.04 eV.[8] Silicon does not form pπ multiple bonds and there is considerable evidence of a double Si-N bond characteristic involving an orbital overlap, i.e., dπ-pπ bonding.[2]

5.4 Summary of Structural Data of Silicon Nitride

The structural data for silicon nitride is summarized in Table 12.4.[12]

Table 12.4: Silicon Nitride Structural Data at 298K

	α-Si_3N_4	β-Si_3N_4
Theoretical Density (g/cm^3)	3.184	3.187
Unit Cell Dimensions (nm)		
a_o	0.7748	0.7608
c_o	0.5617	0.29107
c/a	0.7250	0.3826
Unit Cell Content	$Si_{12}N_{16}$	Si_6N_8
B-N Bond Length (nm)	0.179	0.179
Space Group	p31C	$P6_3/m$
Pearson Symbol	hP28	hP14

REFERENCES

1. Evans, R. C., *An Introduction to Crystal Chemistry,* 2d. edition, Cambridge University Press, Cambridge, UK (1979)
2. Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry,* Interscience Publishers, New York (1972)
3. Adams, D. M., *Inorganic Solids,* John Wiley & Sons, New York (1981)
4. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond and Fullerenes,* Noyes Publications, Park Ridge, NJ (1993)
5. Massalski, T. B., *Binary Alloy Phase Diagrams,* 2d. Edition, ASM International, Metals Park, OH (1990)
6. Thomson, R., *The Chemistry of Metal Borides and Related Compounds,* in *Progress in Boron Chemistry* (R. J. Brotherton and H. Steinberg, eds.), Pergamon Press Ltd., New York (1970)
7. Brookes, C. A., The Mechanical Properties of Cubic Boron Nitride, *Int. Physics Conf. Series,* No. 75 (E. A. Almond, et al., eds.), Adam Hilger Ltd. Bristol, UK (1984)
8. Kisly, P. S., The Chemical Bond Strength and the Hardness of High Melting Point Compounds, in *Science of Hard Materials,* Institute of Physics Conf. Series No. 75, Adam Hilger Ltd., Bristol, UK (1984)
9. Saitoh, H., Yoshida, K., and Yarbrough, W., Crystal Structure of New Composition Boron-Rich Boron Nitride Using Raman Spectroscopy, *J. Mater. Res.,* 8(1):8–11 (Jan. 1993)
10. Ettmayer, P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry,* 5th. Ed. VCH (1985)
11. Pandey, R., et al., Electronic Structure of High Pressure Pahse of AlN, *J. Mater. Res.,* 8(8):1922–1927 (Aug. 1993)
12. Hampshire, S., *Nitride Ceramics,* in *Material Science and Technology,* Vol. 11 (M. V. Swain, Ed.) VCH, New York (1994)
13. Messier, D. R., and Croft, W. J., *Silicon Nitride,* in *Preparation and Properties of Solid State Materials,* (W. R. Wilcox, ed.), 7:131–213, Marcel Dekker Inc., New York (1982)
14. Van Weeren, R., et al., Synthesis and Characterization of Amorphous Si_2N_2O, *J. Am. Ceram. Soc.,* 77(10):2699–2702 (1994)

13

Covalent Nitrides: Properties and General Characteristics

1.0 INTRODUCTION

The previous chapter was a review of the structure and composition of the three refractory covalent nitrides: boron nitride, aluminum nitride, and silicon nitride. This chapter is an assessment of the properties and a summary of the fabrication processes and applications of these three materials.

The refractory covalent nitrides have remarkable properties and are industrial materials of major importance, produced on a large scale in the form of powders, monolithic shapes, and coatings.

2.0 PHYSICAL PROPERTIES OF THE COVALENT NITRIDES

2.1 Discussion and Comparison

In this section and the next three, the properties and characteristics of the covalent nitrides are reviewed and compared whenever appropriate with

those of the parent elements, the covalent carbides, and with the refractory compounds of titanium (for comparison with other carbides, nitrides, or borides, see the appropriate tables in Chs. 4, 5, and 6).[1–5]

2.2 Physical Properties

Physical properties are shown in Table 13.1.

Table 13.1: Density and Melting Point of Covalent Nitrides and Other Refractory Compounds

Material	Density (g/cm^3)	Melting Point °C
BN*	2.25	3000**
AlN	3.26	2200**
Si_3N_4	3.18	1900
B_4C	2.52	2450
βSiC	3.214	2545**
B	2.35	2050
Al	2.70	660
Si	2.329	1414
TiC	4.91	3067
TiN	5.40	2950
TiB_2	4.52	2980

* hexagonal boron nitride
** decomposes

The three covalent nitrides are low-density materials with melting points which are higher than those of their parent elements: boron, aluminum, and silicon. Of the three, boron nitride has the highest melting point

and is more refractory than boron carbide. On the other hand, silicon nitride is not as refractory as silicon carbide.

3.0 THERMAL AND ELECTRICAL PROPERTIES OF COVALENT NITRIDES

3.1 Thermal Properties

The thermal properties of the covalent nitrides are shown in Table 13.2.

Table 13.2: Thermal Properties of Covalent Nitrides and Other Refractory Materials at 20°C

Material	Specific Heat (J/mole·K)	Specific Heat (J/g·K)	Thermal Conductivity (W/m·K)	Thermal Expansion ($\times 10^{-6}$/°C)
h-BN*	21.96	0.885	28–33	0.0**
AlN	36.89	0.9	180–220	2.7
Si_3N_4	98.2	0.7	25–36	2.8–3.2
βSiC	28.63	0.714	43–145	3.8
B_4C	50.88	0.921	20–35	4.3
Si	18.58	0.405	150	2.6
B(β)	11.16	1.032	60	4.8
Al	24.28	0.90	237	23
TiC	33.8	0.563	21.0	7.4
TiN	33.74	0.545	19.2–29.1	9.4
TiB_2	44.29	0.744	24.3	6.6

* Hot-pressed boron nitride (grade HP of Ref. 5)
** Negative thermal expansion has been reported

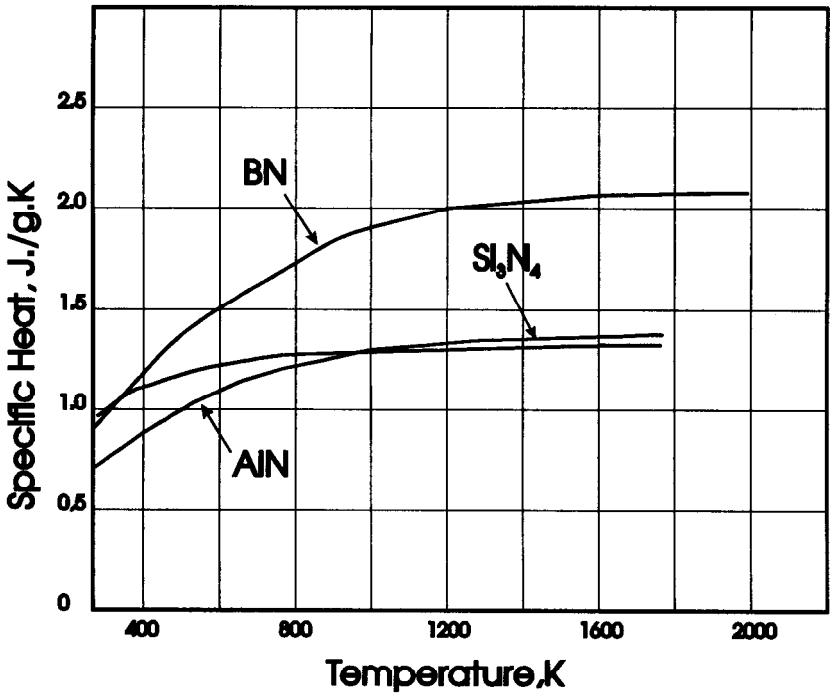


Figure 13.1: Specific heat of the covalent nitrides vs. temperature.

Specific Heat. The specific heat (C_p) of the covalent nitrides as a function of temperature is shown in Fig. 13.1.[4]

Thermal Conductivity. The thermal conductivity (K) of the covalent nitrides, like that of the covalent carbides but unlike that of the interstitial nitrides and carbides, decreases with increasing temperature as shown in Fig. 13.2.[4] The thermal conductivity of the single crystals of c-BN and AlN are extremely high (1300 and 320 W/m·K respectively) and comparable to that of the best conductors such as Type II diamond (2000 W/m·K), silver (420 W/m·K), copper (385 W/m·K), and beryllium oxide (260 W/m·K).[6]

Thermal Expansion. As shown in Fig. 13.3, thermal expansion of the covalent nitrides is low and, like that of the covalent carbides, increases with increasing temperature. This increase is not entirely linear and is slightly more rapid at high temperature.[4] For discussion of thermal expansion, see Sec. 2.5 of Ch. 4.

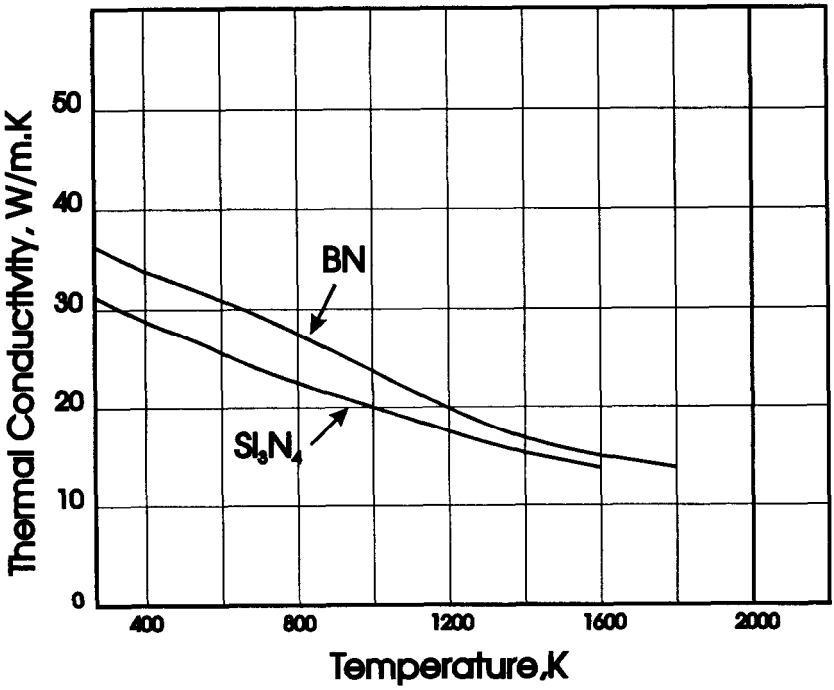


Figure 13.2: Thermal conductivities of the covalent nitrides vs. temperature.

3.2 Electrical Properties

Unlike the transition-metal nitrides and unlike boron carbide and silicon carbide, the covalent nitrides are excellent electrical insulators. Their electrons are strongly and covalently bonded to the nucleus and are not available for metallic bonding (see Sec. 3.1 of Ch. 4).

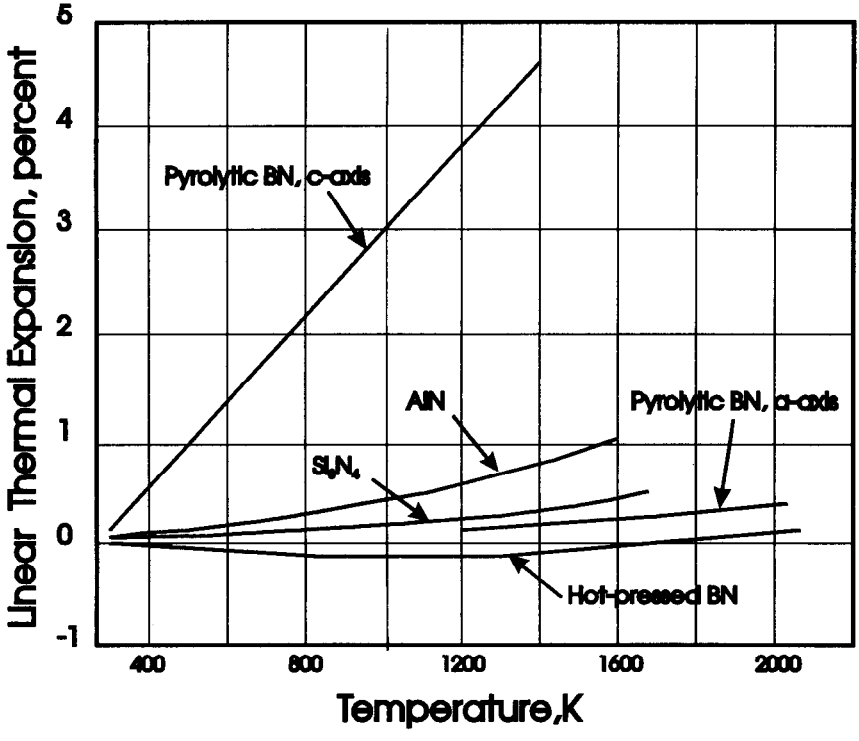


Figure 13.3: Linear thermal expansions of the covalent nitrides vs. temperature.

4.0 MECHANICAL PROPERTIES OF COVALENT NITRIDES

4.1 Property Variables

Relatively little has been reported on the mechanical properties of the covalent nitrides. The reported values often show a large spread due to differences in the fabrication processes and other factors. The values shown here are an average of the data reported in the recent literature (see Sec. 4.1 of Ch. 4 and Sec. 6.1 of Ch. 8).

4.2 Summary of Mechanical Properties

The mechanical properties of the covalent nitrides and other refractory materials are summarized in Table 13.3.

Table 13.3: Mechanical Properties of Covalent Nitrides and Other Refractory Compounds at 20°C.

Compound	Vickers Hardness (GPa)	Young Modulus of Elasticity (GPa)	Flexural Strength (MPa)
h-BN*	0.08–0.09	46.9–73.5	103
c-BN	29.9–43.1	650	
AlN	12	315	590–970
Si_3N_4	16–18	260–30	600–1200
βSiC	24.5–28.2	475	350–600
B_4C	up to 48	290–450	323–430
TiC	28–35	410–510	240–390
TiN	18–21	250	
TiB2	33	575	400

* Hot-pressed boron nitride (grade HP of Ref. 5)

4.3 Strength and Modulus

Unlike h-BN which is a relatively low-strength material, aluminum nitride and especially silicon nitride have high strength and modulus and, in this respect, compare favorably with the other refractory carbides and nitrides. The strength and modulus of silicon nitride drop rapidly above 1100°C (see Figs. 13.4 and 13.5), and creep rate becomes high.[4] It is not as good a high-temperature material as silicon carbide which retains its strength up to 1200°C (see Fig. 8.6 of Ch. 8).

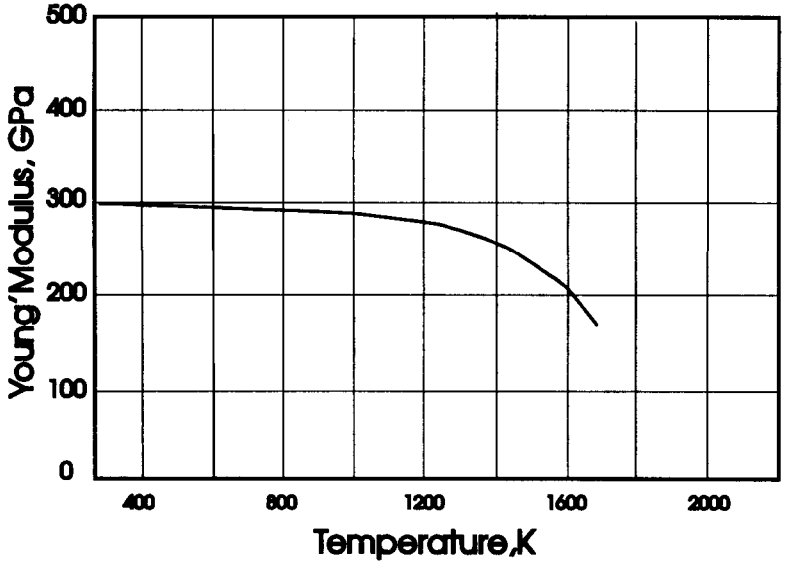


Figure 13.4: Young's modulus of silicon nitride vs. temperature.

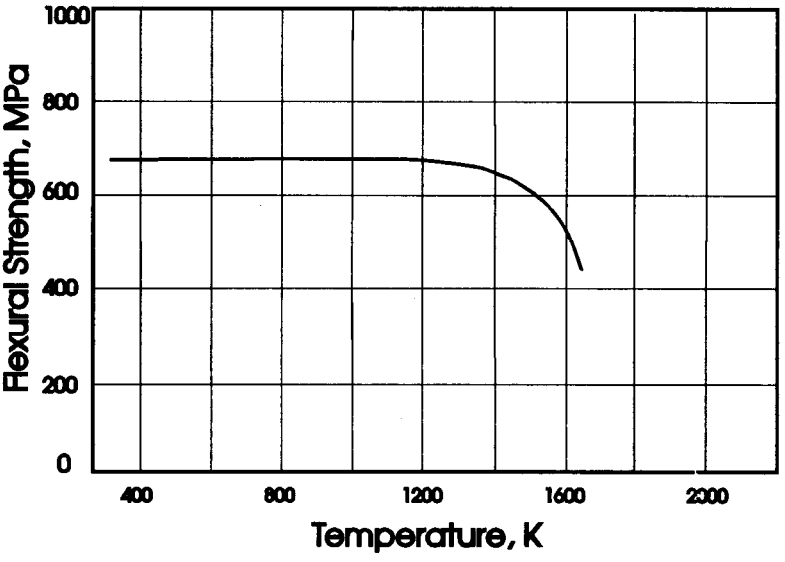


Figure 13.5: Flexural strength of silicon nitride vs. temperature.

Aluminum nitride and silicon nitride, like other refractory carbides and nitrides, have the ability to deform plastically to some degree above the ductile-to-brittle transition temperature. Below that temperature, they are intrinsically brittle (for discussion, see Sec. 4.3 of Ch. 4).

Hexagonal boron nitride, formed by CVD, is highly anisotropic and the basal planes (*ab* directions) can slip over one another as temperature increases. Thus brittle fracture can be avoided. As a result, the strength increases with temperature as shown in Fig. 13.6, while the modulus generally decreases.

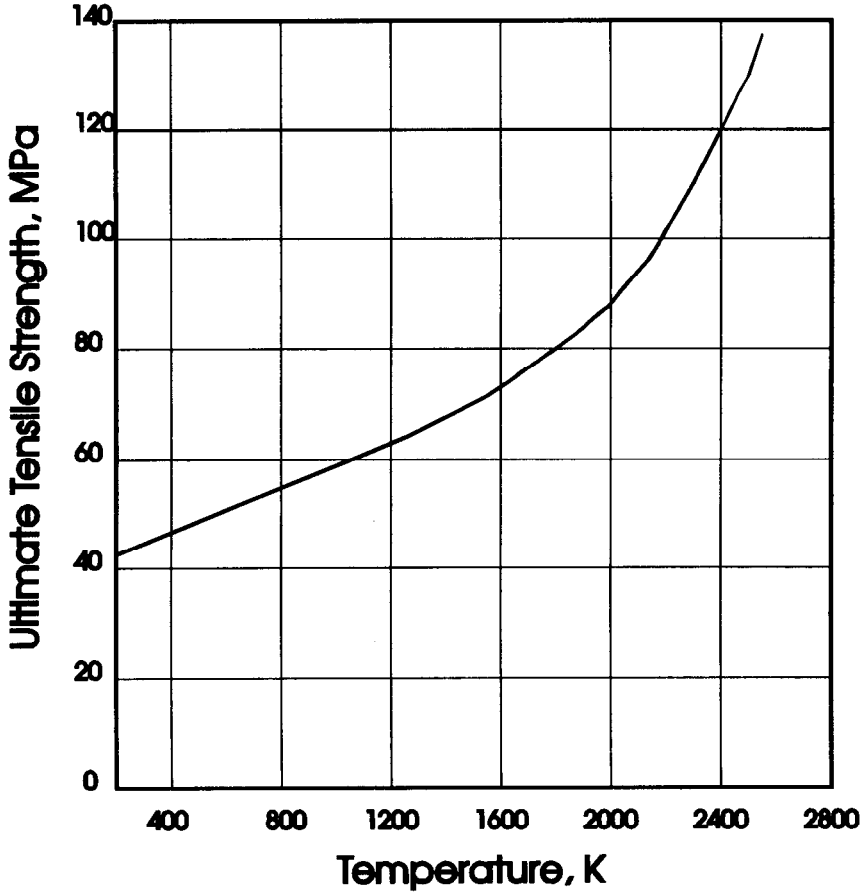


Figure 13.6: Ultimate tensile strength of boron nitride vs. temperature.

4.4 Hardness

Boron nitride is an unusual material since its properties vary considerably depending on its structure (hexagonal or cubic). For instance, h-BN is a soft and lubricious material while c-BN is next to diamond in hardness. Cubic boron nitride maintains its hardness to 1800°C[7][8] (see Sec. 4.4 of Ch. 4).

5.0 CHEMICAL PROPERTIES OF COVALENT NITRIDES

As a rule, the covalent nitrides have excellent chemical resistance and are not wet by most molten metals, salts, or glasses; consequently they are able to withstand corrosive attack for long periods of time.

6.0 CHARACTERISTICS AND PROPERTIES OF BORON NITRIDE

6.1 Historical Background and Present Status

As stated in Ch. 12, boron nitride exists in two crystalline forms: hexagonal and cubic with much different properties.[9]-[13] It was first synthesized as a powder in 1842 but for many years remained a laboratory curiosity since the powder was thought too difficult to mold into useful shapes. In the 1950's, the Carborundum Co. found a way to hot-press the material and the Raytheon Co. developed a chemical vapor deposition process.[9] Boron nitride is now used extensively as a solid lubricant, as a chemically resistant container, and as a dielectric in electronic applications. It should be stressed that the reported property values often vary considerably and the values given here are a general average.

6.2 Hexagonal Boron Nitride

The hexagonal form (h-BN) has considerable crystalline anisotropy resulting in anisotropic properties. It is produced by hot pressing the powder or by chemical vapor deposition (CVD). The processes impart different properties as shown in Tables 13.4 (hot-pressed hBN) and 13.5

(CVD hBN). The properties of the hot-pressed boron nitride show less anisotropy than the single crystal since the powder grains are randomly oriented. The anisotropy is rather the result of the pressing conditions.

Table 13.4: Summary of Characteristics and Properties of Hexagonal Boron Nitride (Hot-Pressed). Notes: *(a)* = tested parallel to pressing direction, ⊥ tested perpendicular to pressing direction; *(b)* test temperature is 20°C unless otherwise stated.

Composition: BN
Molecular Weight (g/mol): 24.816
Pearson Symbol: cF8
Color: white to transparent
X-ray Density (g/cm3): 2.25
Density (g/cm^3): 19.2–29.1
Melting Point: 3000°C (sublimes)

Specific Heat (J/g·K): 0.885 (see Fig. 13.1)
(J·mol·K): 21.96
Thermal Conductivity (W/m·°C): 28–33 (see Fig. 13.2)
Thermal Expansion (× 10^{-6}/°C) in the range of 20–250°C:
= 7.20; ⊥ 0.45 (Grade A of Ref. 5) (see Fig. 13.3)
= 0.0; ⊥ 0.0 (Grade HP of Ref. 5)

Electrical Resistivity (Ω·cm): = 1 × 10^{14}; ⊥ 1 × 10^{15}
Loss Tangent @ 8.8 GHz: = 0.0017; ⊥ 0.0005
Dielectric Constant: = 4.58; ⊥ 4.15
Dielectric Strength (V/mm): 88000 (sample thickness 250 μm)
Loss Factor at 1 MHz: = 0.0012; ⊥ 0.0034

Vickers Hardness (MPa): = 93.7; ⊥ 82
Compressive Strength (MPa): = 143; ⊥ 186
Shear Strength (MPa): = 77; ⊥ 103
Young's Modulus (GPa): = 46.9; ⊥ 73.5
Modulus of Rupture (GPa): = 75.7; ⊥ 113

Oxidation Resistance: no reaction up to 750°C. Above, oxidizes slowly by the formation of a layer of B_2O_3 (see Fig. 13.7)

Chemical Resistance: essentially inert to all reagents at room temperature

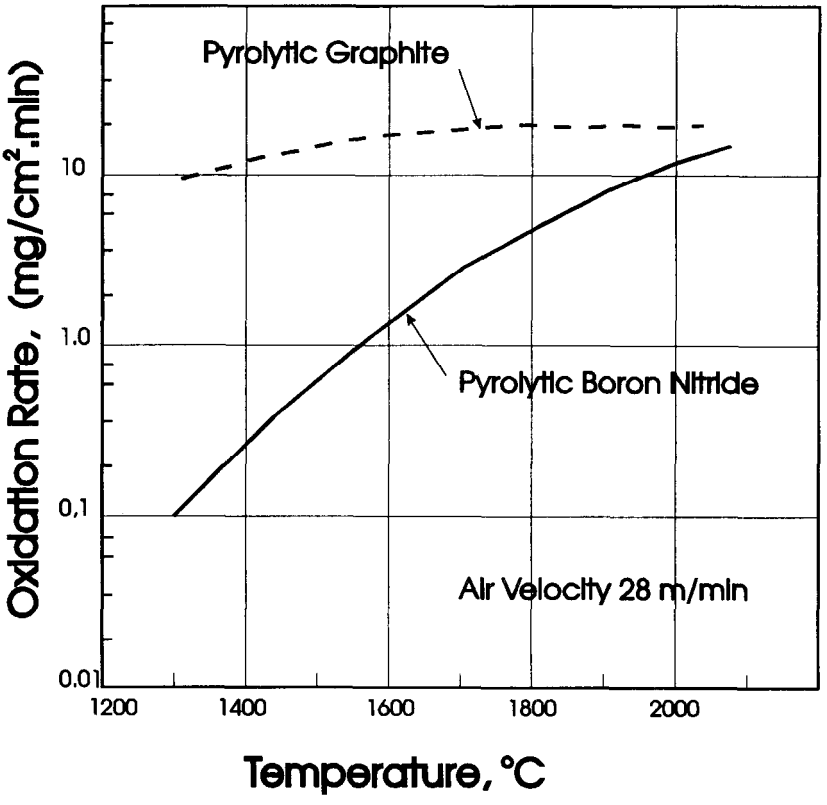


Figure 13.7: Oxidation rate of pyrolytic boron nitride and pyrolytic carbon.

6.3 Phase Diagram

No boron-nitrogen phase diagram is presently available but a tentative pressure-temperature diagram is shown in Fig. 12.1 of Ch. 12.[14][15]

6.4 CVD Boron Nitride

CVD boron nitride (also known as pyrolytic boron nitride) has a structure closely resembling that of the single crystal and shows a considerable degree of anisotropy in many of its properties as shown in Table 13.5 (properties that are similar to the hot-pressed material are not listed). In this respect it is similar to pyrolytic graphite.[6]

Table 13.5: Summary of Characteristics and Properties of Pyrolytic (CVD) Boron Nitride.

Notes: *(a) ab*: tested in *ab* direction (parallel to surface), *c*: tested in *c* direction (perpendicular to the surface);

(b) test temperature is 20°C unless otherwise stated.

Composition: BN
Molecular Weight: 24.816 g/mol
Color: white to transparent
Density: 2.1 g/cm^3
Porosity (helium admittance): 2×10^{-11} cm·sec
Space Group: F43m

Thermal Conductivity (W/m·°C): *ab* 62.8; *c* 1.66 (at 100°C)
Thermal Expansion ($\times 10^{-6}$/°C): *ab* 0; *c* 24 in the range of 20–250°C (see Fig. 13.3)

Electrical Resistivity (Ω·cm): *ab* 10^7, *c* 10^{15} (at 1000°C)
Loss Tangent (100 Hz to 1000 GHz): *ab* 1.5×10^{-4}; *c* $<1 \times 10^{-4}$
Dielectric Constant: *ab* 5.12; *c* 3.4
Dielectric Strength: *c* 2×10^5 dcV/mm

Hardness: soft and lubricious
Compressive Strength (MPa): *c* 234
Tensile Strength (MPa): *ab* 41; *ab* 103 (at 2200°C) (see Fig. 13.6)
Torsional Shear Strength (Mpa): 10 (15 at 1500°C)
Young's Modulus (GPa): *ab* 22
Poisson Ratio: *ab* 0.25

Oxidation Resistance: no appreciable weight loss up to 1300°C. Above, oxidizes slowly by the formation of a layer of B_2O_3 (see Fig. 13.8).

Chemical Resistance: essentially inert to all reagents at room temperature

6.5 Cubic Boron Nitride

Cubic boron nitride (c-BN) is a different material altogether with a structure similar to that of diamond characterized by its extremely high hardness (second to diamond) and thermal conductivity as shown in Table

13.6.[7][13][16] It is a relatively new material (discovered in 1957 and available commercially since the 1970's). Little has been published regarding its properties.

Table 13.6: Summary of Characteristics and Properties of Cubic Boron Nitride.
Note: Test temperature is 20°C unless otherwise stated.

Composition: BN
Molecular Weight: 24.816 g/mol
Color: white
X-ray Density: 3.48 g/cm3
Melting Point: 3000°C (sublimes)
Specific Heat: 12.65 J/mol·K
Thermal Conductivity: 300–600 W/m·°C (theoretical value: 1300)
Thermal Expansion: 4.9×10^{-6}/°C
Electrical Resistivity: insulator
Hardness: 29.89–43.12 GPa (depending on crystal orientation)
Compressive Strength: 2730 MPa
Young's Modulus: 650 GPa
Fracture Toughness: 6.4 MPa·$m^{0.5}$
Chemical Resistance: essentially inert to all reagents at room temperature

6.6 Chemical Resistance of Boron Nitride

Hexagonal boron nitride is one of the most outstanding corrosion-resistant materials. It is inert to gasoline, benzene, alcohol, acetone, chlorinated hydrocarbons, and other organic solvents. It is not wet by molten aluminum, copper, cadmium, iron, antimony, bismuth, silicon, germanium nor by many molten salts and glasses. It has good resistance to oxidation and, in this respect, is far superior to graphite

Cubic boron nitride does not react with carbide formers such as Fe, Co, Ni, Al, Ta, and B at approximately 1000°C (while diamond does); this is a useful characteristic in machining and grinding applications. However, it reacts with aluminum at 1050°C and with Fe and Ni alloys containing Al above 1250°C.[17]

7.0 CHARACTERISTICS AND PROPERTIES OF ALUMINUM NITRIDE

7.1 Historical Background and Present Status

Aluminum nitride was first produced and identified in 1907 but it is only since the 1980's that its cost has been sufficiently reduced to permit the development of industrial applications. Japan is the major supplier.[3][18] Several American companies have recently entered in the competition to supply heat sinks for the electronic industry.

7.2 Summary of Properties

Aluminum nitride is a highly stable material with the unusual combination of high thermal conductivity comparable to that of metals and high electrical insulation comparable to the best insulators. Its characteristics and properties are summarized in Table 13.7 (see Ch. 12 for structural data). The reported property values often vary considerably and the values given here are a general average.[3][4][19]

7.3 Phase Diagram

The phase diagram of Al-N is shown in Fig. 13.8.[14][15]

7.4 Chemical Resistance of Aluminum Nitride

Fine AlN powder is susceptible to hydrolysis by atmospheric humidity. This is no longer the case once the material is sintered. Densified AlN begins to oxidize in air above 1100°C and is stable in inert atmosphere to 1800°C. It is highly resistant to molten copper, silver, tin, lead, bismuth, and nickel. It is wet by but does not react with aluminum.[3]

Table 13.7: Summary of Characteristics and Properties of Aluminum Nitride.
Note: Test temperature is 20°C unless otherwise stated.

Composition: AlN
Molecular Weight: 40.99 g/mol
Color: White when pure, tan or gray with impurities
X-ray Density: 3.16 g/cm^3
Space Group: F43m
Pearson Symbol: hP4
Direct band gap (2H polytype): 6,28 eV
Melting Point: 2200°C at 4 atm. N_2 (sublimes at atm. pressure)
Specific Heat: 0.7–0.9 J/g·K (see Fig. 13.1)
28.7–36.9 J/mol·K
Thermal Conductivity (W/m·°C): up to 320 for pure single crystal
180–220 hot pressed material
Thermal Expansion (10^{-6}/°C): 2.7 at 25°C (matches that of silicon) (see Fig. 13.3)

Electrical Resistivity: 10^{13} Ω·cm
Direct Bandgap: 6.28 eV
Dielectric Constant: 8.9 at 1 MHz, 8.2 at 7 GHz
Dielectric Strength: 10 kV/mm
Surface Acoustic Velocity, Raleigh V_R: 6–6.2 km/s, V_L = 11–12 km/s[20]
Electromechanical Coupling Coefficient: to 1%[20]
Optical: transparent in the visible and near IR range.
Piezoelectric characteristics

Vickers Hardness: 12 GPa
Young's Modulus: 315 GPa
Poisson's Ratio: 0.25
Flexural Strength: 590–970 MPa
Compressive Strength: 2070 MPa

Oxidation Resistance: resistant to 1350°C[21]

Chemical Resistance: decomposes slowly in boiling water; essentially inert to most other reagents at room temperature

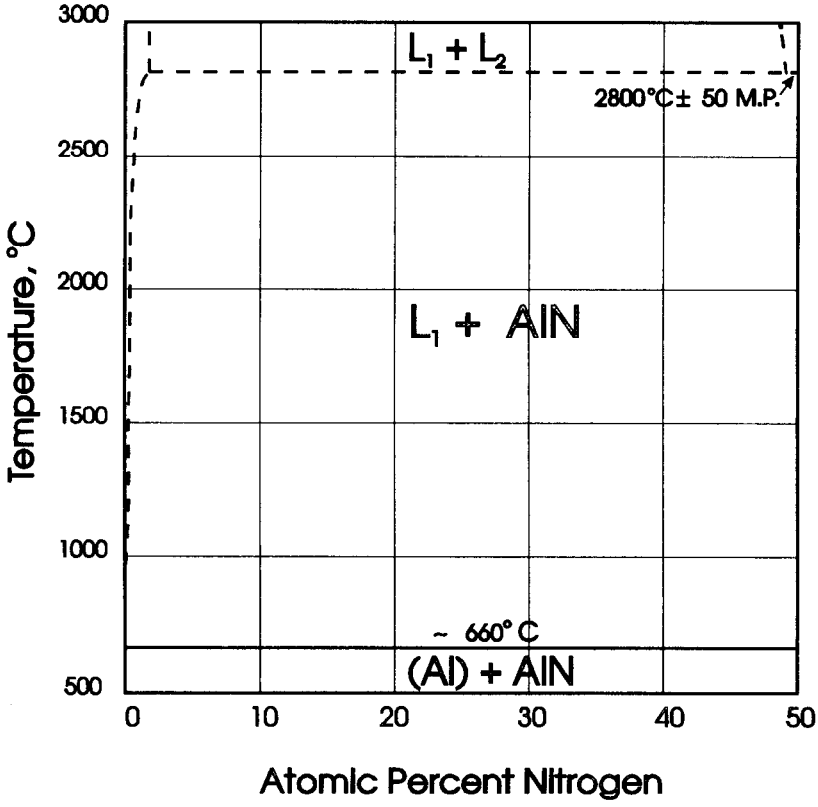


Figure 13.8: Nitrogen–aluminum phase diagram.

8.0 CHARACTERISTICS AND PROPERTIES OF SILICON NITRIDE

8.1 Historical Background and Present Status

Silicon nitride was first produced in 1857 but remained in the laboratory until after World War II when it was developed as a crucible for molten

metals. In 1971, a program was started to develop silicon-nitride components for gas turbines and since then considerable progress has been achieved in the processing of the material.[18] Japan remains the major supplier of silicon-nitride powder.

8.2 Summary of Properties

Silicon nitride can be obtained as an amorphous material or in two hexagonal crystalline forms, α and β, the latter being the high-temperature form. An irreversible transformation from α to β occurs at 1600°C. The material has excellent overall properties such as:

- Light weight
- High strength and toughness (for a ceramic material)
- High chemical resistance to acids, bases, salts and molten metals
- Good resistance to oxidation to 1500°C
- High electrical resistivity

Its characteristics and properties are summarized in Table 13.8 (see Ch. 12 for structural data).[22]–[25] As stated above, the reported property values often vary considerably especially as a function of processing characteristics, and the values given here are a general average.

8.3 Phase Diagram

The phase diagram of Si-N is shown in Fig. 13.9.[14][15]

8.4 Chemical Resistance of Silicon Nitride

Silicon nitride has good corrosion resistance and is not attacked by most molten metals as shown in Table 13.9.[26]

Table 13.8: Summary of Characteristics and Properties of Silicon Nitride.

Note: Test temperature is 20°C unless otherwise stated; material is bSi_3N_4 unless specified..

Composition: Si_3N_4
Molecular Weight: 140.28 g/mol
Color: colorless if pure
Theoretical Density (g/cm^3): 3.187 (β), 3.184 (α)
Melting Point: 1900°C
Specific Heat (J/g·K): 0.54–0.7 (see Fig. 13.1)
(J/mole·K): 75.7–98.2
Thermal Conductivity: 25–36 W/m·°C (see Fig. 13.2)
Thermal Expansion (10^{-6}/°C): 2.8–3.2 over the range of 0–100°C (see Fig. 13.3)

Electrical Resistivity: 10^{14} Ω·cm
Dielectric Constant @ 35 GHz: 7.9–8.14
Loss Tangent @ 35 GHz: 0.0017–0.0006

Vickers Hardness: 16–18 GPa
Weibull Modulus: 15–30 MPa
Fracture Toughness 5–7.5 MPa
Young's Modulus: 260–330 GPa (see Fig. 13.4)
Poisson's Ratio: 0.23–0.27
Flexural Strength: 600–1200 MPa (see Fig. 13.5)

Oxidation Resistance: to 1350°C
Chemical Resistance: Resistant to most reagents at room temperature[24]

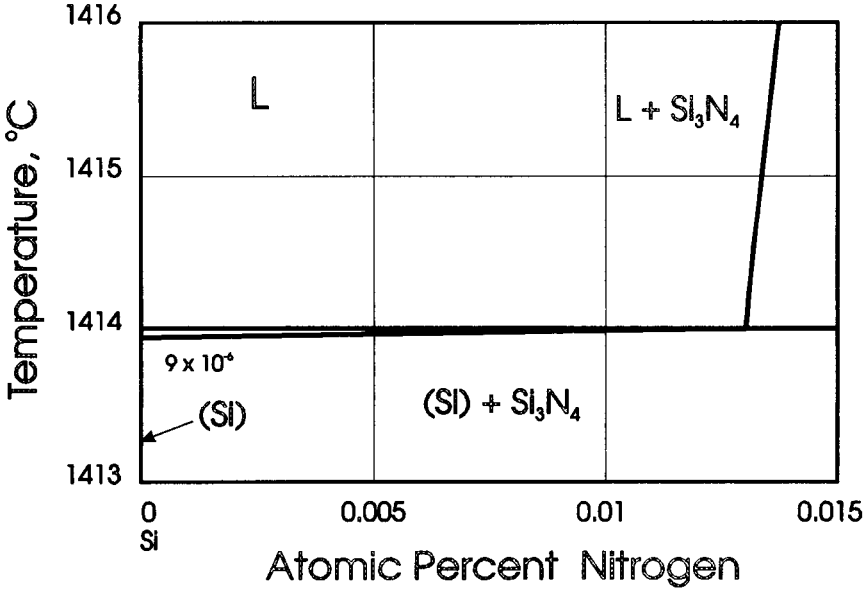


Figure 13.9: Nitrogen–silicon phase diagram.

Table 13.9: Resistance of Silicon Nitride to Molten Metals.

Metal	Temperature (°C)	Time (hr)	Degree of Attack
Al	800	950	none
Al	1000	100	none
Pb	400	144	none
Sn	300	144	none
Zn	550	500	none
Mg	750	20	slight
Cu	1160	7	severe

8.5 Sialons

The term *sialon* was adopted in the seventies to describe solid-solution compositions containing the elements Si-Al-O-N. The crystal lattice of β-Si_3N_4 can readily accommodate other atoms such as Al and O, and the Sialons are formed by the addition of alumina (Al_2O_3) or aluminum nitride (AlN) to β-Si_3N_4. An empirical formula for this family of materials is $Si_{6-x}Al_xO_xN_{8-x}$. The sialons show promise as high-temperature engineering materials.[4][25]

9.0 SUMMARY OF FABRICATION PROCESSES

The fabrication processes for the three covalent nitrides are also reviewed in Chs. 14 and 15.

9.1 Boron Nitride

Boron nitride powder is produced directly from the elements or from the reaction of boron and ammonia or boric oxide and ammonia. The powder is difficult to process and expensive and requires a sintering agent such as boric oxide.[17]

Coatings and monolithic components of boron nitride are usually produced by CVD by the reaction of a boron halide with ammonia. MOCVD and plasma-CVD are also used.[27]

Cubic boron nitride is obtained by high pressure processing from h-BN powder with lithium nitride as a catalyst.[2]

9.2 Aluminum Nitride

Aluminum nitride powder is obtained by the carbothermal reduction of alumina, the decomposition of aluminum chloride and ammonia, and the reaction of aluminum powder with ammonia or nitrogen.

Coatings of AlN are produced by atmospheric and low-pressure CVD by the reaction of ammonia and an aluminum halide. They are also produced by MOCVD by the reaction of an aluminum alkyl with ammonia.[27]

9.3 Silicon Nitride

Silicon nitride powder is produced by the reaction of silicon chloride and ammonia, by the nitridation of silicon, and by the thermal decomposition of silicon diimide. It is also produced by laser CVD from halogenated silanes and ammonia. Shapes are produced by sintering, reaction bonding, and hot pressing. Thin films are deposited by reactive sputtering, and by CVD by using ammonia or nitrogen reacting with silane.

10.0 SUMMARY OF APPLICATIONS AND INDUSTRIAL IMPORTANCE

The following is a summary of applications the three covalent nitrides presently in production or development. More details are given in Ch. 16.

10.1 Boron Nitride

The applications of boron nitride form a growing market estimated at over $20 million in 1994, most of it as powder for lubricants and additives.[28][29]

- Solid lubricants, fillers and mold releases (powder form)
- Break rings in steel casting
- Insulators for high-frequency electrical equipment
- Masks for x-ray lithography
- High-temperature furnace hardware and boats for molten metals, glasses and ceramic processing
- Radar windows and antennas
- Crucibles for aluminum evaporation and for molecular beam epitaxy
- Vessels for Czochralski crystal growth of III-V and II-VI compounds (i.e., gallium arsenide)
- Insulating substrate in ribbon heaters in combination with a pyrolytic graphite resistance heating element
- Powder and bonded abrasive, and cutting material for high hardness steel and alloys (cBN)

- Release agent
- Filler for plastics

10.2 Aluminum Nitride

The major application of aluminum nitride is for electronic components. The market for powder was estimated at 147 metric tons with a value of $8.8 million, most of it produced and used by the Japanese industry.[30]

- Heat-sink substrates and packaging materials for electronic devices (major application)
- Passivation and dielectric layers
- High-frequency acoustic wave devices (piezoelectric)
- Traveling-wave tubes
- Microwave-absorbing components
- Experimental high-power and high-temperature material for electronic and optoelectronic devices especially in the UV region of the spectrum

10.3 Silicon Nitride

The market for silicon nitride is fast growing particularly in structural and chemical resistance applications and as a thin film in semiconductor devices.[31]

- Crucibles for silicon single-crystal processing
- Crucibles and vessels for handling corrosive chemicals and molten metals
- High-temperature gas-turbine components
- Diesel-engine components
- Rotors for turbocharger
- Cutting tools (Si_3N_4 and Sialons)
- Components for welding, tube drawing, and extruders
- Ball and roller bearings
- Bearing seals and check valves
- Blast nozzles

- Thermocouple tubes
- Heat exchangers, pumps, seal faces
- Passivation layers, multilayer resist stacks, diffusion barriers, interlevel dielectrics, side-wall spacers, trench masks, oxidation masks, etc., in semiconductor devices
- Whiskers for high strength reinforcement

REFERENCES

1. Benesovsky, F., Kiefer, R., and Ettmayer, P., Nitrides, in *Kirk-Othmer's Encyclopedia of Industrial Chemistry,* 4th. Ed., John Wiley & Sons (1993)
2. Ettmayer, P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed. VCH (1985)
3. *Handbook of Advanced Ceramic Materials,* Advanced Refractory Technologies, Inc., Buffalo, NY (1994)
4. *Engineering Property Data on Selected Ceramics, Vol. 1, Nitrides,* MCIC HB-07-1, Battelle Institute, Columbus, OH (1976)
5. Combat Boron Nitride, *Technical Brochure,* Carborundum, Amherst, NY (1994)
6. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes,* Noyes Publications, Park Ridge, NJ (1993)
7. Brookes, C. A., The Mechanical Properties of Cubic Boron Nitride, *Int. Physics Conf. Series*, No. 75 (E. A. Almond et al, eds.), Adam Hilger Ltd., Bristol, UK (1984)
8. Makarenko, G. N., Borides of the IVb Group, in *Boron and Refractory Borides* (V. L. Matkovich, ed.), Springer-Verlag, Berlin (1977)
9. Li, P. C., Capriulo, A. J., and Lepie, M. P., Chemically Vapor Deposited Boron Nitride, *Proc. OSU-RTD Symp. on Electro-Magnetic Windows*, Vol. 1 (June 1964)
10. Boralloy Pyrolytic Boron Nitride, Technical Brochure, Union Carbide, Cincinnati, OH (1994)
11. Pyrolytic Boron Nitride, Technical Brochure, Atomergic Chemical Corp., Plainview, NY (1990)
12. Kempfer, L., The Many Faces of Boron Nitride, *Mater. Eng.*, 41–44 (Nov. 1990)
13. Noaker, P. M., Hard Facts on Hard Turning, *Manufacturing Engineering*, 43–46 (Feb. 1992)

14. Moffatt, W. G., *The Handbook of Binary Phase Diagrams,* Genum Publishing Corp, Schenectady, NY (1984)
15. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. Edition, ASM International, Metals Park, OH (1990)
16. Naka, S., Ceramic Processing Overview, in *Fine Ceramic* (S. Saito, ed.), 1–15, Elsevier (1988)
17. Gardinier, C., Physical Properties of Superabrasives, *Ceramic Bull.*, 67(6):1006–1009 (1988)
18. Sheppard, M., Aluminum Nitride, A Versatile but Challenging Material, *Ceramic Bulletin*, 60(11):1801–1812 (1990)
19. Hampshire, S., Nitride Ceramics, in *Material Science and Technology*, Vol. 11 (M. V. Swain, ed.) VCH, New York (1994)
20. Rowland, L. B. et. al., Epitaxial Growth of AlN by Plasma-Assisted, Gas Source Molecular-Beam Epitaxy., *J. Mater. Res.*, 8(9):2310–22314 (1993)
21. Bellosi, A., Landi, E., and Tampieri, A., Oxidation Behavior of Aluminum Nitride, *J. Mater. Res.*, 8(3):565–572 (Mar. 1993)
22. Silicon Nitride, Technical Brochure, Ceradyne Inc., Costa Mesa, CA (1994)
23. Komaya, K., and Matsui, M., High-Temperature Engineering Ceramics, in *Material Science and Technology*, Vol. 11 (M. V. Swain, ed.) VCH, New York (1994)
24. Messier, D. R., and Croft, W. J., Silicon Nitride, in *Preparation and Properties of Solid State Materials* (W. R. Wilcox, ed.), 7:131–213, Marcel Dekker Inc., New York (1982)
25. Torti, M. L., The Silicon Nitride and Sialon Family of Structural Ceramics, in *Treatise on Materials Science and Technology*, 29:161–194, Academic Press, New York (1989)
26. Campbell, I., and Sherwood, E., *High Temperature Materials and Technology,* John Wiley & Sons, New York (1967)
27. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
28. Boron carbide and Boron Nitride, *Mitchell Market Reports,* Monmouth, UK (1993)
29. Lelonis, D. A., Boron Nitride Tackles the Tough Ones, *Ceramic Industry*, 57–60 (April 1989)
30. Mroz, T. J., Jr., Aluminum Nitride, *Ceramic Bull.*, 70(6):849 (1991)
31. Silicon Nitride and the Sialons, *Mitchell Market Reports,* Monmouth, UK (1989)

14

Processing of Refractory Carbides and Nitrides (Powder, Bulk, and Fibers)

1.0 INTRODUCTION

1.1 Synthesis Characteristics

Unlike many ceramic materials such as oxides which can be produced from raw materials found in nature, the refractory carbides and nitrides generally do not exist in the natural state. A few minor exceptions include a form of silicon carbide found in the meteorite field of Canyon Diablo in Arizona[1] and titanium nitride detected in some silicate meteorites as the mineral osbornite.[2] These exceptions can be considered as curiosities and the refractory carbides and nitrides must be synthesized for scientific or commercial use.

This synthesis is costly and exacting since, as shown in previous chapters, these materials are highly refractory and chemically inert, with strong covalent bonds and a general tendency to decompose upon melting. As a result, they cannot be readily processed by common metallurgical techniques such as casting or forging nor can they normally be sintered without sintering aids. Even under the best conditions, it is difficult to obtain a material free of porosity and with uniform and controlled grain

structure. The properties are often degraded and may vary considerably from batch to batch due to processing differences, small as they may be.

These factors have long hindered the development and commercial applications of these materials. It is only with the recent advances in processing techniques such as chemical-powder production, cold and hot isostatic pressing, chemical- and physical-vapor deposition, and thermal spray that industry is now able to take better advantage of their remarkable properties.

1.2 Forms and Processing of Refractory Carbides and Nitrides

The refractory carbides and nitrides are available in the form of powders, monolithic (or bulk) shapes, coatings, fibers, and whiskers. Each of these categories is produced by one or more specific processes as summarized in Table 14.1.

Table 14.1: Fabrication Processes of Refractory Carbides and Nitrides

Form	Process
Powder	Chemical preparation Vapor-phase chemical reaction RF-plasma torch Sol-gel Self-propagating high-temperature synthesis
Bulk/monolithic	Powder forming Reaction bonding Sintered reaction bonding Hot pressing Hot-isostatic pressing
Fiber/whisker	Chemical-vapor deposition Sol-gel
Coatings	Chemical-vapor deposition (CVD) Physical-vapor deposition (PVD) Thermal spray

The processes listed in Table 14.1 are complex and each is the subject of much investigation and numerous reports and books. Their complete description is outside the scope of this book and they can only be summarized here. More information can be obtained from the references.

2.0 PRODUCTION OF REFRACTORY CARBIDE AND NITRIDE POWDERS

2.1 General Considerations

The bulk/monolithic and thermal spray processes for refractory carbides and nitrides are two-step operations which first require the preparation of powders. Powders are also used as such in grinding and polishing applications (mostly silicon carbide and boron carbide).

These powders are produced by a variety of experimental or production processes which can offer controlled composition, small particle size, and high purity. These processes are outlined in Table 14.1 and summarized below.

2.2 Chemical Preparation

Refractory carbide and nitride powders are usually produced by chemical reaction between the elements or compounds of the elements. These processes are moderate in cost but do not generally produce materials of the highest purity and consistency.

Refractory Carbides. The various chemical preparation reactions for refractory carbide powders are summarized in Table 14.2.[5]

As shown in the table, a common method of preparing transition-metal carbide powders is to react the metal oxide (i.e., TiO_2, ZrO_2, etc.) with carbon in the form of powders in the presence of hydrogen and in the temperature range of 1500°C to 2400°C, depending on the metal.[5]

Beta-SiC powder can be produced in a microwave oven (2540 MHz) by simple solid-state reaction between silicon and charcoal powder at temperature lower than 1000°C.[11]

Table 14.2: Chemical Preparation of Refractory Carbide Powders

Carbide	Process
TiC	Reaction of TiO_2 with carbon at 2000°C or above in hydrogen Carburization of titanium sponge
ZrC	Reaction of ZrO_2 with carbon at 1800–2400°C in hydrogen Carburization of zirconium sponge
HfC	Reaction of HfO_2 with carbon at 1800–2200°C in hydrogen Carburization of hafnium sponge Carburization of hafnium hydride at 1600–1700°C
VC	Reaction of vanadium oxide or ammonium vanadate with carbon at 1500–1700°C in hydrogen followed by a vacuum heat-treatment Reaction of vanadium metal with carbon under vacuum
NbC	Reaction of niobium oxide with carbon at 1700°C in hydrogen Reaction of niobium metal or niobium hydride with carbon under vacuum
TaC	Reaction of Ta_2O_3 with carbon at 1700°C in hydrogen usually in two steps Direct carburization of tantalum Reaction of tantalum hydride with carbon
Cr_3C_2	Reaction of Cr_2O_3 with carbon up to 1600°C hydrogen (below 1300°C, Cr_7C_3 is obtained) Carburization of the chromium metal
Mo_2C	Direct heating of Mo and carbon powders in hydrogen at 1500°C
WC	Direct carburization of W with carbon such as lamp black or graphite at 1400–2000°C in hydrogen or vacuum Other precursors: tungsten oxide, tungstic acid, ammonium paratungstate
SiC	Electrochemical reaction of high-purity silica sand and carbon in electric furnace with addition of saw dust and chlorine (see Ch. 8, Sec. 8)[6] αSiC produced above 2100°C βSiC produced at 1500–1600°C[7]
B_4C	Reduction of B_2O_3 with carbon in electric furnace at high temperature (to 2300°C)[8] Same reduction reaction with magnesium Direct synthesis of the elements[9][10]

Refractory Nitrides. The various chemical preparation reactions for refractory nitride powders are summarized in Table 14.3.[2][5][12]-[16]

Table 14.3: Chemical Preparation of Refractory Nitride Powders

TiN	Nitridation of Ti metal with nitrogen or ammonia at 1200°C
ZrN	Nitridation of Zr metal with nitrogen or ammonia at 1200°C
HfN	Nitridation of Hf metal with nitrogen or ammonia at 1200°C
VN	Nitridation of V metal with nitrogen or ammonia at 1200°C
NbN	Nitridation of Nb metal with nitrogen or ammonia at 1200°C
TaN	Nitridation of Ta metal with nitrogen or ammonia at 1200°C
AlN	Carbothermal reduction of alumina in nitrogen Thermal decomposition of aluminum chloride and ammonia followed by calcination to remove chlorine, and high temperature crystallization Reaction of aluminum powder with ammonia or nitrogen at 800–1000°C
Si_3N_4	Thermal decomposition of silicon chloride and ammonia followed by calcination to remove chlorine and crystallization at 1500°C (αSi_3N_4) Nitridation of silicon at 1200–1400°C (αSi_3N_4) Thermal decomposition of $Si(NH)_2$ ($\alpha S_{i3}N_4$)
BN	Synthesis from elemental boron and ammonia Reaction between boric oxide and ammonia[17]

As shown in the table, most refractory nitride powders may be produced by the reaction of the metal halide with ammonia. Another common production method is the reaction of an oxyhalide (i.e., CrO_2Cl_2),

an oxide (i.e., B_2O_3, V_2O_3), or an ammonium-oxo complex (i.e., NH_4VO_3) with ammonia.

Conventional Comminution (Grinding). The materials prepared by chemical means may require *comminution* (grinding) to obtain smaller and more uniform particles. This is usually accomplished by jaw crushers or crushing rollers and ball and attrition mills. The mill and ball material is often the same as that to be ground in order to minimize contamination. The resulting powder is a mixture of coarse and fine particles. The advantages of comminution are a relatively inexpensive process, the production of unaggregated powder, and wide applicability. Disadvantages are limited purity, the inability to grind much below one micrometer, and limited homogeneity.[3][4]

2.3 Vapor-Phase Chemical Reactions

High-quality powders of refractory carbides and nitrides can be obtained by the more recent processing techniques of chemical-vapor deposition (CVD), RF-plasma torch, combustion synthesis, and sol-gel.[4][18]

The CVD process is reviewed in more detail in Ch. 15. In a CVD reaction, if the temperature and supersaturation are sufficiently high, the product is primarily powder precipitated from the gas phase.[19] Such powders have few impurities, small diameter, and great uniformity. In addition, the temperatures required to sinter CVD powders are generally lower than those for conventional powders.

The following powders are made experimentally or on a production basis.

- Beta-SiC powder from the decomposition of methyl-trichlorosilane (MTS) in the presence of hydrogen in an argon plasma. Also from the gaseous thermal decomposition of tetramethylsilane, $Si(CH_3)_4$, in a flow-through reactor between 850 and 1500°C[20] and by the reaction of acetylene and silane
- Submicron βSiC powder by reacting silane and acetylene in a 10–50 W continuous-wave CO_2 laser beam[21]
- Amorphous Si_3N_4 powder from silicon halides and ammonia at high temperature.[15][22] The powder can also be produced by using the same reaction at 1000°C in an RF plasma with a mean particle size of 0.05–0.1 μm[23]

- Si_3N_4 powder by laser CVD from halogenated silanes and ammonia with an inert sensitizer such as SF_6[24]
- Aluminum nitride submicron powder from aluminum alkyl[25] and from the reaction of aluminum powder, lithium salt and nitrogen at 1000°C[26]

How much of an impact CVD carbide and nitride powders will have is not clear at this time since applications have yet to reach the commercial stage in any significant manner. Still, the success of a number of development programs strongly suggests that CVD may soon become a major powder-production technology. This is already evident in Japan which is a recognized leader, particularly in refractory nitrides.

2.4 RF Plasma Torch

Ultrafine refractory carbide and nitride powders can be produced in an inductively coupled radio-frequency (rf) plasma torch.[4][27] A schematic drawing of a plasma torch for the production of silicon carbide powder is shown in Fig. 14.1.

2.5 Self-Propagating High-Temperature Synthesis (SHS)

With the proper conditions, highly exothermic reactions, once initiated, will spread as a combustion wave throughout the reactants mixture.[4][8] These reactions, originally developed in Russia, are used to produce powders of almost all the refractory carbides and nitrides.

The adiabatic temperature (T_{ad}) of the compound, i.e., the processing temperature at which no heat enters or leaves the system, can be used as an indication of the temperature at the combustion front. As shown in Table 14.4, this temperature can be very high, particularly with the refractory nitrides.

It has been empirically determined that T_{ad} should be greater than 1800 K for the reaction to be self-sustaining. However weakly exothermic reactions such as those forming SiC or B_4C can be initiated by preheating the reactant mixture. For nitride powders to be formed, the nitrogen pressure must be higher than the dissociation pressure of the nitride at the adiabatic temperature. For instance, a nitrogen pressure greater than 10 GPa is necessary to form Si_3N_4, and greater than 0.1 MPa to form AlN.

Table 14.4: Adiabatic Temperature of Refractory Carbides and Nitrides

Compound	T_{ad}(K)	Compound	T_{ad}(K)
TiC	3210	TiN	4900
HfC	3900	ZrN	4900
TaC	2700	HfN	5100
WC	1000	NbN	3500
SiC	1800	TaN	3360
B_4C	1000	Si_3N_4	4300
		BN	3700
		AlN	2900

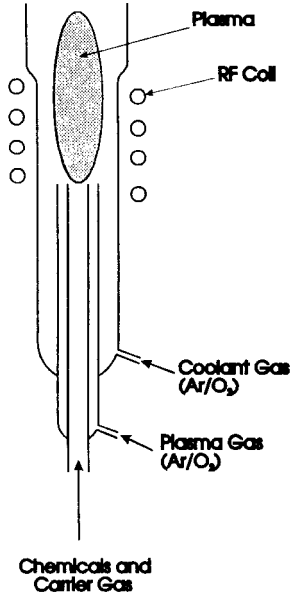


Figure 14.1: Schematic drawing of a RF–plasma torch.[4]

2.6 Sol-Gel

The sol-gel process uses a liquid reactive precursor material that is converted to the final product by chemical and thermal means. This precursor is prepared to form a colloidal suspension or solution (sol) which goes through a gelling stage (gel) followed by drying and consolidation. The process requires only moderate temperatures, in many cases less than half the conventional refractory-ceramic processing temperatures. It also permits close control of the composition and structure on the molecular level.[29]

At the present time, most of the work is centered on the development of silicon carbide and silicon-nitride powders. Polysilanes are the basic precursor for the synthesis of silicon carbide from sol-gel. This was first achieved by the conversion of polydimethyl silane through a carbosilane intermediate. However this silane has poor solubility and low char yield and considerable shrinkage occurs during conversion to the final product. Precursors are being developed with a much larger SiC yield notably those based on trifunctional alkoxides and chlorosilanes. These materials are being evaluated for the production of powders.[30][31]

Silicon nitride powder can be produced by sol-gel by using volatile silazanes as precursors. These materials are converted to silicon nitride and carbide. By the introduction of oxygen during the conversion process, the silicon carbide is reduced and the nitride is left. Other precursors of interest are as follows:

- Tungsten carbonyl and dimethyl acetylene dicarboxylate react to produce tungsten carbide
- Boron-nitride powder produced from substituted borazene with silyl amine cross linking groups

3.0 PRODUCTION OF BULK/MONOLITHIC SHAPES OF REFRACTORY CARBIDES AND NITRIDES

The fabrication of refractory carbides and nitrides (and ceramics in general) entails two major steps: *(a)* pressing the powder to the required shape and *(b)* sintering (or firing) it at high temperature.[4][32]

3.1 Powder Pressing

Many techniques are used to consolidate a ceramic powder to the desired shape (green shape). The most commonly used can be summarized as follows.

- Isostatic pressing to 150–300 MPa (i.e., carbide tools)
- Slip casting (mostly for thin-wall hollow parts)
- Tape casting (mostly for flat thin plates)
- Extrusion (for constant cross-section shapes)
- Injection molding (for complicated shapes such as turbine rotor blades)

3.2 Sintering

Sintering is a complex physical and chemical phenomenon and can only be summarized here.[33] It causes the loose powder particles to bond together and usually results in shrinkage, densification, and grain growth. The characteristics of the powder govern to a great degree the physical and chemical properties of the final ceramic product. To optimize these properties, a powder should have the following characteristics:

- Small particle size ($\approx$10 nm)
- Equiaxed particle shape
- Narrow size distribution
- Freedom from agglomeration
- High purity

The various sintering processes presently used with refractory carbides and nitrides are outlined below.[34][35]

Liquid-Phase Sintering. Liquid-phase sintering is an important industrial process used in the production of items such as silicon-carbide glow plugs and aluminum-nitride structural parts. A liquid, able to wet the solid (i.e., molten aluminum), must be present at sintering temperature. The solid must have substantial solubility in the liquid. Further densification may be accomplished by pressure-assisted sintering methods. An example of liquid-phase sintering is the sintering of aluminum nitride using an additive such as CaO, Y_2O_3, CeO_2, or ZrO_2.[2]

Reaction Sintering (Reaction Bonding). In reaction sintering, consolidation occurs by a chemical reaction between the constituents. Large and complex shapes can be fabricated to near-net shape, thus reducing or eliminating the need for machining. A sintering additive is often required to promote the reaction. For instance the addition of Mg_3N_2 and Ca_3N_2 facilitates the sintering of aluminum nitride. Undesirable amorphous grain boundary phases can be almost entirely prevented in silicon nitride ceramics by the use of Be_3N_2 or $BeSiN_2$. These compounds however are toxic.[2][12] Some typical examples of reaction sintering are:

- Beta-SiC from boron and carbon-doped SiC powder
- αSiC and βSiC from aluminum or aluminum compounds and carbon or rare-earth elements[7]
- SI_3N_4 from silicon powder under high nitrogen pressure (see below)
- B_4C from submicron B_4C powder and amorphous carbon powder[10]

Pressure Sintering. Densification of refractory carbides and nitrides can be achieved by external pressure with techniques such as uniaxial hot pressing, hot-isostatic pressing (hipping), and gas-pressure sintering.

In the case of hot-isostatic-pressing (hipping), the part must be encapsulated in a vacuum-tight envelope (usually a foil of a refractory metal such as tungsten, tantalum, or molybdenum, or a high-viscosity glass) if any open porosity is present.[36] Typical hipping processing conditions are shown in Table 14.5.[2][32][34][37]

Table 14.5: Typical Pressure Hipping Sintering Conditions.

Material	Pressure (MPa)	Temperature (°C)
TiN	100–200	1000–1600
TiC/WC	70–100	1500–1760
SiC presintered	138	1850–2100
Si_3N_4/Be_2N_3	2.7–200	1950-2050
Si_3N_4	0.1–2	1730–1950
B_4C presintered	~100	1950–2100

Sintering of Silicon Nitride. Silicon nitride (Si_3N_4) is a major industrial material with great potential. Its processing is typical of refractory carbides and nitrides and it is outlined here in more detail. The strongly bonded covalent structure of the material is such that the self-diffusion of nitrogen is extremely slow. To accelerate the diffusion, gas-pressure sintering at high temperature and high nitrogen pressure is necessary.[2] A common process is to pre-sinter a preform made of silicon powder in nitrogen until all the silicon is converted to silicon nitride. This conversion begins above 1000°C but the temperature must not rise above 1410°C (the melting point of silicon). The reaction is accompanied by a 22% volume decrease and, as a result, the preform is partially densified. The part is then sintered under high nitrogen pressure. This increased partial pressure of nitrogen raises the thermal-decomposition temperature of Si_3N_4 and, consequently, less decomposition gases are produced and the porosity is reduced. Sintering temperature up to 2000°C are possible, thereby reducing the need for sintering aids. A typical cycle is 3 hours at $P_N = 2$ MPa followed by 2 hr. at $P_N = 6$ MPa at 2000°C.[38] A typical flow-sheet of the sintering process in shown in Fig. 14.2.[12][39]

If sintering agents such as oxides (MgO, Y_2O_3, CeO_2, ZrO_2, Al_2O_3) or nitrides (AlN, TiN, ZrN, CrN, Mg_2N_3) are added to the starting powder, it is possible to further densify the material by additional sintering at 1880°C to 2130°C and at pressures up to 2 MPa with reported resulting density >99.3% of theoretical.

With these processes, silicon nitride can be produced to near-net shape, often within ± 1%. If closer dimensional tolerances are required, the material can be diamond ground. If the silicon nitride is alloyed with a small amount of titanium nitride, it acquires sufficient electrical conductivity to allow electrical discharge machining (EDM).

The properties of a material may vary considerably depending on the sintering process. This is illustrated in the case of silicon nitride in Table 14.6.[40] This table shows that both the sintered-reaction-bonded and the hot-pressed materials have excellent properties. The sintered reaction-bonded appears to be the superior process since it is generally cheaper and more versatile than hot-pressing. The microstructure of the sintered-reaction-bonded material is shown in Fig. 14-3.[40] The interlocking needle structure is noticeable and likely to be the reason for the excellent fracture toughness of the material.

Table 14.6: Properties of Silicon Nitride (Si_3N_4)

	Reaction Bonded	Sintered Reaction Bonded	Hot Pressed
Density (% theoretical)	75	>99.3	>98.5
Rupture Modulus (MPa)			
at 25°C	240	800	931
at 1400°C	240	366	498
Weibull Modulus (MPa)			
at 25°C	10	15–20	15–20
Poisson's Ratio	0.22	0.28	0.28
Hardness (R45N)	54	89–91	90–92
Fracture Toughness (MPa$\sqrt{m}$)	2.5	6–7.5	5-6
Thermal Expansion ($\times 10^{-6}$/°C)	3.2	3.5	3.5
Thermal Conductivity (W/mK)			
at 25°C	14	35	35
at 1000°C	11	17	17
Electrical Resistivity (Ω·cm)	$>10^{14}$	$>10^{14}$	$>10^{14}$
Dielectric Constant @ 35 GHz		7.9	8.14
Loss Tangent @ 35 GHz		0.0017	0.0006

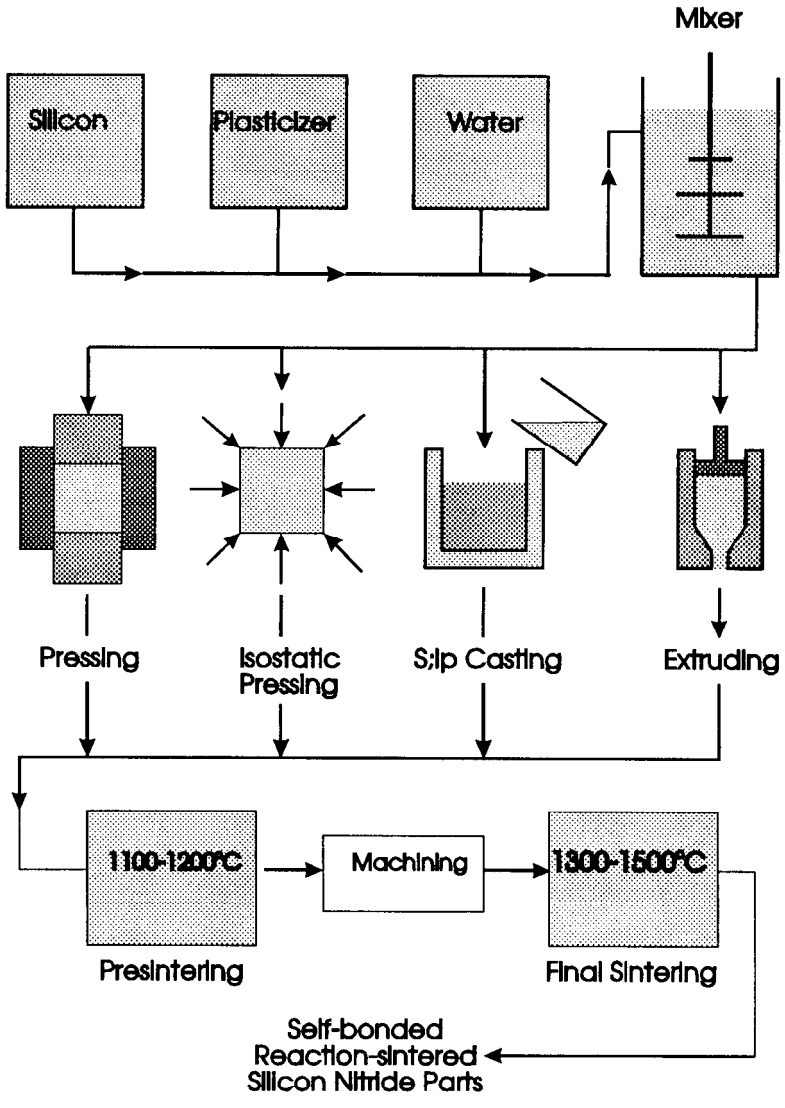


Figure 14.2: Schematic flow–sheet of the production of self–bonded, reaction–sintered silicon nitride [12]

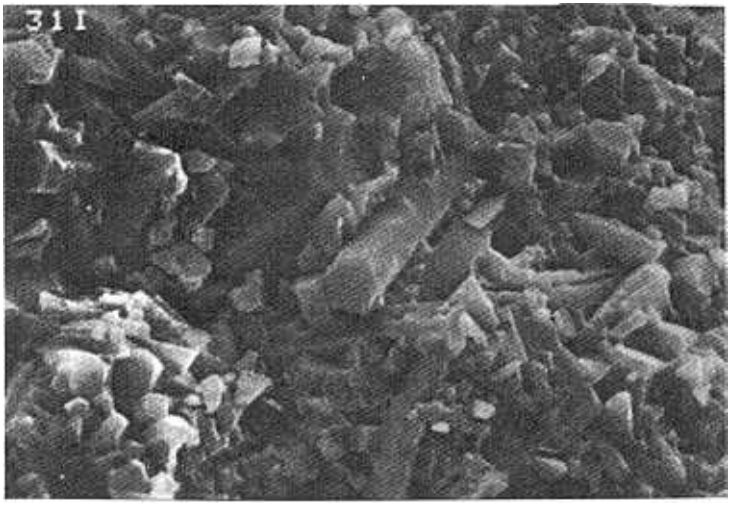


Figure 14.3: Microstructure of sintered reaction–bonded silicon nitride.[40]

4.0 FIBER PRODUCTION

4.1 State of the Art

Until recently, the great majority of ceramic fibers were made from oxides such as alumina or mullite. But in the last few years, much work has been done to develop practical processes for the production of other fiber materials, especially the refractory carbides and nitrides. This work is beginning to bear results especially with silicon-carbide fibers which have now reached full-scale production. Other materials such as silicon nitride, boron nitride, aluminum nitride, titanium carbide, hafnium carbide, and hafnium nitride are at the development stage or in pre-production.[41]

Competing Inorganic Fibers. The competitors to carbide and nitride fibers are glass, ceramic oxides, carbon, and boron. Table 14.7 summarizes their processing, characteristics, and typical applications.[42]

Table 14.7: Characteristics and Applications of Inorganic Fibers

Material	Processing	Main Characteristics	Typical Applications
Glass	Melt blowing and spinning	High strength Low modulus Low temperature Low cost	Insulation Reinforced plastics
Oxides	Melt spinning Sol-gel	Medium strength Good oxidation resistance High cost	Ceramic composites High-temp. insulation Filtration
Boron	CVD	High strength High modulus High cost	Plastic and metal composites
Carbon	Pyrolysis	High strength High modulus Low density Low oxidation resistance Medium cost	Reinforced plastics Carbon-carbon High-temp. insulation
Silicon carbide	CVD Sol-gel	High strength High modulus High cost	High-temp. composites

The tensile properties and densities of typical inorganic fibers are shown in Table 14.8 (data supplied by the manufacturers).

Table 14.8: Tensile Strength, Modulus and Density of Selected Inorganic Fibers

Major Constituent	Tensile Strength (MPa)	Tensile Modulus (GPa)	Density (g/cm^3)
Glass (a)	4580	86	2.5
Alumina (b)	1750	154	2.7
Alumina (c)	2275	224	3.0
Boron (d)	3600	400	2.5
Carbon (e)	5500	330	1.7
Silicon carbide (f)	3920	406	3.0

(a) S-Glass, Corning Glass, Corning NY
(b) Nextel 312, 3M, Minneapolis MN
(c) Nextel 400
(d) Avco Boron
(e) MS-40, Grafil, Sacramento CA
(f) Avco SCS 6, Textron Inc., Lowell MA
(carbon-fiber substrate)

These two tables show that the major competitor to silicon-carbide fiber is carbon as both fibers have similar properties and are in the same cost bracket. Another competitor is boron but it is very expensive and may eventually be replaced by silicon carbide.

Production Processes. Because of the very refractory nature of these materials, the standard production processes of melt blowing and spinning are not practical. In these processes, the precursor material is melted, usually in an arc furnace, drawn through spinnerets and spun in a high-pressure air stream. Instead, the fibers (and whiskers) are produced by sol-gel or by chemical-vapor deposition (CVD).

4.2 Refractory-Carbide and Nitride Fibers by Sol-Gel

The principle of sol-gel processing is summarized in Sec. 2.6. Sol-gel is used on a large scale in the production of alumina-based fibers (*Nextel* by the 3M Co.) and more recently of silicon-carbide and silicon-nitride fibers.

The chemistry is similar to that of powder production. The basic precursor is usually polycarbosilane which is a pale-yellow solid with a melting point of 225°C. A typical process flowchart is shown in Fig. 14.4. The chemical solution is partially thickened by polymerization or by additives and spun directly into fibers. The resulting green fibers are dried and pyrolized.[43][44] These fibers are produced commercially by Nippon Carbon Co. and distributed in the US under the trade name of *Nicalon* by Dow Corning Corp., Midland MI. They are also produced by another Japanese firm, UBE Industries under the tradename of *Tyranno*.

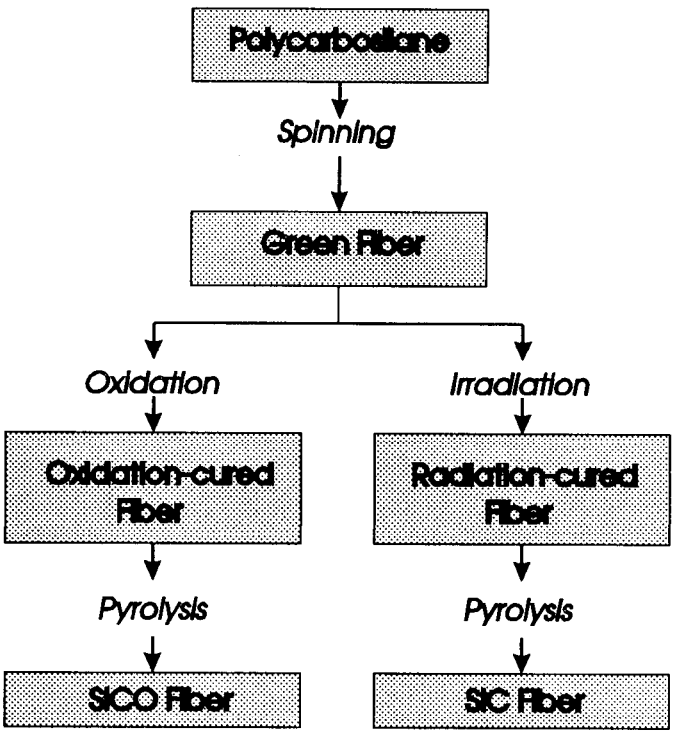


Figure 14.4: Melt–spinning process for the production of Nicalon fibers.[43]

The Nicalon fibers have variable composition which includes a substantial amount of oxygen and free carbon and consist of microcrystalline SiC in Si-C-O glassy matrix together with thin plates of turbostratic carbon. Their properties vary with the composition.[45] They generally have high electrical conductivity.

The precursor for the Tyranno fibers is also polycarbosilane but it is cross-linked with a titanium alkoxide which provides a more thermochemically stable fiber. Final composition is (by weight): 51% Si, 28% C, 18% O, and 3% Ti.[45][46]

Another group of fibers in the development stage is the type HPZ produced by Dow Corning Corporation.[47] These fibers are prepared from a hydridopolysilazane polymer. With an elemental composition of 58% silicon, 28% nitrogen, 10% carbon, and 4% oxygen, they should be regarded as carbonitride. They have high volume resistivity and excellent strength and modulus retention at temperature up to 1400°C in inert atmosphere.

The properties of Nicalon, HPZ, and CVD-SiC fibers (in Sec. 4.3) are summarized in Table 14.9.

Table 14.9: Properties of Monofilament Fibers Derived from the Carbide and Nitride of Silicon

Fiber Type	Diameter (μm)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Density (g/cm^3)
Nicalon	15	2960	193	2.55
Tyranno	8	3000	200	2.40
HPZ	10–12	2410–3100	150–193	2.3–2.5
CVD SiC*	140	3920	406	3.0

* Carbon-fiber substrate

A major advantage of these fibers is good strength retention at high temperature is shown in Fig. 14.5.[47]

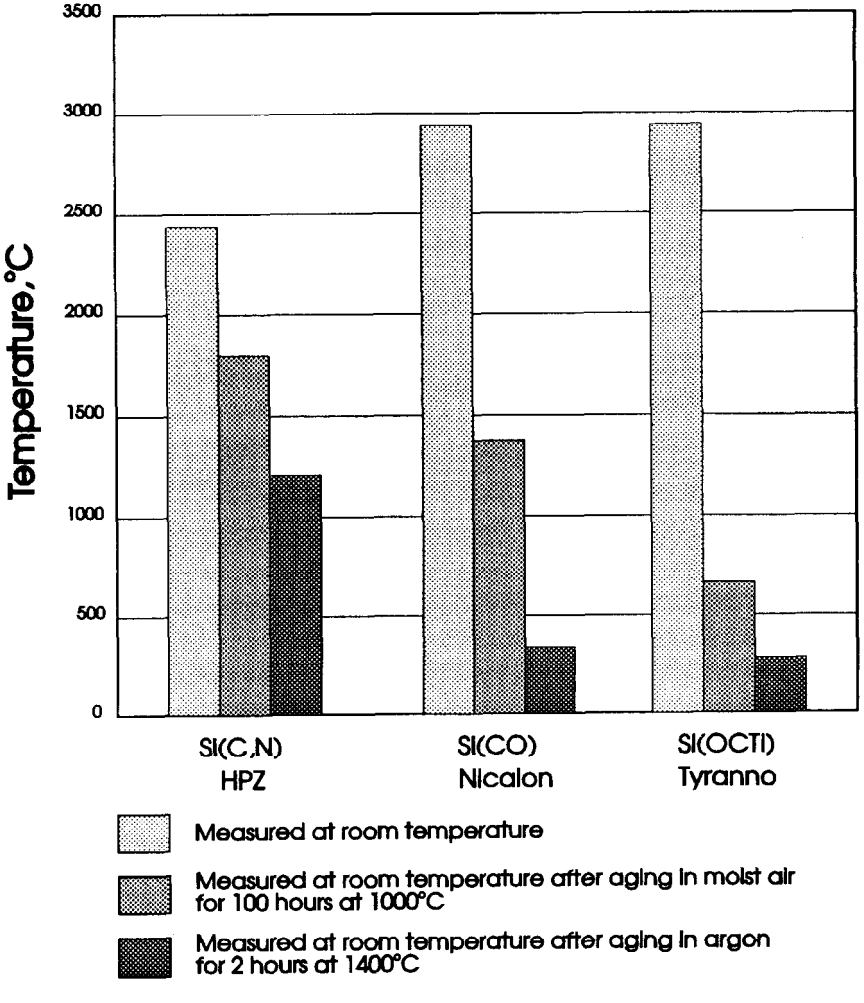


Figure 14.5: Tensile strength of silicon–carbide and silicon–nitride fibers before and after exposure to high temperature.[47]

4.3 Silicon-Carbide Fibers by Chemical-Vapor Deposition (CVD)

A competitor to sol-gel in the production of SiC fibers is chemical vapor deposition (CVD). Each process has its own advantages and drawbacks and, at this stage of development, it is difficult to forecast which one will prevail. The CVD process is reviewed in Ch. 15. Cost reduction in both cases is an important factor.

Processing. The process requires a monofilament carbon-fiber core which is heated resistively in a tubular glass reactor shown schematically in Figure 14.6.[41] The carbon monofilament is pre-coated with a 1 μm layer of pyrolytic graphite to insure a smooth deposition surface and a constant resistivity.[48] SiC is then deposited by the reaction of silane and a hydrocarbon. Other precursors such as $SiCl_4$, CH_3SiCl_3 are also being investigated.[49]

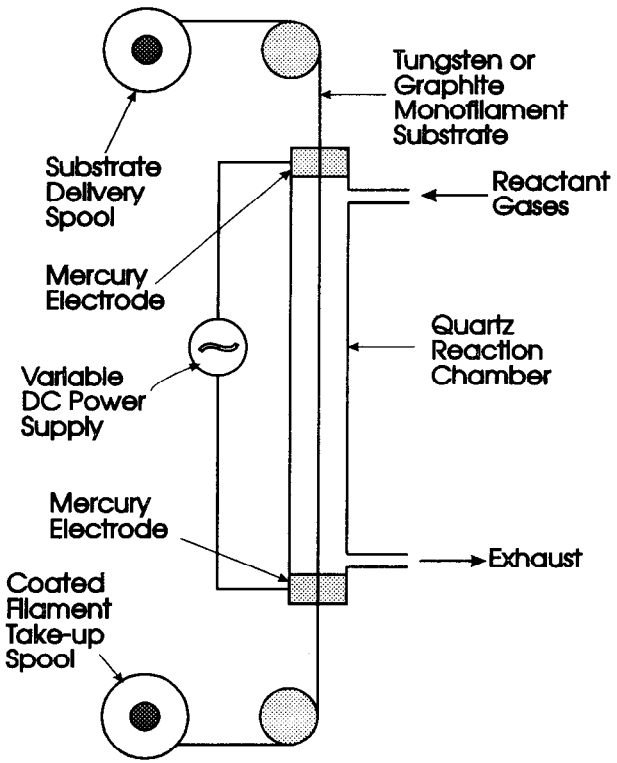


Figure 14.6: Deposition apparatus for the deposition of silicon carbide fibers.[41]

Fiber Diameter. Since a core is required, it is impractical to produce small-diameter fibers (150 μm vs 8–15 μm for sol-gel derived fibers). Being stiff with a high modulus and large diameter, CVD-SiC fibers cannot readily be bent to a small radius or along compound shapes. They are difficult to weave into fabrics. Their use is limited to parts having a simple geometry such as plates, rods or tubes. A fiber cross-section is shown in Fig. 14.7.[50]

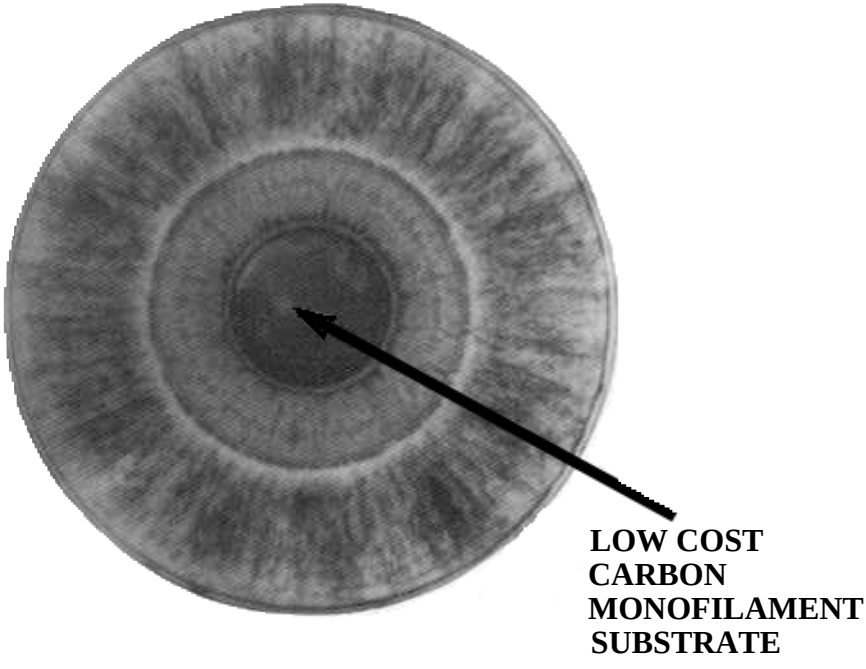


Figure 14.7: Cross section of a CVD silicon–carbide fiber, courtesy of Textron Specialty Materials.[50]

Properties. As shown in Table 14.9, the properties of CVD-SiC fibers are slightly superior to those of Nicalon or Tyranno fibers. The CVD-SiC fibers retain much of their mechanical properties when exposed to high temperature in air up to 800°C for as long as one hour as shown in Figure 14.8.[50]

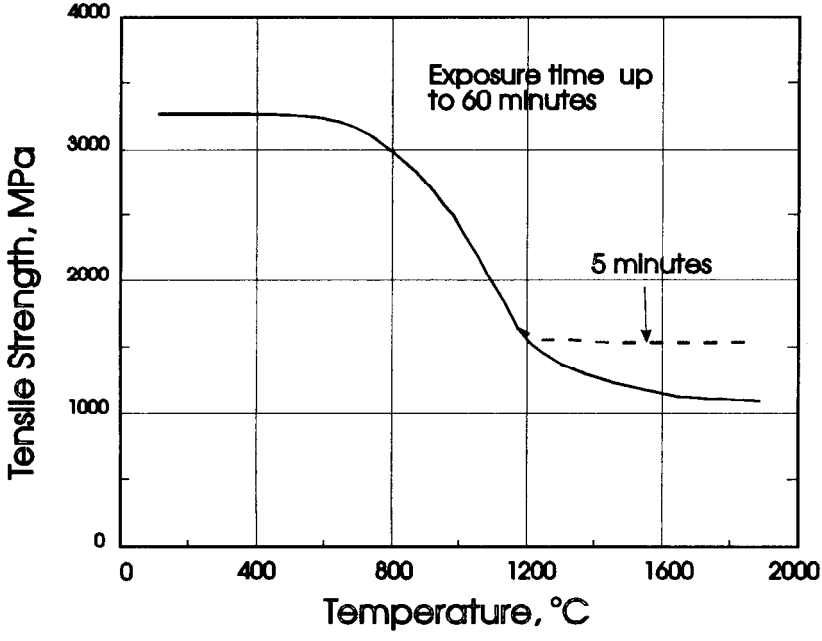


Figure 14.8: Tensile strength of a CVD silicon–carbide fiber as a function of temperature.[48]

4.4 Other Refractory-Fiber Materials

Other materials besides boron and SiC with potential for CVD fiber production are being investigated. They include B_4C, TiC and TiB_2 deposited on a heated core filament, generally by the hydrogen reduction of the chlorides.[49][51] Typical properties of the resulting experimental fibers are shown in Table 14.10. Fiber diameter varies from 20–200 μm.

Table 14.10: Selected Properties of CVD Fibers[49]

	B_4C	TiC
Melting Point (°C)	2450	3180
Deposition Temperature (°C)	1300	1400
Thermal Expansion (10^{-6}/°C)	5.0	7.6
Tensile Strength (GPa)	2.07–2.76	1.38–2.07
Tensile Modulus (GPa)	172–241	172–241

5.0 WHISKER PRODUCTION

Whiskers are short fibers, usually single crystals, with an aspect ratio of 10/1 or greater. They have high strength and are used as a random reinforcement for ceramics or metals, especially SiC whiskers in alumina cutting tools

5.1 Silicon Carbide Whiskers

Silicon-carbide whiskers are produced by a variety of methods including the following:

- By plasma-arc based on the reaction of SiO(g) and CO[52]
- By carbothermal reduction of silica with the addition of a halide as an auxiliary bath, forming β-SiC[53]
- By the vapor-liquid-solid process using an iron catalyst[54]
- By the thermal decomposition of rice hulls, a waste product of rice milling[54]

A typical SiC whisker has a diameter of 0.7–1.2 μm, an aspect ratio of 10–25 and a density of 3.26 g/cm^3. Its surface is smooth and metallic impurities are <1000 ppm.

5.2 Other Whisker Materials

Silicon-carbide whiskers comprise the bulk of all ceramic whiskers. Other whisker materials are produced on an experimental basis and include:

- Titanium carbide whiskers from $TiCl_4$, CH_4 and H_2 in the presence of a nickel catalyst at 1220–1450°C[55]
- Hafnium carbide and hafnium nitride whiskers from $HfCl_4$, CH_4 or N_2, and H_2 in the presence of a nickel catalyst at 1000–1450°C[56]
- Silicon nitride whiskers in both the α-phase (mostly as reinforcement for ceramics) and the β-phase (mostly as reinforcement for metals) produced by Japan's Ube Industries

REFERENCES

1. Parche, M. C., Facts About Silicon Carbide, *The Carborundum Co.*, Niagara Falls, NY (1961)
2. Ettmayer, P., and Lengauer, W., Nitrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed. VCH (1985)
3. Johnson, D. W., Jr., Powder Preparation, Ceramics, in *Advance in Powder Technology*, (G. Y. Chin, ed.), American Society for Metals (1981)
4. Biswas, D. R., Development of Novel Ceramic Processing, *J. Materials Sci.*, 24:3791–98 (1989)
5. Tulhoff, H., Carbides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. Ed., Vol. 15, VCH (1985)
6. Krstic, V., Production of Fine High-Purity Beta Silicon Carbide Powder, *J. Am. Ceram. Soc.*, 75(1):170–174 (1992)
7. Divakar, R., et al., Silicon Carbide, in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)
8. Wentorf, R. H., Jr., Refractory Boron Compounds, in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)

9. Makarenko, G. N., Borides of the IVb Group, in *Boron and Refractory Borides* (V. L. Matkovich, Ed.), Springer-Verlag, Berlin (1977)
10. Schwetz, K. A., and Lipp, A., Boron Carbide, Boron Nitride, and Metal Borides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., Vol. A4, VCH (1985)
11. Ramessh, P. D., et al., Synthesis of β-SiC Powder by the Use of Microwave Radiation, *J. Mater. Res.*, 9(12) (Dec. 1994)
12. Benesovsky, F., Kiefer, R., and Ettmayer, P., Nitrides, in *Kirk-Othmer's Encyclopedia of Industrial Chemistry*, 4th. Ed., John Wiley & Sons (1993)
13. Millberg, L. S., The Synthesis of Ceramic Powders, *J. of Metals*, pp. 9–13, (Aug. 1987)
14. Ault, N. N., Silicon Nitride, *Ceram. Bull.*, 70(6):882 (1981)
15. Hampshire, S., Nitride Ceramics, in *Materials Science and Technology*, Vol. 11 (M. V. Swain, Ed.) VCH, New York (1994)
16. Komeya, K., and Matsui, M., High-Temperature Engineering Ceramics, in *Materials Science and Technology*, Vol. 11 (M. V. Swain, Ed.), VCH, New York (1994)
17. Thompson, R., The Chemistry of Metal Borides and Related Compounds, in *Progress in Boron Chemistry*, (R. J. Brotherton and H. Steinberg, eds.), Pergamon Press (1970)
18. *Ceramic Technology Newsletter*, 37831–6050, Oak Ridge National Lab., Oak Ridge, TN (Apr., Jun. 1990)
19. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
20. Wu, H. D. and Ready, D. W., Silicon Carbide Powders by Gaseous Pyrolysis of, Tetramethylsilane, in *Silicon Carbide 87, Ceramic Transactions*, 2:35–46 (1987)
21. Fantoni, R. et al., Laser Synthesis and Crystallographic Characterization of Ultrafine SiC Powder, *J. Mater Res.*, 5(1) (1990)
22. Schwier, G., On the Preparation of Fine Silicon Nitride Powders, in *Progress in Nitrogen Ceramics*, (F. Riley, ed.), pp. 157–156, Martinus Nijhoff, Boston, MA (1983)
23. Hussain, T., and Ibberson, V., Synthesis of Ultrafine Silicon Nitride in an RF Plasma Reactor, in *Advances in Low-Temperature Plasma Chemistry, Technology, Applications*, 2:71–77, (H. Boenig, Ed.), Technomic, Lancaster (1984)
24. Bauer, R., Smulders, R., Geus, E., van der Put, J. and Schoomman, J., Laser Vapor Phase Synthesis of Submicron Silicon and Silicon Nitride Powders from Halogenated Silanes, *Ceram. Eng. Sci. Proc.*, 9(7–8):949–956 (1988)
25. *Japan Chemical Week*, p. 5, (July 13, 1989)

26. Haussone, J. M., et al., Synthesis Process for AlN, *Am. Ceram. Soc. Bull.*, 72(5) May 1993
27. Hollabaugh, C. M., et al., RF-Plasma System for the Production of Ultrafine Ultrapure Silicon Carbide Powder, *Am. Ceram. Soc. Bull.*, 61:814 (1982)
28. Munir, Z. A., Synthesis of High-temperature Materials by Self-Propagating Combustion Methods, *Ceram. Bull.*, 67(2):342–349 (1988)
29. Brinker, C. J., and Scherer, G. W., *Sol-Gel Science*, Academic Press, San Diego, CA (1990)
30. Lee, B. I., and Hench L. L., Molecular Composites of SiC/SiO_2, SiC/Al_2O_3 and SiC/TiC, *Ceramic Bulletin*, 66(10) (1987)
31. White, D. A., et al., Preparation of Silicon Carbide from Organosilicon Gels, *Advanced Ceramic Materials*, 2(1) (1987)
32. Srinivasan, M., The Silicon Carbide Family of Structural Ceramics, in *Structural Ceramics,* (J. B. Wachtman, Jr., Ed.) Vol. 29, Academic Press (1989)
33. Coblenz, W. S., and German, R. M., in *Engineered Materials Handbook*, ASM International, 4:242, 260 (1991)
34. Spriggs, R. M., Ceramic Sintering, Proceedings of the Workshop on Microwave-Absorbing Materials for Accelerators, *CEBAF*, Newport News, Va (1993)
35. Haggerty, J. S., in *Engineered Materials Handbook*, ASM International, 4:291 (1991)
36. Gazza, G. E., in *Engineered Materials Handbook*, ASM International, 4:296 (1991)
37. Schwetz, K. A., Grellner, W., and Lipp, A., Mechanical Properties of HIP-treated Sintered Boron Carbide, *Inst. Phys. Conf. Series* No. 75, Ch. 5, Adam Hilger Ltd. Bristol, UK (1984)
38. Lewis, C. F., *Silicon Nitride, the Rock-Solid Performer*, ME 30–33 (May 1989)
39. Tiegs, T. N., et al., Effects of Processing Parameters on Densification and Mechanical Properties of Gas-Pressure Sintered Silicon Nitride, in *Ceramic Engineering and Science Proc.,* Am. Ceram. Soc. Publishers, pp. 677-685 (1994)
40. Silicon Nitride, *Technical Brochure, Ceradyne Inc.*, Costa Mesa, CA (1994)
41. Buck, M. E., Advanced Fibers for Advanced Composites, *Advanced Materials and Processes*, pp. 61–65 (Sept. 1987)
42. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes,* Noyes Publications, Park Ridge, NJ (1992)

43. Peterson, A. L., and Rabe, J. A., *Silicon Carbides Ceramic Fibers Offer Tailored Electrical Properties at High Temperatures*, Technical Report, Dow Corning Corp., Midland, MI (1992)

44. Mah, T., Mendiratta, M., Katz, A. and Mazodiyasni, K., Recent Developments in Fiber-Reinforced High Temperature Ceramic Composites, *Ceramic Bull.*, 66(2):304–317 (1987)

45. Bender, B. A., and Jensen, T. L., A comparison of the Interphase Development and Mechanical Properties of Nicalon and Tyranno SiC Fiber-Reinforced $ZrTiO_4$ Matrix Composites, *J. Mater. Res.*, 9(10):2670–2676 (Oct. 1994)

46. Yamamura, T. et al., Development of a New Continuous Si-Ti-C-O Fibre Using an Organometallic Polymer Precursor, *J. Mater. Sci.*, 23:2589–2594 (1988)

47. Jones, R. E., Rabe, J. A., and Peterson, A. L., *New Ceramic Fiber Maintains Physical Properties at High Temperatures*, Technical Report, Dow Corning Corp., Midland, MI (1992)

48. Sheppard, L. M., Progress in Composites Processing, *Ceramic Bulletin*, 69(4):666–673 (1990)

49. Gatica, J. E., and Hlavacek, V., Laboratory for Ceramic and Reaction Engineering: A Cross-Disciplinary Approach, *Ceramic Bulletin*, 69(8):1311–1318 (1990)

50. AVCO Silicon-Carbide Fiber, Technical Brochure, *Textron*, Lowell, MA, 01851 (1990)

51. Revankar, V., Scholtz, J., and Hlavacek, V., Synthesis of High-Performance Ceramic Fibers by CVD, in *Ceram. Eng. Sci. Proc.*, 9(7–8):919–930 (1988)

52 Pickles, C. A., and Toguri, J. M., The Plasma-Arc Production of Si-based Ceramic Whiskers, *J. Mater. Res.*, 8(8) (Aug. 1993)

53. Wang, L., Wada, H., and Allard, L. F., Synthesis and Characterization of SiC Whiskers, *J. Mater. Res.*, 7(1) (Jan. 1992)

54. Urretaviscaya, G., and Porto López, J. M., Growth of SiC whiskers by VLS Process, *J. Mater. Res.*, 9(11):2981–2986 (Nov. 1994)

55. Wokulski , Z., and Wokulska, K., On the Growth and Morphology of TiC_x Whiskers, *J. Cryst. Growth*, 62(2):439–446 (July 1983)

56. Futamoto, M., Yuito, I. and Kawabe, U., Hafnium Carbide and Nitride Whisker Growth by Chemical Vapor Deposition, *J. Cryst. Growth*, 61(1):69–74 (Jan., Feb. 1983)

15

Processing of Refractory Carbides and Nitrides (Coatings)

1.0 COATING PROCESSES

In the previous chapter, the processing of refractory carbides and nitrides in the form of powders, bulk/monolithic shapes, fibers, and whiskers was reviewed. These materials have one other major form, i.e., coatings, and the review of coating processes is the objective of this chapter.

Coatings of refractory carbides and nitrides have great industrial importance with a wide range of applications in semiconductors and other electronic components, in cutting tools, gas-turbine vanes and blades, precision bearings, punch sets, extruders, prostheses, and many other products.

1.1 Composite Nature of Coatings

The surface of a material may be exposed to wear, corrosion, radiation, electrical or magnetic fields and other phenomena and must have the ability to withstand these environments. In addition, the surface may be required to provide certain desirable properties such as reflectivity or high thermal conductivity. This can be accomplished by coating the base material to obtain a composite in which the surface properties may be considerably different from those of the substrate.[1]

An example of such composite material is a cutting tool such as a twist drill coated with titanium nitride. The drill must be made of a tough and strong material such as high-speed tool steel which is able to withstand the stresses associated with drilling, yet its surface must be very hard and chemically resistant to withstand wear, abrasion, and corrosion. However hardness and toughness are inverse properties and no single material can have both to any appreciable degree. A solution is to coat the drill with titanium nitride which protects the steel substrate from high-temperature oxidation and reaction with the material to be cut and provides the necessary hardness, wear resistance, and low coefficient of friction which reduces the required cutting forces.

Table 15.1 summarizes the surface properties that can be obtained or modified by the use of refractory carbide and nitride coatings.

Table 15.1: Properties Affected by Refractory Carbide and Nitride Coatings

Electrical	Resistivity
Optical	Refraction and reflectivity Emissivity
Mechanical	Wear and friction Toughness and ductility Strength and hardness Adhesion
Chemical	Diffusion Oxidation and corrosion Electrochemical reactivity

1.2 Major Coating Processes

The major coating processes for refractory carbides and nitrides are listed in Table 15.2.[2]–[4]

Table 15.2: Major Coating Processes for Refractory Carbides and Nitrides

Chemical-Vapor Deposition (CVD)	Thermal CVD
	Plasma CVD
	MOCVD
	Photo and Laser CVD
Physical-Vapor Deposition (PVD)	Sputtering
	Evaporation
	Ion plating
Thermal Spray	Plasma spray
	D-gun spray
	Flame spray

CVD and PVD belong to the class of vapor-transfer processes which are atomistic in nature, that is the deposition species are atoms or molecules or a combination of these. The coatings are also commonly known as *thin-films* when their thickness is less than 10 μm. This is an arbitrary limitation and perhaps a better definition would be a coating that adds essentially nothing to the mass of the substrate. CVD and PVD coatings of TiC, TiN, Si_3N_4, and Al_2O_3, have major industrial applications (see Ch. 16).

Thermal-spray coatings consist mostly of WC, Cr_2C_3, and to a lesser degree TiC and AlN. They are relatively inexpensive and widely used in corrosion and wear applications particularly in the gas-turbine industry.

These processes, CVD, PVD, and thermal spray have reached the stage of large industrial production with a constant R&D effort, particularly in the development of new source materials with greater purity, the refinement of processing parameters, and the improvement of the equipment. In the next sections, the processes are reviewed as they pertained to the refractory carbides and nitrides. This review can only touch on the major aspects of these extended and complex technologies and the references should be consulted for further information.

2.0 GENERAL CHARACTERISTICS OF CHEMICAL VAPOR DEPOSITION (CVD)

2.1 The CVD Process

CVD is a versatile process, well adapted to the production of all the refractory carbides and nitrides not only as coatings but also as powders, bulk/monolithic components, and fibers.[2][3] It may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. Its advantages are:

- It is not restricted to a line-of-sight deposition. Deep recesses, holes and other difficult three-dimensional configurations can be coated readily
- The deposition rate is high and thick coatings are possible (in some cases centimeters thick)
- The CVD equipment is relatively simple, does not require ultrahigh vacuum and generally can be adapted to many process variations. Changes in composition during deposition and codeposition of two or more materials are possible

The drawbacks of CVD are:

- It is most efficient at temperatures > 600°C and generally not recommended for the coating of substrates with low melting point (i.e., plastics)
- It requires chemical precursors (the starter materials) with high vapor pressure which are often hazardous and toxic. The by-products can also be toxic and corrosive and must be neutralized, which may be a costly operation

2.2 General Characteristics

Thermodynamic and Kinetic Considerations. As with all chemical reactions, the constraints of thermodynamics and kinetics apply to chemical vapor deposition, i.e., the reaction must have a negative heat of formation ($-\Delta G^o$). An analysis of these constraints is necessary before any CVD reaction is considered.

Contamination. A general problem in the CVD of refractory carbides and nitrides is oxygen contamination during deposition. These materials can dissolve considerable quantities of oxygen by lattice substitution for carbon or nitrogen.[5] To avoid this, it is essential to maintain a deposition system that is free of oxygen. Likewise, hydrogen can dissolve readily in the lattice defects and, since many CVD reactions are carried out in hydrogen, this may easily occur. It may be necessary to vacuum anneal the coating to remove the hydrogen. Finally, composition uniformity is not easily obtained and careful control of coating stoichiometry is necessary.

Thermal Expansion Matching. The coefficients of thermal expansion (CTE) of coating and substrate should match as closely as possible. The CTE of the coating is usually lower than that of a metallic substrate and, upon cooling from the deposition temperature, thermal stresses are produced which may cause cracks and delamination. Such considerations have led to the development of low-temperature deposition processes such plasma-CVD or metallo-organic CVD (MOCVD) which minimizes these stresses and reduces the chance of coating failure (see Sec. 3.1).[2]

Low Deposition Pressure. In any CVD reaction, when the partial pressure of the reactants and carrier gases is low, the boundary layer becomes thinner and, as a result, the diffusion of the reactants through this layer is increased.[2] The mass transfer variables become less critical and a more uniform coating is obtained. This is an important factor especially if many components are to be coated in one operation. Such low pressure CVD is the most common CVD process for the deposition of refractory carbides and nitrides.

3.0 THE CVD OF REFRACTORY CARBIDES

3.1 Titanium Carbide

Titanium carbide is one of the most important coating materials and its deposition reactions are similar to those of other interstitial carbides.[6] A

common deposition system is the reaction of the metal chloride with a hydrocarbon such as methane as follows:

Reaction (1) $TiCl_4(g) + CH_{4(g)} \rightarrow TiC(s) + 4HCl(g)$

This reaction is usually carried out in the temperature range of 850–1050°C in a hydrogen atmosphere with pressure varying from less than 100 Pa to 1 atm. A common pressure is 4 kPa.[7]

Equipment. A typical CVD apparatus for the coating of cutting tools with TiC, TiN, or Ti(CN) is shown schematically in Fig. 15.1. Resistance heating maintains a uniform temperature throughout the furnace. The parts to be coated are loaded on trays or racks; a vacuum is applied and the temperature is raised to the desired level; the reaction gases are then introduced. The coating materials can be deposited alternatively when graded-composition coatings are required, under precise, computer-controlled conditions. Such CVD reactors can be large and the coating of thousands of parts in one operation is common.

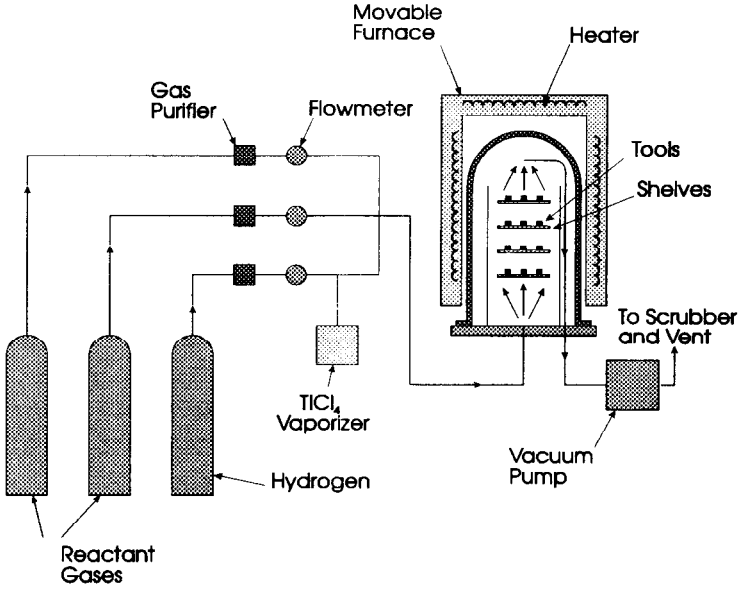


Figure 15.1: CVD apparatus for the coating of cutting tools.[6]

To deposit TiC, titanium tetrachloride (which is a liquid at room temperature) is vaporized and transported by flowing hydrogen into the reaction vessel where it reacts with a gaseous carbon source such as methane (CH_4), toluene ($C_6H_5CH_3$), or propane (C_3H_8).[8]

The high-temperature requirement places restrictions on the type of substrate that can be used. For instance some steels will lose their mechanical properties at these temperature and will require a heat treatment after coating. They may also change dimensions sufficiently to require post-deposition machining.

Metallo-Organic CVD (MOCVD)[9] It is possible to lower the deposition temperature of titanium carbide (i.e., 700°C) by using metallo-organic precursors such as:

- Tris-(2.2'-bipyridine) titanium (decomposes at 370–520°C)
- Tetraneopentyl titanium (decomposes at 150–300°C)
- Dichlorotitanocene, $(C_5H_5)_2TiCl_2$ (substrate temperature is 700°C)

Plasma CVD. In plasma CVD, the chemical reaction takes place in a plasma produced by a high-frequency electric field. The gases are ionized, causing the atoms to lose or gain one or more electrons. The reaction of these ionized gases requires much less energy, and reaction temperatures consequently are lower than those for standard CVD, usually by 300–350°C. TiC has been deposited successfully by plasma CVD in the temperature range of 500°C to 900°C and a pressure of 100 Pa.[10][11] This broadens the range of suitable substrates and the number of potential applications. The schematic of a typical plasma CVD reactor for the deposition of TiN on silicon wafers is shown in Fig. 15.2.

Substrates. Suitable substrates for TiC deposition are the cemented carbides, such as tungsten carbide (WC) bonded with cobalt (Co), which are widely used as cutting-tool materials (see Ch. 16). Other substrates coated by TiC are molybdenum and graphite.[6] In the case of molydenum, it is essential to maintain the deposition temperature below 950°C, otherwise recrystallization of the metal and reduction in mechanical strength will occur.

Deposition of Titanium Carbonitride. Titanium carbonitride (TiC_xN_{1-x}) combines the wear properties of TiC with the low friction and oxidation and chemical resistance of TiN. It can be obtained by the following simplified reaction:

Reaction (2) $TiCl_4 + xCH_4 + \frac{1}{2}(1\text{-}x)N_2 + 2(1\text{-}x)H_2 \rightarrow TiC_xN_{1\text{-}x} + 4HCl$

This reaction is carried out in a hydrogen atmosphere and at a temperature of approximately 1000°C.

If acetonitrile (CH_3CN) is used as a carbon and nitrogen source, the deposition temperature is greatly reduced and the process can be used to coat tool steel.[12][13] The reaction is carried out at low pressure and in a temperature range of 700–900°C. A simplified reaction is described as follows:

Reaction (3) $TiCl_4 + CH_3CN + 2.5H_2 \rightarrow TiCN + CH_4 + 4HCl$

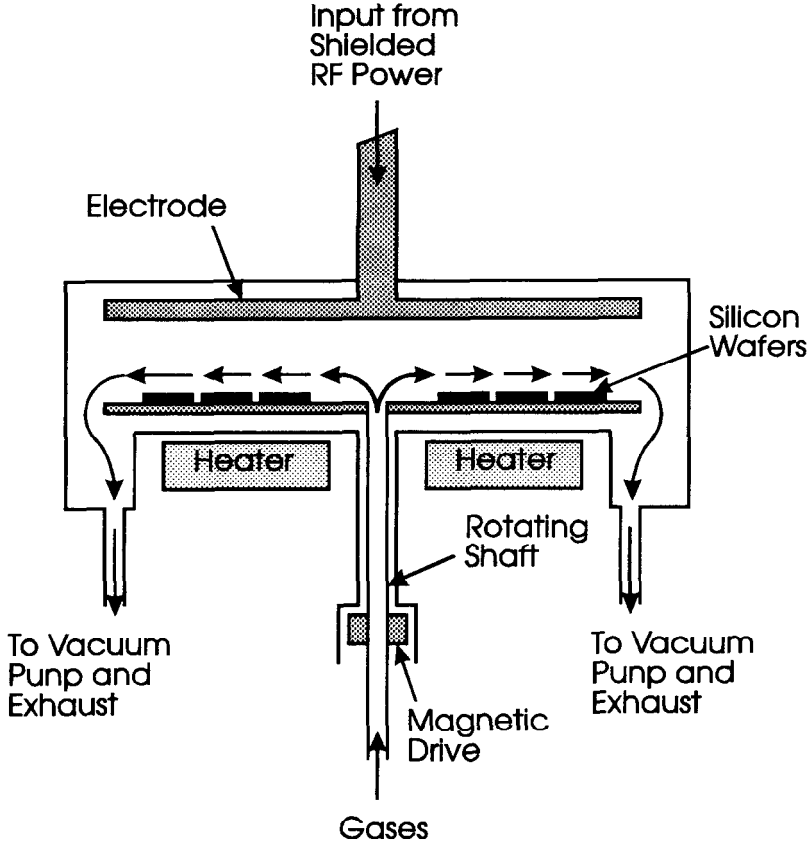


Figure 15.2: RF–plasma CVD reactor for the deposition of TiN on semiconductor devices.

3.2 The CVD of Other Interstitial-Metal Carbides

The CVD of other refractory metal carbides is essentially similar to that of TiC. The metal halide is reacted with a hydrocarbon, usually methane, although propane, propene and toluene have been used also. Pressure varies from 1 kPa to 1 atm. (composition closest to stoichiometry are usually obtained at the lower pressures).

Metal Chlorination. With the exception of titanium and vanadium chlorides ($TiCl_4$ and VCl_4), the chlorides of the refractory metals are solids at room temperature and it is often expedient to chlorinate the metal in situ with chlorine or HCl as shown schematically in Fig. 15.3. A typical reaction is the formation of hafnium chloride as follows:

Reaction (4) $\quad Hf + 2Cl_2 \rightarrow HfCl_4$

The reaction occurs between 500°C and 600°C and is exothermic. It is only necessary to heat the metal (in the form of sponge or chips) to the starting temperature, after which it becomes self-sustaining.

Deposition Reactions. The most common deposition reactions are similar to reaction 1:

- Zirconium carbide from the reaction of $ZrBr_4$ with methane at 1350–1550°C in an atmosphere of hydrogen and argon[14] or from the reaction of $ZrCl_4$ with methane or cyclopropane as the carbon source[15]
- Hafnium carbide from the reaction of $HfCl_4$ with a hydrocarbon which can be propane (C_3H_8), propene (C_3H_6), toluene (C_7H_8) or methane (CH_4) at 900–1500°C)[16]–[18]
- Hafnium carbide from the reaction of methyl chloride (CH_3Cl) with $HfCl_4$ in hydrogen at 1200°C and 1–3 kPa
- Niobium carbide from the reaction of carbon tetrachloride (CCl_4) with $NbCl_5$ at 1500–1900°C[19]
- Tantalum carbide from the reaction of methyl chloride (CH_3Cl) with $TaCl_4$ in hydrogen at 1150–1200°C and 1–3 kPa
- Chromium carbide from the reaction of $CrCl_2$ with butane at 1000°C[20] or from the decomposition of chromium dicumene $Cr[(C_6H_5)C_3H_7]_2$ at 300–550°C and at low pressure[21]

- Molybdenum carbide (Mo_2C) by the decomposition of molybdenum carbonyl ($Mo(CO)_6$)[22]
- Tungsten carbide from the reaction of WCl_6 with methane in hydrogen at 670–720°C and low pressure or from the reaction of WF_6 with methanol (CH_3OH) in hydrogen[23][24]
- Tungsten carbide from the decomposition of tungsten carbonyl ($W(CO)_6$ at 350–400°C although carbon tends to remain incorporated in the structure

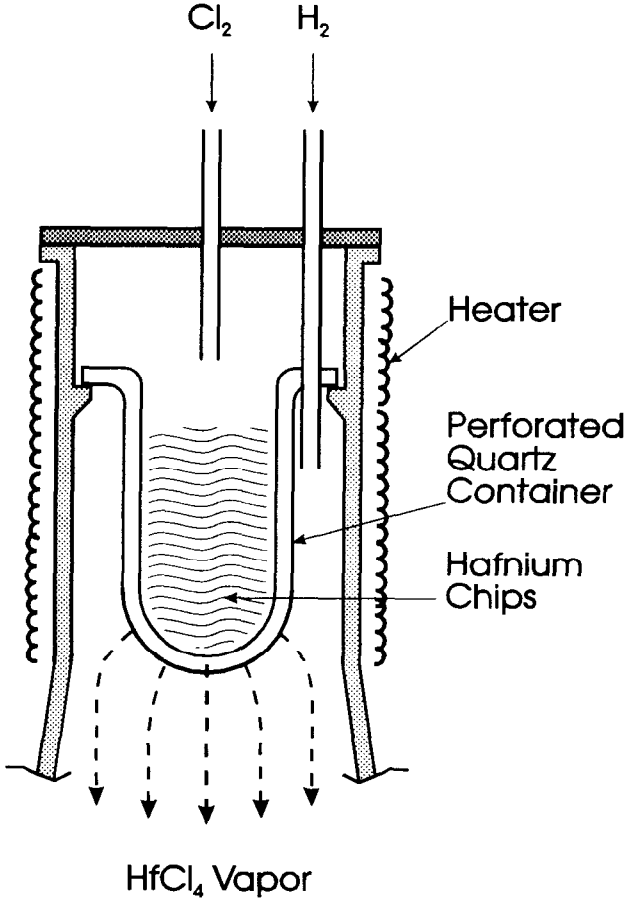


Figure 15.3: In-situ chlorinator for the generation of hafnium chloride.

3.3 The CVD of Silicon Carbide

Silicon carbide (SiC) is a major industrial material with many applications. CVD plays a major role in its development and production.

A common CVD reaction is the decomposition of methyl trichlorosilane (MTS) at 900–1400°C (optimum 1100°C) and 1–6 kPa in a hydrogen atmosphere:[25]–[27]

Reaction (5) $CH_3SiCl_3 \rightarrow SiC + 3HCl$

The deposition rate and the crystallite size increase with increasing partial pressure of MTS.

Another common deposition system is the reaction of silane with a hydrocarbon such as propane or benzene at ≈800°C and ≈1 kPa in the following simplified forms:[25][28][29]

Reaction (6) $3SiH_4 + C_3H_8 \rightarrow SiC + 10H_2$

Reaction (7) $6SiH_4 + C_6H_6 \rightarrow 6SiC + 15H_2$

Plasma CVD has been used with reactions 6 and 7 to deposit SiC at considerably lower temperatures (200–500°C).[30]

The decomposition of methyl silane (CH_3SiH_3) produces an amorphous SiC at 800°C and a crystalline SiC at 900°C.[31] Other possible CVD systems are: $SiCl_4/CH_4$, $SiCl_4/CCl_4$, SiH_2Cl_2/C_3H_8, and $SiHCl_3/C_3H_8$.[32]

3.4 The CVD of Boron Carbide

The following CVD reactions are used to deposit boron carbide.[33]–[36] All three reactions use excess hydrogen. The most common reactions are:[8]

Reaction (8) $4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl$
(temperature range 1200–1400°C, pressure 1–3 kPa)

Reaction (9) $4BCl_3 + CH_3Cl + 5H_2 \rightarrow B_4C + 13HCl$
(temperature range: 1150–1250°C, pressure: 1–3 kPa)

Reaction (10) $4BCl_3 + CCl_4 + 8H_2 \rightarrow B_4C + 16HCl$
(temperature range: 1050–1650°C, pressure: to 1 atm.)

Boron carbide has also been deposited from diborane as a boron source in a plasma at 400°C as follows:

Reaction (11) $2B_2H_6 + CH_4 \rightarrow B_4C + 8H_2$

4.0 THE CVD OF REFRACTORY NITRIDES

4.1 The CVD of Titanium Nitride

All refractory nitrides can be produced as coatings by CVD and, for most of them, CVD remains a major production process. CVD titanium nitride (TiN) is the most important nitride coating from an application standpoint. It is used extensively mainly for wear- and erosion-resistant applications and as a diffusion barrier and antireflection coating in semiconductor devices.[37]

Titanium nitride coatings are produced by reactive sputtering (see Sec. 7.0) and by CVD with titanium tetrachloride as the metal source and either nitrogen gas or ammonia as a source of nitrogen, as follows:

Reaction (1) $TiCl_4 + \frac{1}{2}N_2 + 2H_2 \rightarrow TiN + 4HCl$

Reaction (2) $TiCl_4 + NH_3 + 0.5H_2 \rightarrow TiN + 4HCl$

The range of temperature for reaction 1 is 900–1200°C with best results obtained at 1000°C. An argon diluent is used at pressures up to 1 atm.[38][39] Reaction 2 takes place at lower temperature (480–700°C) and is usually carried out at low pressure (≈1 kPa) with excess hydrogen.[40] The ammonia reaction generally has a higher deposition rate, owing to the high reactivity of the monatomic nitrogen released in the ammonia decomposition.

Reaction 1 is also obtained in a high frequency plasma (13.56 MHz) at 150 Pa pressure and at a low deposition temperature of 500°C.[41]–[43]

The availability of two metallo-organic titanium compounds, tetrakis-diethylamino titanium (TDEAT) and tetrakis-dimethylamino titanium (TDMAT) makes possible the deposition of TiN at lower temperature[37][44] with the following reactions (both at 320°C):

Reaction (3) $Ti[N(CH_2CH_3)_2]_4 + NH_3 \rightarrow TiN + \text{gaseous organics}$

Reaction (4) $Ti[N(CH_3)_2]_4 + NH_3 \rightarrow TiN + \text{gaseous organics}$

These low-temperature reactions are being developed for semiconductor applications to replace sputtering. In reaction 4, the level of impurities (C and O_2) remains high and reaction 3 is preferred.

4.2 The CVD of Other Interstitial Nitrides

The CVD of refractory interstitial nitrides other than TiN remains mostly on an experimental basis. The principal reaction is that of the metal chloride with nitrogen (or ammonia) in excess hydrogen at low pressure (≈1 kPa) (see Sec. 3.2 for a discussion on the metal halides). A typical reaction is:

Reaction (5) $2HfCl_4 + N_2 + 4H_2 \rightarrow 2HfN + 8HCl$

Other reactions are:

- Zirconium nitride (ZrN) from the reaction of $ZrCl_4$ with nitrogen in hydrogen at 1150–1200°C[45]
- Hafnium nitride (HfN) from the reaction of $HfCl_4$ with nitrogen and hydrogen at 900–1300°C[46] or with ammonia as nitrogen source at 1100°C
- Niobium nitride (NbN) from the reaction of $NbCl_4$ with nitrogen or ammonia in excess hydrogen at 1000–1100°C[47][48]
- Tantalum nitride (TaN) from the metal chloride reaction with nitrogen at 800–1500°C[45]

4.3 The CVD of Aluminum Nitride

Aluminum nitride (AlN) is deposited by CVD both experimentally and on a production basis. Coatings of aluminum nitride (AlN) are produced at high-temperature by the reaction of ammonia with either the chloride or the bromide as metal sources in a hydrogen atmosphere at low pressure (≈100 Pa):[49][50]

Reaction (1) $AlCl_3 + NH_3 \rightarrow AlN + 3HCl$ (1000–1100°C)

Reaction (2) $AlBr_3 + NH_3 \rightarrow AlN + 3HBr$ (900°C)

Reaction 2 is also used with a plasma at a deposition temperature of 200–800°C.[30]

AlN can be produced by MOCVD by reacting ammonia with trimethyl aluminum at low pressure (<130 Pa) at 900–1400°C:[51]

Reaction (3) $(CH_3)_3Al + NH_3 \rightarrow AlN + 3CH_4$

The pyrolysis of aluminum-nitrogen organic complexes such as diethyl aluminum azide $[(C_2H_5)_2AlN_3]$ is also used successfully at low deposition temperatures (450–870°C).[52] Another metallo-organic, hexakis(dimethylamido)dialuminum, reacting with ammonia allows deposition at 200–250°C at atmospheric pressure.[53]

4.4 The CVD of Silicon Nitride

Silicon nitride (Si_3N_4) is a major industrial material which is produced extensively by CVD for electronic and structural applications. It is an excellent electrical insulator and diffusion barrier (to sodium and water vapor) and has replaced CVD oxides in many semiconductor devices.[54]

Silicon nitride coatings are produced by the reaction of silicon tetrachloride ($SiCl_4$) with ammonia:

Reaction (1) $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$

The optimum deposition temperature is 850°C. Pressure may be up to 1 atm.. A hydrogen or nitrogen atmosphere is used with a high ratio of N_2 to reactants.[45][55]–[57]

Another reaction uses dichlorosilane (SiH_2Cl_2), also with ammonia:

Reaction (2) $3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$

The range of deposition temperature is 755–810°C with a high dilution of nitrogen.[58] When a high-frequency plasma (13.56 MHz) is used, the deposition temperature is lower (400–600°C).[59]

Another common deposition reaction combines ammonia with silane as the silicon source:

Reaction (3) $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$

Deposition temperature ranges from 700–1150°C and pressure up to 1 atm. Excess ammonia is used since it decomposes more slowly than silane. The ammonia-to-silane ratio should be greater than 10:1 over stoichiometric.[45] Plasma activation of this reaction considerably lowers the deposition temperature (≈300°C) and is used widely in semiconductor processing.[60]

The use of ammonia as a source of nitrogen has a tendency to deposit silicon nitride with a high ratio of included hydrogen, especially at the lower temperatures and if a plasma is used. This tendency is often detrimental but it can be remedied, at least to some degree, by using nitrogen instead of ammonia:

Reaction (4) $3SiH_4 + 2N_2 \rightarrow Si_3N_4 + 6H_2$

However, the nitrogen molecule has a far greater bonding energy than ammonia and is more difficult to dissociate into free atomic nitrogen active species. Consequently, the deposition rate is extremely slow. This can be offset by plasma activation at high frequency (13.56 MHz), by electron-cyclotron resonance (ECR), and with microwave activation.[61]–[64]

A CVD-plasma reactor is shown schematically in Fig. 15.2 and several variations are used on a large scale for the deposition of silicon nitride for semiconductor devices. The reactor generally operates at 450 kHz or 113.56 MHz. Typical deposition conditions are 360°C and 260 Pa.[65]

Deposition at low temperature (200–400°C) is possible by plasma-CVD from the reaction of ammonia and a metallo-organic precursor: tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$. The films are essentially featureless.[66]

4.5. The CVD of Boron Nitride

Boron nitride is usually deposited by the reaction of boron trichloride or boron trifluoride with ammonia:[67]

Reaction (1) $BCl_3 + NH_3 \rightarrow BN + 3HCl$

Reaction (2) $BF_3 + NH_3 \rightarrow BN + 3HF$

At a deposition temperature of 1300°C, a low-density boron nitride is obtained (1.5 g/cm^3) (theoretical density is 2.28 g/cm^3). Density increases with increasing temperature and reaches 2.0 g/cm^3 at 1600°C. Vapor phase precipitation can be a problem in the high-temperature range.

Reaction 2 is used in an electron cyclotron (ECR) plasma to produce c-BN at 675°C on an experimental basis.[68] Cubic boron nitride has a structure similar to diamond with extreme hardness and chemical resistance and is normally obtained by high-pressure processing.

Low-temperature deposition is possible from diborane as a boron source:[69]

Reaction (3) $B_2H_6 + 2NH_3 \rightarrow 2BN + 6H2$
(300-400°C, < 1 Torr)

Another useful deposition reaction is the decomposition of borazine. This is a condensation reaction which produces an amorphous BN with residual hydrogen incorporation:[70]

Reaction (4) $B_3H_3N_3 \rightarrow 3BN + 1.5H_2$
(700°C, < 1 Torr)

MOCVD has also been used with triethyl boron as the boron source in a hydrogen and argon atmosphere:[71]

Reaction (5) $B(C_2H_5)_3 + NH_3 \rightarrow BN +$ hydrocarbons
(750-1200°C)

5.0 PHYSICAL VAPOR DEPOSITION (PVD)

Like CVD, PVD is a vapor deposition process. The distinction between these processes is that in CVD deposition occurs by chemical reaction, whereas in PVD deposition is by condensation.

An important recent trend is the tendency for the two processes to merge. For instance, CVD now makes extensive use of plasma (a physical phenomenon) and conversely, during the PVD processes of reactive evaporation and reactive sputtering, a chemical reaction takes place. Semiconductor processing equipment now often combine CVD and PVD reactors in

one single piece of equipment and the difference between the two processes becomes blurred. The major PVD processes for the deposition of refractory carbides and nitrides are evaporation, sputtering, and ion plating.

6.0 EVAPORATION

6.1 Principle of Evaporation

The principle of evaporation is relatively simple.[3][72] The coating material (known as the source) is heated at low pressure ($<10^{-3}$ Pa) above its boiling point, sending atoms or molecules, through a cosine distribution of trajectories, in a straight line to the substrate, where these condense to form a thin film. At such low pressure, the mean-free path is large compared to the distance between source and substrate and few collisions occur before the species condense on the substrate. This leads to uneven thickness buildup since the thickest part of the coating will that which is closest to the source. To compensate for that, planetary substrate holders and multiple sources may be used.

To evaporate the source material, various heating methods are used such as resistance heating, electron beam, laser, or cathodic arc (where the source is the cathode). An evaporation system using an electron-beam heater is shown schematically in Fig. 15.4.

6.2 Reactive Evaporation

Compounds such as the refractory carbides and nitrides have extremely high boiling points and generally dissociate during evaporation. The condensation of the molecular fragments on the substrate depends on many factors and the stoichiometry of the deposit may be different from that of the source. To minimize this problem, the process known as *reactive evaporation* is used where the nonmetallic element of the coating (carbon or nitrogen) is introduced into the gas phase and a pure metal source is used. For instance TiN is deposited when a titanium target is evaporated in an atmosphere of nitrogen or ammonia. Likewise to produce a carbide, evaporation occurs in a hydrocarbon atmosphere.

As with CVD, the reaction must have a negative free energy of formation ($-\Delta G^o$) in order to proceed. This is usually the case as shown by the following typical reactions for the deposition of TiC and TiN (at 298 K):

Reaction (1) $Ti + 1/2\ C_2H_2 \rightarrow TiC + 1/2\ H_2\ \Delta G^o = -76.5$ kcal·mol C_2H_2

Reaction (2) $Ti + 1/2\ N_2 \rightarrow TiN\ \Delta G^o = -73.5$ kcal·mol N_2

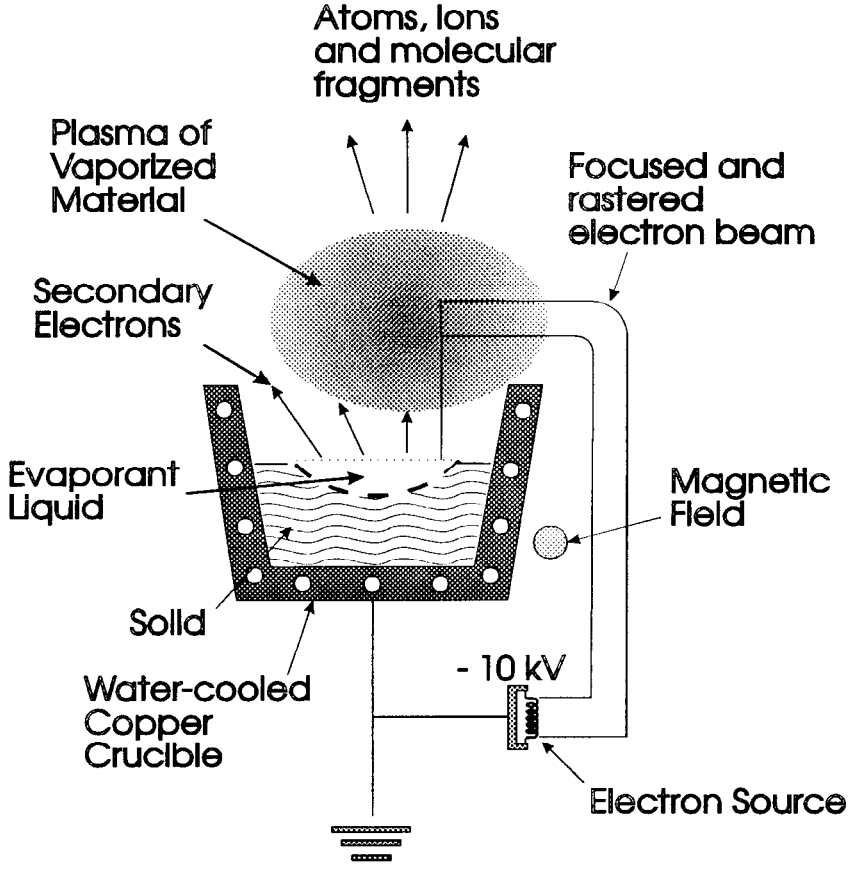


Figure 15.4: Schematic representation of evaporation apparatus using an electron–beam heater.

6.3 Reactive Evaporation of TiN

A typical example of reactive evaporation is the deposition of TiN. The source is evaporated resistively or more commonly by electron-beam heating in a nitrogen atmosphere.[73] Deposition rate is reduced with

increasing nitrogen pressure and hardness of the TiN film is a function of the nitrogen pressure, as shown in Fig. 15.5. Resistivity also varies with nitrogen pressure.

Composition is not constant and in order to form stoichiometric TiN, nitrogen pressure should be above 3×10^{-2} Pa. The substrate is usually heated to 550°C which increases the surface diffusivity, the rate of reaction, and the grain size of the deposit. It also results in a smoother coating surface.

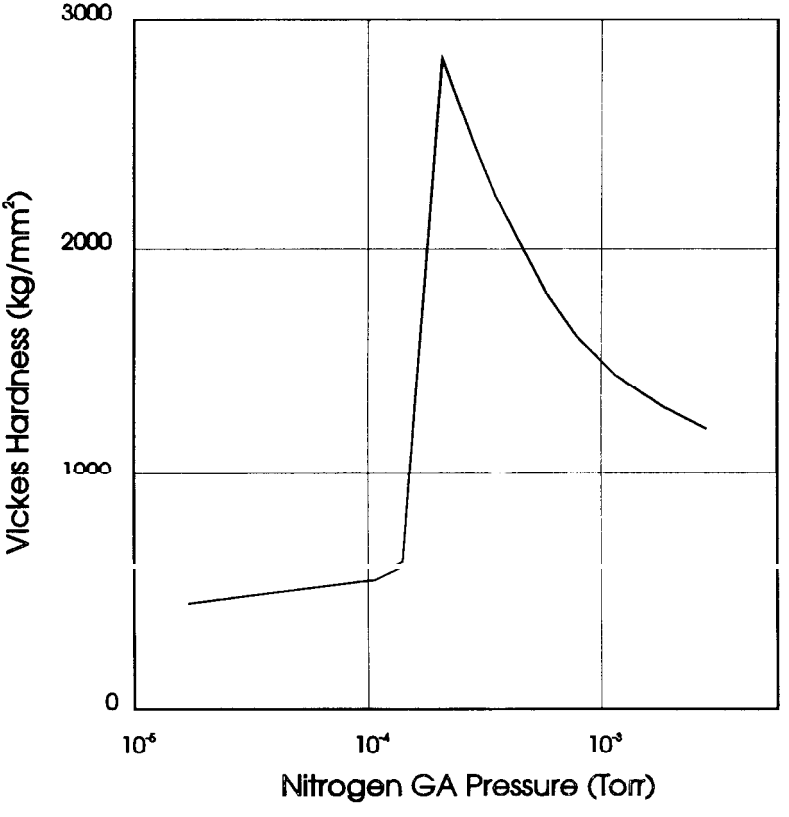


Figure 15.5: Hardness of TiN film obtained by reactive evaporation as a function of nitrogen pressure.

6.4 Plasma Evaporation

In some cases, the deposition rate can be increased by the action of a plasma in a process known as *activated reactive evaporation* (ARE).[3][72] The plasma enhances the reactions (such as the reactions listed in Sec. 2.2) and modifies the growth kinetics of the deposit.

6.5 Molecular-Beam Epitaxy

Another evaporation technique is *molecular beam epitaxy* (MBE). MBE produces extremely pure and very thin films with abrupt composition changes.[74] Deposition rate however is very slow and the process is still considered experimental. It has been used for the deposition of AlN and SiC films.[75][76]

6.6 Examples of Evaporated Films

Evaporation is used extensively for the deposition of hard coatings such as TiN for cutting tools and decorative coatings (jewelry) (see Ch. 16).

7.0 SPUTTERING

Sputtering is an important thin-film process used extensively in the semiconductor and tool-coating industries and for decorative and jewelry coatings.[3][77][78] Coatings of all the refractory carbides and nitrides can be readily produced by sputtering with excellent adhesion and good composition control without the high temperature requirements of CVD.

7.1 Principle of Sputtering

The principle of sputtering is relatively simple. A source (or target) is bombarded in a high vacuum with gas ions (usually argon) which have been accelerated by a high voltage, producing a glow discharge or plasma. Atoms from the target are physically ejected by momentum transfer and move across the vacuum chamber to be deposited on the substrate (Fig. 15.6). Unlike CVD or evaporation, the process is not thermally activated.

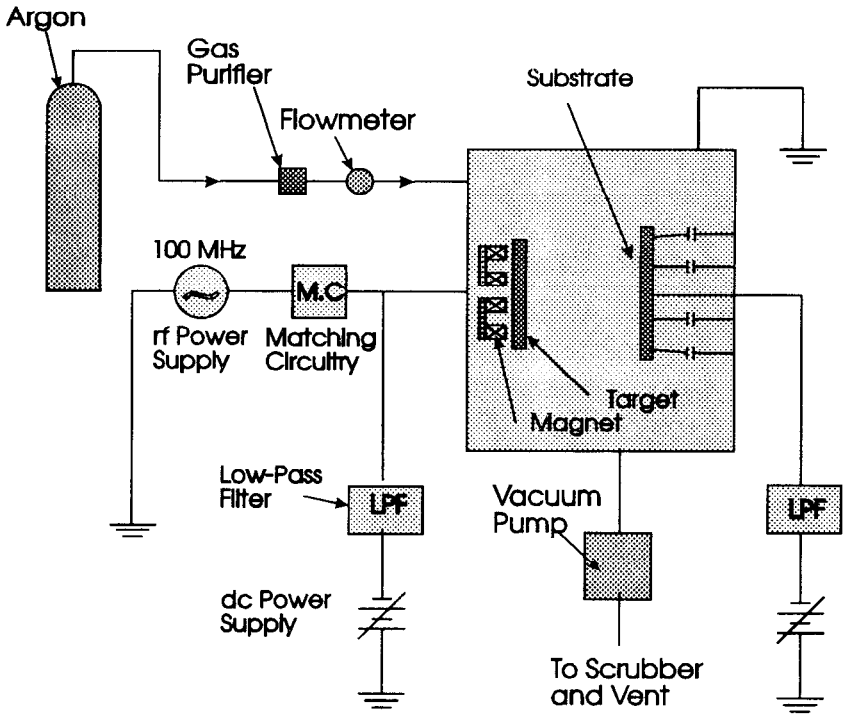


Figure 15.6: Schematic representation of bias sputtering system using RF–DC coupled mode.

The disadvantages of sputtering are a relatively low deposition rate and a line-of-sight deposition characteristic which makes the coating of deep holes and trenches difficult. This can be overcome to some extent by operating at higher pressure (but at some sacrifice in deposition rate) or by the use of three-dimensional grids. On the other hand, the high energy of sputtered particles improves adhesion and produces a denser and more homogenous coating than does evaporation.

Low-Pressure Requirements. Sputtering requires low pressure to remove all traces of background and contaminant gases which could degrade the coating. This is achieved by cryogenic pumps capable of producing a vacuum of 10^{-5} Pa with good pumping speed. After evacuation, the system is refilled with argon to a partial pressure of 0.1–10 Pa. Higher pressure, by placing too many argon atoms in the path of the ions and ejected

atoms, would not allow these to travel relatively unimpeded by collision. In other words, the mean-free path would be too short.

Reactive Sputtering. Like reactive evaporation reviewed in Secs. 6.2 and 6.3, reactive sputtering is used in the deposition of refractory carbides and nitrides by providing a small partial pressure of hydrocarbons or nitrogen. A problem is target poisoning caused by the reaction of the target with the reactive gas.

7.2 Sputtering Techniques

Several techniques are used in sputtering.[77]

- *Diode sputtering* is the simplest but requires an electrically conductive target; it has low energy efficiency and electron bombardment may cause significant damage of the substrate
- *Radio-Frequency (RF)* sputtering, using frequencies above 50 kHz, can sputter insulators but the process gives low deposition rates
- *Triode sputtering* uses an additional cathode to sustain the plasma but is more complicated and may cause contamination of the deposit
- *Magnetron sputtering* uses a magnetically enhanced cathode (magnetron). This process has considerably expanded the potential of sputtering. The magnetron sends the electrons into spiral paths to increase collision frequency and ionization. Deposition rates are high and the process does not cause radiation damage. A typical apparatus for the deposition of TiN is shown schematically in Fig. 15.7.[79]

7.3 Examples of Sputtered Films (see Ch. 16)

- Si_3N_4 diffusion barriers for semiconductor devices
- TiN for hard coatings for cutting tools and semiconductor applications[37]
- TaN resistive films for hybrid circuits deposited by planar magnetron sputtering

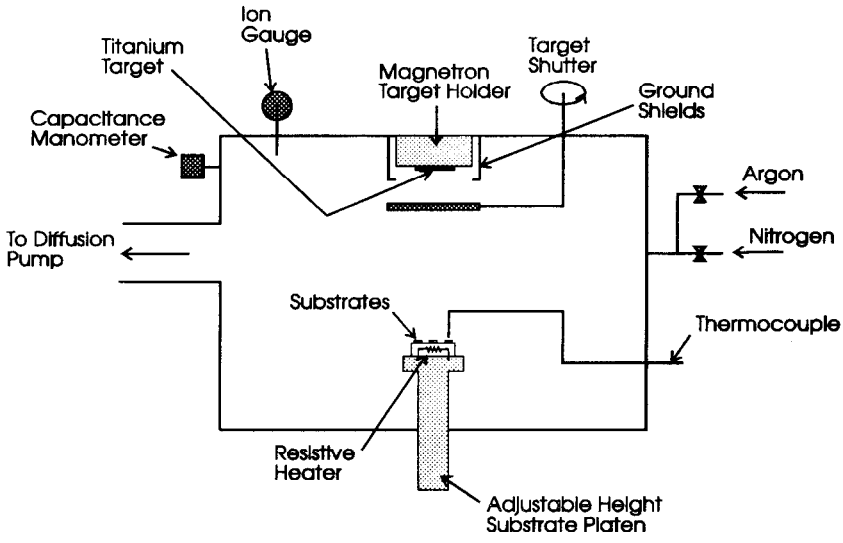


Figure 15.7: Schematic representation of magnetron sputtering apparatus.

8.0 ION PLATING

In ion-plating deposition, the substrate and the deposited film (as it forms) are subjected to bombardment by particles (ions, atoms, molecules) which alter the formation process and the properties of the coating.[80][81] The process is also called *ion-beam assisted deposition* (IBAD). Two basic versions of the process, plasma-based ion plating and vacuum-based ion plating, are illustrated in Figs. 15.8 and 15.9.

The coated material is vaporized in a manner similar to evaporation. Typically, the plasma is obtained by biasing the substrate to a high negative potential (5 kV) at low pressure. The constant ion bombardment of the substrate sputters off some of the surface producing better adhesion and reducing impurities. Surface coverage of discontinuities is also improved.

Reactive ion plating is used to produced several refractory carbides and nitride coatings, especially TiN, TiC, and TiC_xN_y (see Sec. 6.2) for wear, abrasion, and decorative coatings.[82][83]

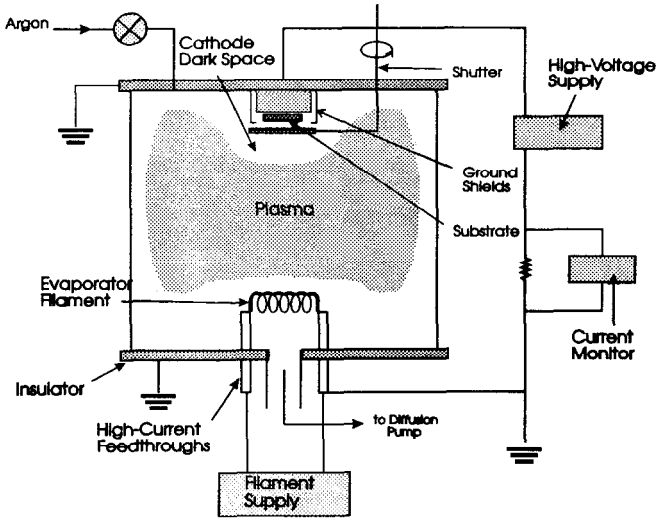


Figure 15.8: Schematic representation of ion–plating apparatus using a plasma–based configuration with resistance–heating evaporator.

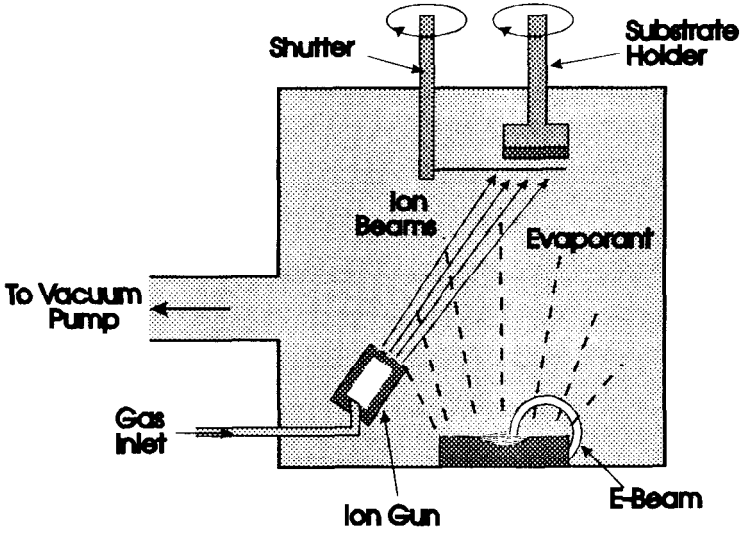


Figure 15.9: Schematic representation of ion–plating apparatus using a vacuum–based configuration with electron–beam evaporator.

9.0 THERMAL SPRAY

9.1 Principle of Thermal Spray

Thermal spraying is a well-established, relatively low-cost, industrial process which is used widely for the deposition of metals and compounds, including the refractory carbides and nitrides. An example is coatings of tungsten carbide with a cobalt binder which are of major industrial importance.[84][85]

The coating material in the form of powder is metered into a compressed-gas stream and fed into the heat source where it is heated to its melting point and projected onto the substrate. Refractory carbides and nitrides have very high melting points and, at these temperatures, they are extremely reactive and must be sprayed in an inert atmosphere to avoid detrimental chemical reactions such as oxidation.

The properties of thermal-sprayed coatings vary as a function of processing parameters such as temperature and particle velocity. Generally, such coatings have greater porosity than CVD or PVD coatings and thickness control is more difficult to achieve.

9.2 Heat Sources

Because of the refractory nature of carbides and nitrides, equipment capable of providing high temperatures is required. These include:

- Detonation gun (D-gun) shown schematically in Fig. 15.10.[84] It uses the energy of continuous, controlled explosions of oxyacetylene mixtures to obtain the necessary kinetic energy
- High-velocity oxy-fuel (HVOF) shown schematically in Fig. 15.11. It operates at high pressure (10 MPa) and high particle velocity (~315 m/s)
- Plasma spray using a DC-plasma torch or an RF inductively coupled torch. The materials are sprayed in an argon atmosphere at torch pressure close to 0.1 MPa[86]

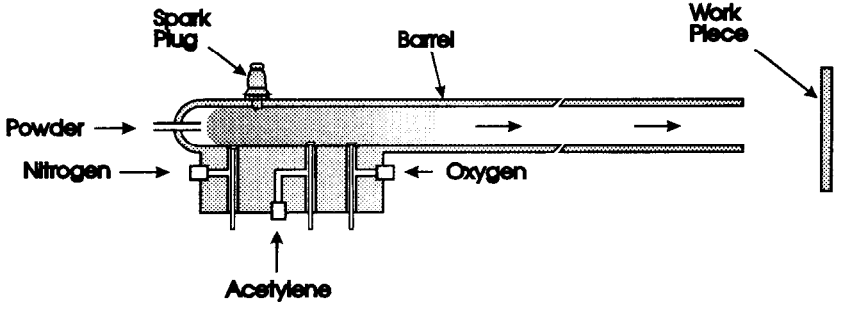


Figure 15.10: Cross–section of a detonation spray gun.

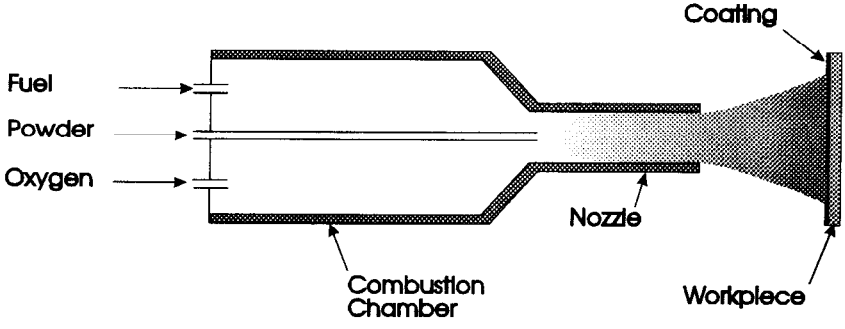


Figure 15.11: Schematic representation of a high–velocity oxyfuel (HVOF) spray gun.

9.3 Reactive Thermal Spray

Coatings of refractory carbides and nitrides can be deposited reactively in a manner similar to reactive evaporation and sputtering by spraying the pure metal in an atmosphere of either a hydrocarbon or nitrogen (see Secs. 6.2 and 6.3).

9.4 Examples of Thermal-Sprayed Coatings

Among the refractory carbides and nitrides, tungsten carbide with a cobalt binder is the most important material used widely in the coating of gas-turbine components for aircraft and industrial use, components of steam turbines and diesel engines, components for the oil and gas industry, paper and pulp industry, and chemical processing industry (see Ch. 16).

Next in importance is chromium carbide also used in the coating of steam turbines. Mixtures of WC, TiC, and Cr_3C_2 are used to a lesser degree.

REFERENCES

1. Picreaux, S., and Pope, L., Tailored Surface Modifications by Ion Implantation and Laser Treatment, *Science*, 226:615–622 (1986)
2. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
3. *Handbook of Deposition Technologies for Films and Coatings,* Second Edition, (R. Bunshah, Ed.), Noyes Publications, Park Ridge, NJ (1993)
4. *Thermal Spraying,* Publications of the American Welding Society, Miami, FL (1985)
5. Storm, E. K., *The Refractory Carbides*, Academic Press, New York (1967)
6. Pierson, H. O., The CVD of Refractory Metal Carbides, *High-Temp Materials and Processes,* 11(1–4) (1993)
7. Dariel, M., Aparicio, R., Anderson, T., and Sacks, M., CVD of TiC_x on Refractory Materials, *Proc. 11th. Int. Conf. on CVD*, (K. Spear and G. Cullen, Eds.) pp. 659–669, Electrochem. Soc., Pennington, NJ (1990)
8. Kim, D., Yoo, J., and Chun, J., Effect of Deposition Variables on the Chemical Vapor Deposition of TiC Using Propane, *J. Vac. Sci. Technol.* A, 4(2):219–221 (Mar.-Apr. 1986)
9. Huchet, G., and Teyssandier, F., Crystalline TiC Obtained at 700°C by MOCVD, *Proc. 11th. Int. Conf. on CVD,* (K. Spear and G. Cullen, eds.) pp. 703–809, Electrochem. Soc., Pennington, NJ (1990)
10. Ikegawa, A., Tobioka, M., Doi, A., and Doi, Y., TiC and TiN Coated Cemented Carbides by RF Plasma Assisted CVD, *Proc. 5th. European Conf. on CVD* (J. Carlsson and J. Lindstrom, eds.) pp. 413–410, Univ. of Uppsala, Sweden (1985)
11. Bhat, D. G., *Surface Modification Technologies*, Publ. of the Metallurgical Soc. (1988)

12. Pierson, H. O., Titanium Carbonitride Obtained by Chemical Vapor Deposition, *Thin Solid Films*, 40:41–47 (1977)

13. Chatterjee-Fischer, R., and Mayr, P., Investigations of TiCN-Layers Obtained at Moderate Temperatures, *Proc. 5th. European Conf. on CVD*, (J. Carlsson and J. Lindstrom, eds.) pp. 395–404, Univ. of Uppsala, Sweden (1985)

14. Ogawa, T, Ikawa, K., and Iwamoto, K., Chemical Vapor Deposition of ZrC within a Spouted Bed by Bromide Process, *J. Nucl. Mater.*, 97(1-2):104–112 (Mar. 1981)

15. Hollabaugh, C., Wahman, L., Reiswig, R., White, R., and Wagner, P., Chemical Vapor Deposition of ZrC Made by Reactions of $ZrCl_4$ with CH_4 and with C_3H_6, *Nuc. Technol.*, 35(2):527–535 (Sept. 1977)

16. Hertz, D., Spitz, J., and Besson, J., Elaboration du Carbure de Hafnium par Depot Chimique en Phase Vapeur, *High Temp. High Press.*, 6:423-433 (1974)

17. Hakim, M., Chemical Vapour Deposition of Hafnium Nitride and Hafnium Carbide on Tungsten Wires, *Proc. 5th Int. Conf. on CVD*, (J. Blocher et al., Eds), pp. 634-649, Electrochem. Soc., Pennington, NJ 08534

18. Lackey, W., Hanigofsky, J., and Freeman, G., Experimental Whisker Growth and Thermodynamic Study of the Hafnium-Carbon System for Chemical Vapor Deposition Applications, *J. Amer. Ceram. Soc.*, 73(6):1593–98 (1990)

19. Caputo, J., *Thin Solid Films*, pp. 40–49 (1977)

20. Motojima, S., and Kuzuya, S., Deposition and Whisker Growth of Cr_7C_3 by CVD Process, *J. Crystal Growth*, 71(3):682–688 (1985)

21. Maury, F., Oquab, D., Morancho, R., Nowak, J., and Gauthier, J., Low Temperature Deposition of Chromium Carbide by LPCVD Process using Bis-Arene Chromium as Single Source, *Proc. 10th Int. Conf. on CVD*, (G. Cullen, Ed.) pp. 1213–1219, Electrochem Soc., Pennington, NJ (1987)

22. Nutt, S., and Wawner, F., CVD Coating from Metal Carbonyls on SiC Filaments, *Proc. 10th. Int. Conf. on CVD* (G. Cullen, ed.) pp. 840-848, Electrochem. Soc., Pennington, NJ (1987)

23. Teysandier, F., Ducarroir, M., and Bernard, C., Investigation of the Deposition Conditions for Pure Tungsten Monocarbide, *Proc. 7th. Int. Conf. on CVD* (T. Sedgwick and H. Lydtin, eds.) pp. 398–411, Electrochem. Soc. Pennington, NJ (1977).

24. Roman, O. V., Kirilyuk, L., and Chernousova, S., Gas-Phase Precipitation of Tungsten Carbide Coatings, *Poroshk. Metall.* (6):53–56 (1987)

25. Langlais, F., and Prebende, C., On the Chemical Process of CVD of SiC-based Ceramics from the Si-C-H-Cl System, *Proc. 11th. Int. Conf. on CVD*, (K. Spear and G. Cullen, eds.) pp. 686–695, Electrochem. Soc., Pennington, NJ (1990)

26. Schintlmeister, W., Wallgram, W., and Gigl, K., Deposition of CVD-SiC Coatings at Intermediate Coating Temperatures, *High Temp., High Press.*, 18(2):211–222 (1986)

27. Fischman, G., and Petuskey, W., Thermodynamic Analysis and Kinetic Implications of Chemical Vapor Deposition of SiC from Si-C-Cl-H Gas Systems, *J. Am. Ceram. Soc.*, 68(4):185–190 (1985)

28. Komiyama, H., Oyamada, H., Tanaka, S., and Shimogaki, Y., Low Temperature Synthesis of SiC Films by Low Pressure Chemical Vapor Deposition, *Proc. 11th. Int. Conf. on CVD*, (K. Spear and G. Cullen, eds.) pp. 361–367, Electrochem. Soc., Pennington, NJ (1990)

29. Allendorf, M., and Kee, R., A Model of Silicon Carbide Chemical Vapor Deposition, *Proc. 11th. Int. Conf. on CVD* (1990), (K. Spear and G. Cullen, eds.) pp. 679–685, Electrochem. Soc., Pennington, NJ (1990)

30. Stinton, D., Besmann, T., and Lowden, R., Advanced Ceramics by Chemical Vapor Deposition Techniques, *Ceram. Bul.*, 67-2:350–355 (1988)

31. Angelini, P., Chemical Vapor Deposition of Silicon Carbide from Methylsilane and Coating of Nuclear Waste Ceramics, *Diss. Abstr. Int.*, 46(9):170, (Mar. 1986)

32. Furumara, Y., Doki, M., Mieno, F., Eshita, T., Suzuki, T., and Maeda, M., Heteroepitaxial beta-SiC on Si, *Proc. 10th. Int. Conf. on CVD*, (G. Cullen, ed.) pp. 435-444, Electrochem. Soc., Pennington, NJ (1987)

33. Janson, U., Chemical Vapor Deposition of Boron Carbides, *Materials and Manufacturing Processes,* 6(3):481–500 (1991)

34. Lartigue, S., Cazajous, D., Nadal, M., and Male, G., Study of Boron Carbide Vapor-Deposited under Low Pressure, *Proc. 5th. European Conf. on CVD,* (J. Carlsson and J. Lindstrom, eds.) pp. 403–410, Univ. of Uppsala, Sweden (1985)

35. Koumoto, K., Thermoelectric Properties of CVD Boron Carbide, *Am. Ceram. Soc. Bull.*, 73(10):84–87 (1994)

36. Mullendore, A., Chemical Vapor Deposition of Boron-based Refractory Solids, *AIP Conf. Proc.*, 4-140, Am. Inst. of Physics, New York (1986)

37. Singer, P., The Interconnect Challenge: Filling Smnall, High Aspect Ration Contact Holes, *Semiconductor International,* pp. 57–64 (Aug. 1994)

38. Bhat, D. G., A Thermodynamic and Kinetic Study of CVD TiN Coating on Cemented Carbide, *Proc. 11th. Int. Conf. on CVD,* (K. Spear and G. Cullen, eds.) pp. 648–655, Electrochem. Soc., Pennington, NJ 08534 (1990)

39. Glejbol, K. Pryds, N. H., and Tholen, A. R., Nucleation of CVD-TiN on Tungsten, *J. Mat. Res.*, 8(9):2239–2244, (Sept. 1993)

40. Sherman, A., and Ranijmakers, J., Step Coverage of Thick, Low Temperature LPCVD TiN Films, *Proc. 11th. Int. Conf. on CVD,* (K. Spear and G. Cullen, eds.), pp. 373–380, Electrochem. Soc., Pennington, NJ (1990)

41. Ianno, N. J., Ahmed, A. U., and Englebert, D. E., Plasma-Enhanced Chemical Vapor Deposition of TiN from $TiCl_4/N_2/H_2$ Gas Mixtures, *J. Electrochem. Soc.*, 136–1 (Jan. 1989)

42. Shizhi, L., Cheng, Z., Yulong, S., Xiang, X., Wu, H., Yan, X., and Hongshun, Y., The Deposition of TiN Coatings by Plasma Chemical Vapor Deposition and its Applications, *Proc. 10th. Int. Conf. on CVD,* (G. Cullen Ed.) pp. 1233–1243, Electrochem. Soc., Pennington, NJ (1987)

43. Mayr, P., and Stock, H. R., Deposition of TiN and Ti(O,C,N) Hard Coatings by a Plasma-Assisted Chemical Vapor Deposition Process, *J. Vac. Sci. Technol.*, 4(6):2726–2730 (Nov. Dec. 1986)

44. Roberts, B, Harrus, A., and Jackson, R., Interconnect Metallization for Future Device Generations, *Solid State Technology*, pp. 69–78 (Feb. 1995), see also Technical Brochures, *TDEAT* and *TDMAT*, Schumacher, Carlsbad, CA (1994)

45. Kern, W., and Ban, V. S., Chemical Vapor Deposition of Inorganic Thin Films, in *Thin Film Processes*, (J. Vossen and W. Kern, Eds.), Academic Press, New York (1978)

46. Hakim, M., Chemical Vapor Deposition of Hafnium Nitride and Hafnium Carbide on Tungsten Wires, *Proc. 5th. Int. Conf. on CVD,* (J. M. Blocher, Jr., et al., Eds.) pp. 634–649, Electrochem. Soc. Pennington, NJ, 08534 (1975)

47. Kieda, N., Mizutani, N., and Kato, M., CVD of 5a Group Transition Metal Nitrides, *Proc. 10th. Int. Conf. on CVD,* (G. Cullen, Ed.) pp. 1203–1209, Electrochem. Soc., Pennington, NJ, 08534 (1987)

48. Funakubo, H., Kieda, N., and Mizutani, N., Preparation of Niobium Nitride Films by CVD, *Yogyo Kyokaishi*, Japan, 95(1):55–8 (1987)

49. Nickel, K., Riedel, R., and Petzow, G., Thermodynamic and Experimental Study of High-Purity Aluminum Nitride Formation from Aluminum Chloride by Chemical Vapor Deposition, *J. Amer. Ceram. Soc.*, 72(10):1804–1810 (1989)

50. Pauleau, Y., Bouteville, A., Hantzpergue, J., Remy, J., and Cachard, A., Composition, Kinetics and Mechanism of Growth of Chemical-Vapor-Deposited Aluminum Nitride Films, *J. Electrochem. Soc.*, 129(5):1045–1052 (May 1982)

51. Susuki, M., and Tanji, H., CVD of Polycrystalline Aluminum Nitride, *Proc. 10th. Int. Conf. on CVD*, (G. Cullen, Ed.) pp. 1089–1097, Electrochem. Soc., Pennington, NJ 08534 (1987)

52. Ho, K., Annapragada, A., and Jensen, K., MOCVD of AlN using Novel Precursors, *Proc. 11th. Int. Conf. on CVD,* (K. Spear and G. Cullen, Eds.) pp. 388–394, Electrochem. Soc., Pennington, NJ, 08534 (1990)

53. Gordon, R. G., Hoffman, D. M., and Riaz, U., Atmospheric Pressure CVD of AlN Thin Films at 200-250°C. *J. Mater. Res.*, 6(1) (Jan. 1991)

54. Rosler, R. S., The Evolution of Commercial Plasma-Enhanced CVD Systems, *Solid State Technology*, pp. 67–71 (June 1991)

55. Bhat, D. G., and Roman, J. E., Morphological Study of CVD Alpha-Silicon Nitride Deposited at One Atmosphere Pressure, *Proc. 10th. Int. Conf. on CVD,* (G. Cullen, Ed.) pp. 579–585, Electrochem. Soc., Pennington, NJ, 08534 (1987)

56. Kim, J., Yi, K., and Chun, J., The Effects of Deposition Variables in the Chemical Vapor Deposition of Si_3N_4, *Proc. 5th. European Conf. on CVD,* (J. Carlsson and J. Lindstrom, eds.) pp. 482–491, Univ. of Uppsala, Sweden (1985)

57. Unal, O., Petrovic, J. J., and Mitchell, T. E., CVD Si_3N_4 on Single Crystal SiC, *J. Mater. Res.*, 7(1) Jan. 1992

58. Kaplan, W., and Zhang, S., Determination of Kinetic Parameters of LPCVD Processes from Batch Depositions, Stoichiometric Silicon Nitride Films, *Proc. 11th. Int. Conf. on CVD* (K. Spear and G. Cullen, Eds.), pp. 381–387, Electrochem. Soc., Pennington, NJ (1990)

59. Marks, J., Witty, D., Short, A., Laford, W., and Nguyen, B., Properties of High Quality Nitride Films by Plasma Enhanced Chemical Vapor Deposition, *Proc. 11th. Int. Conf. on CVD,* (K. Spear and G. Cullen, Eds.), pp. 368–373, Electrochem. Soc., Pennington, NJ, 08534, (1990)

60. Kiermasz A., and Beekman, K., Plasma CVD of Silicon Nitride, *Semiconductor International*, pp. 108–111 (June 1990)

61. Chang, M., Wong, J., and Wang, D., Low Stress, Low Hydrogen Nitride Deposition, *Solid State Technol.*, pp. 193–195 (May 1988)

62. Manabe, Y., and Yamazaki, O., Silicon-Nitride Thin Films Prepared by ECR Plasma CVD, *Proc. 10th. Int. Conf. on CVD* (G. Cullen, Ed.), pp. 885–893, Electrochem. Soc., Pennington, NJ, 08534 (1987)

63. Tsu, D. V., and Lucovsky, G., Silicon Nitride and Silicon Diimide Grown by Remote Plasma-Enhanced Chemical Vapor Deposition, *J. Vac. Sci. Technol. A*, 4(3-1):480–485 (May–June 1986)

64. Grannen, K. J., Xiong, F., and Chang, R., The Growth of Silicon-Nitride Crystalline Films using Microwave Plasma-Enhanced CVD, *J. Mater. Res.*, 9(9):2341–2348 (1994)

65. Rosler, R. S., and Engle, G. M., Plasma-Enhanced CVD in a Novel LPCVD-Type System, *Solid State Technology*, pp. 172–177 (Apr. 1981)

66. Hoffman, D. M. et al., Plasma-Enhanced CVD of Silicon Nitride Films from a Metallo-Organic Precursor, *J. Mater. Res.*, 9(12):3019–3021 (1994)

67. Pavlovic, V., Kotter, H. R., and Meixner, C., CVD of Boron Nitride using Premixed Borothrichloride and Ammonia, *J. Mater. Res.*, 6(11):2393–2396 (Nov. 1991)

68. Kempfer, L., The Many Faces of Boron Nitride, *Mater. Eng.*, pp. 41–44 (Nov. 1990)

69. Adams, A., and Capio, C., The Chemical Deposition of Boron-Nitrogen Films, *J. Electrochem. Soc.*, 127(2):399–405 (1980)

70. Hirano, S., Yogo, T., Asada, S., and Naka, S., Synthesis of Amorphous Boron Nitride by Pressure Pyrolysis of Borazine, *J. Am. Ceram. Soc.* 72(1):66–70 (1989)

71. Nakamura, K., Preparation and Properties of Boron Nitride Films by Metal Organic Chemical Vapor Deposition, *J. Electochem. Soc.*, 133-6:120–1123 (1986)

72. Mattox, D. M., Vacuum Deposition, Reactive Evaporation and Gas Evaporation, in *ASM Handbook, Vol. 5, Surface Engineering,* pp. 556–572, ASM Publ. (1994)

73. Wittmer, M., *Properties and Microelectronic Applications of Thin Films of Refractory Metal Nitrides,* Am. Inst. of Physics, Conf. Proc. No. 149, New York (1986)

74. Moustakas, T., Molecular Beam Epitaxy: Thin Film Growth and Surface Studies, *MRS Bulletin*, pp. 29–34, (Nov. 1988)

75. Kern, R. S. et al., Solid Solutions of AlN and SiC Grown by Plasma-Assisted GAs-Source Molecular Beam Epitaxy, *J. Mater. Res.*, 8(7):1477–1480 (July 1993)

76. Rowland, L. B., et al., Epitaxial Growth of AlN by Plasma-Assited Molecular Beam Epitaxy, *J. Mater. Res.,* 8(9):2310–2324 (Sept. 1993)

77. Rohde, S. L., Sputter Deposition, in *ASM Handbook, Vol. 5, Surface Engineering,* pp. 573–581, ASM Publ. (1994)

78. Wasa, K., and Hayakawa, S., *Handbook of Sputter Deposition Technology*, Noyes Publications, Park Ridge, NJ (1992)

79. Johansson, B. O., et al., Growth and Properties of Single Crystal TiN Films Deposited by Reactive Magnetron Sputtering, *J. Vac. Sci. Technol. A,* 3(2):303–307 (Mar.-Apr. 1985)

80. Rossnagel, S. M., and Cuomo, J. J., Ion-Beam Deposition Film Modification and Synthesis, *MRS Bulletin*, pp. 40–45 (Dec. 1988)

81. Mattox, D. M., Ion Plating, in *ASM Handbook, Vol.5, Surface Engineering,* pp. 583–592, ASM Publ. (1994)

82. Sproul, W. D. et al., Reactive Sputtering in the ABS System, *Surface Coating Technol.,* 66:179 (1993)

83. Kincel, E. S., A Coat of Many Colors, *Gun World,* 23 (Mar. 1993)

84. Tucker, R. C., Jr., Thermal Spray Coatings, in *ASM Handbook, Vol.5, Surface Engineering,* pp. 497–509, ASM Publ. (1994)

85. Longo, F. N., Thermal Spray Coatings, Markets, Trends, and Forecasts, in *Thermal Spray Coatings Conf.*, Gorham Advanced Materials Inst., Gorham, ME (1992)

86. Bordeaux, F., et al., Thermal Shock Resistance of TiC Coatings Plasma-Sprayed onto Macroroughened Substrates, *Surface and Coating Technology,* 53:49–56 (1992)

16

Applications of Refractory Carbides and Nitrides

1.0 OVERVIEW OF APPLICATIONS OF REFRACTORY CARBIDES AND NITRIDES

1.1 Applications Classification

Major industrial applications of refractory carbides and nitrides have entered the market in the last twenty years or so and new applications are continuously being developed. As seen in Chs. 14 and 15, these applications take the form of powders, bulk/monolithic shapes, coatings, fibers, whiskers, and coatings. They can be associated with a specific property such as strength (structural applications), hardness and chemical resistance (wear and corrosion applications), high-temperature stability and resistance to radiation (nuclear applications), or high thermal conductivity and electrical insulation (semiconductor applications). The classification of these applications is summarized in Table 16.1. It should be noted that some of these categories overlap.

Table 16.1: Application Classification of Refractory Carbides and Nitrides

Application Category	Typical Form	Typical Property	Typical Material	Industrial Category
Structural	Bulk Fibers	Strength Hardness Refractoriness	SiC Si_3N_4 B_4C BN	Automotive Aerospace Chemicals Armor
Wear and Erosion	Bulk Coating Powder	Hardness Chemical resistance	TiC TiN SiC c-BN	Machinery Cutting Tools Aerospace Abrasives
Nuclear	Bulk Coatings	Refractoriness Neutron resist.	B_4C TiC	Nuclear power
Semiconductor and Optical	Coatings	Elect. cond. Thermal cond.	Si_3N_4 TiN AlN SiC	Semiconductor Opto-electronic Optics

This chapter is a review of the applications of refractory carbides and nitrides in each of the following industrial categories: automotive and aerospace, industrial machinery and equipment, cutting and grinding tools, armor, nuclear, semiconductor, and optical.

1.2 Industrial Importance

It is often difficult to assess and compare the industrial importance of refractory carbides and nitrides. In some cases, the analysis is relatively straightforward. A case in point would be a silicon-nitride blast nozzle. The cost of producing such a part can be exactly determined and its advantages over a metal unit in terms of wear resistance and useful life accurately plotted.

In many cases however, the analysis is more difficult and subjective. Tonnage statistics are often meaningless; for instance, one cannot equate the production of thousands of tons of coarse silicon-carbide powder used as an inexpensive abrasive with that of high-cost coatings of silicon nitride or titanium nitride for semiconductor devices which demand exacting processing and critical property control and require only a few grams of material. These coatings are widely used as effective passivation and diffusion barriers. Their fabrication is an integral part of a complicated and lengthy sequential operation which may involve hundreds of steps.[1] To isolate their cost in terms of add-on value and determine the relative importance of such a processing step is difficult. What can be said though is that nitride coatings, with their unique properties, are an essential factor in the production of modern semiconductor devices even though the total quantity of material required may be minute.

1.3 Status of Industrial Production

The five covalent refractory carbides and nitrides, silicon carbide, boron carbide, aluminum nitride, silicon nitride, and boron nitride are all produced on an industrial scale and all have a number of successful large-volume applications. Of these five, the latecomer silicon nitride, either in bulk/monolithic form or as a coating, may have the most promising future.

On the other hand, not all the interstitial carbides and nitrides have large-volume applications; in fact, some have never developed much beyond the laboratory stage and only tungsten carbide, titanium carbide, chromium carbide, and titanium nitride have found large-scale applications at this time.

The success of a material for a given application depends on its properties, its processing characteristics, and its ability to meet the design requirements as well as on its cost and availability. But occasionally, success or failure have more subtle causes, such as consumer acceptance. For instance, silicon-nitride rotors for passenger-car turbochargers are now the standard in Japan but remain at the laboratory stage in the USA, perhaps due to the greater awareness of technological advances among Japanese motorists and the unwillingness of the American customer to pay the higher cost.

A proper analysis of cost is a crucial factor. An example is the production of balls for ball bearings. Balls made of monolithic silicon

nitride or titanium-carbide-coated steel greatly outperform steel balls but their cost is considerably higher. Steel balls in passenger-automobile applications are satisfactory and normally last the life of the car and the far-longer life of the ceramic balls is not needed.

The data presented here is based on available statistics from governmental agencies, industrial organizations, and directly from the manufacturers. These sources do not always use the same standards; essential data is often lacking or conflicting especially when it concerns the reporting of properties. In some cases, with good reason, a shroud of industrial secrecy prevails. The information reported in this chapter should be regarded with these considerations in mind.

2.0 AUTOMOTIVE AND AEROSPACE APPLICATIONS

Many of the automotive and aerospace applications of refractory carbides and nitrides are of a structural and chemical nature especially in applications involving high temperature and/or corrosive environments where most metals are no longer suitable. These applications are usually in the bulk form and are made possible by recent advances in processing technology. Relatively large parts can now be produced to near-net shape with little machining required. Yet these materials are still intrinsically brittle due to their strong covalent atomic bonds and the difficulty of obtaining fully dense and flaw-free structures. Much work remains to be done before full advantage can be taken of their outstanding properties.

2.1 Silicon Nitride in Automobile and Aircraft Engines

As previously mentioned, silicon nitride rotors for turbochargers of passenger cars are in production in Japan (Nissan Motor Co.). In a turbocharged engine, compressed air from the turbocharger is fed into the engine when rapid acceleration is necessary. The rotor operates at 600°C. Engines equipped with a standard metal-alloy rotor have a noticeable lag as the heavy rotor accelerates to the required high rotational speed (close to 180,000 rpm).

Silicon nitride rotors have proved superior to steel rotors in this application. The advantage of silicon nitride lies in its low density which allows lower torque, more rapid acceleration, and reduced lag (the silicon

nitride rotor weighs 40% less than the steel). In addition, it is more resistant to the corrosive and abrasive environment. The rotors are 6–8 cm. in diameter (Fig. 16.1)

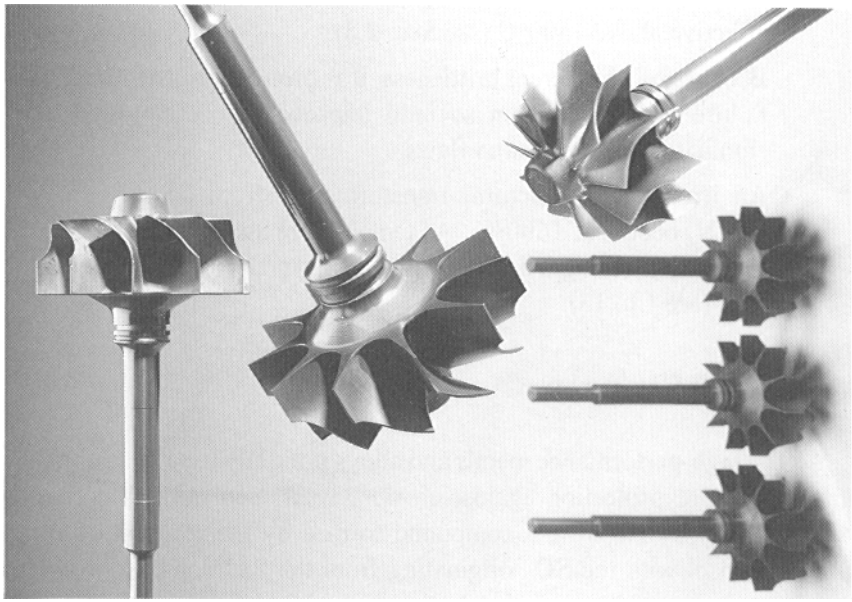


Figure 16.1: Silicon–nitride turbocharger rotor. *(Photograph courtesy of ESK Engineered Ceramics.)*

Diesel engines, particularly for trucks, may soon be required to operate for up to one million miles. This almost mandates the use of ceramics, specifically silicon nitride, in several components. A recent joint Japanese-American effort (NGK Spark Plug Co. and Garrett Automotive Group) involves the development and production of a large rotor for use in the turbochargers of Caterpillar Inc.'s 400-hp diesel truck engines. The part has an outside diameter of 9.6 cm.[2] Other silicon-nitride components for

diesel engines now in production include engine valves and cam-roller followers. Complete ceramic diesel engines may eventually become a reality.

Much work is being done on the development of silicon nitride for more demanding applications such as load-bearing parts in aircraft and industrial turbines where corrosion is severe and temperature is >1000°C.[3] But in spite of its advantages of low density (3.18 g/cm^3), high strength, and high melting point (1900°C), the material has yet to be used on any large scale. This may be due to the following factors:

- Although at high temperature Si_3N_4 oxidizes to form a film of SiO_2 which protects from further oxidation, this film is not effective above 1500°C (see Sec. 2.3).
- Because of its inherent brittleness, it is prone to catastrophic failure and will remain so until improved processing can eliminate all porosity and flaws.
- An irreversible structural transformation from αSi_3N_4 to βSi_3N_4 occurs at 1600°C. As temperature increases beyond 1200°C, its strength drops drastically and creep rate becomes high (see Ch. 13).

2.2 Aircraft Gas Turbines

The high-performance metals and alloys presently used in aircraft gas turbines require protection against erosion, wear, and hot-gas corrosion caused mostly by Na_xSO_y, a compound formed by the reaction of atmospheric aerosol with the SO_2 originating from the fuel combustion. This protection is generally provided by coatings of high-temperature metal alloys and ceramics including partially stabilized zirconia (as thermal-barrier coating) and refractory-interstitial carbides and nitrides, usually tungsten carbide (with a cobalt binder), chromium carbide, titanium carbide, and titanium nitride. These coatings are an effective barrier against corrosion and protect the substrate from damage caused by erosion and foreign particle impact.[4][5] A recent trend is the increasing use of ternary systems based on aluminum such as (Ti,Al)N which offer enhanced corrosion and oxidation resistance.[6] The coatings are applied by low-pressure plasma-spraying, electron-beam evaporation, reactive sputtering, and in some cases CVD.

An estimated 75% of the components of modern aerospace gas turbines are coated, in both the hot and cold sections. This includes stator shrouds and vanes, blade platform edges, blade z-notches, blade tips and shroud tops, and combustor-liner interior surfaces. The use of ceramic coatings in aerospace turbines is being expanded to marine and industrial gas turbines which have similar (and often more acute) environmental problems.

2.3 High-Temperature and Oxidation Protection Applications

Protection of Carbon-Carbon. A common aerospace material used in aircraft brakes, rockets, and reentry systems is carbon-carbon which comprises a carbon-fiber reinforcement and a carbon matrix. It has the highest specific strength of any material above 1000°C.[7] But like all carbon materials, it is susceptible to oxidation and oxidizes rapidly above 500°C. Oxidation protection is provided by silicon carbide which is normally applied by pack cementation or CVD, usually in combination with other materials such as boron to promote self-healing characteristics.

During oxidation, a layer of vitreous silicon dioxide (SiO_2) is formed which provides good oxidation protection up to 1500°C. Above that temperature, the viscosity of the SiO_2 protecting layer decreases rapidly with increasing temperature. This is a severe problem in the case of components subjected to high dynamic loads. Another limitation is the formation of the volatile suboxide SiO which occurs rapidly by simple gasification at temperatures above 1600°C and at low oxygen partial pressure.[8]

Oxidation protection of carbon-carbon can be enhanced by the codeposition of a hafnium-carbide and silicon-carbide coating. During oxidation, intermediate oxide and silicide compounds are formed which provide an effective oxygen barrier up to 1800°C.[9]

High-Temperature Applications of SiC and Si_3N_4. Under most conditions, the thermal decomposition of SiC and Si_3N_4 occurs well below their intrinsic melting point and can become significant at approximately 1700°C. As a result, high-temperature applications are limited. Yet in some cases such as a nonoxidizing atmosphere, these materials may be satisfactory. For instance, because of its strength retention at high-temperature, CVD silicon carbide is the material of choice for many rocket nozzles operating in a nonoxidizing atmosphere.

2.4 Ball Bearings

In some applications, steel-ball bearings do not have the necessary hardness and corrosion resistance. Microwelds tend to occur between the balls and the race which roughen the surfaces and contaminate the lubricant. These problems can be alleviated by coating the steel balls with titanium carbide or by using monolithic silicon-nitride balls.

TiC Coatings. TiC coatings by CVD on steel balls (usually SAE 52100 or AISI 440C) provide much increased hardness, a smoother surface, and a lower coefficient of friction.[10][11]

Monolithic Silicon Nitride. Solid Si_3N_4 balls are replacing steel balls because of their high hardness, chemical resistance, and low density (a feature important in high-speed applications).[12] Further improvement results from coating the silicon nitride with CVD TiN.[11]

Applications. Typical applications of TiC-coated and solid silicon nitride balls are:

- Spin-axis gyroscope with oil lubrication (TiC)
- Bearings in space vehicles operating in vacuum with fluid or solid lubricant (TiC)
- Balls for high-speed machine-tool bearings (Si_3N_4)
- Balls for valves of oil-field sucker-rod pumps (Si_3N_4)

2.5 Composites

Ceramic composites, which consist of a ceramic fiber or whisker reinforcement embedded in a ceramic matrix, are less susceptible to the brittle failure which is characteristic of bulk ceramics because the reinforcement intercepts, deflects, and slows crack propagation (see Ch. 14, Secs. 6 and 7). At the same time, the load is transferred from the matrix to the fibers to be distributed uniformly. A common ceramic composite consists of a SiC-fiber array and SiC or Si_3N_4 matrices produced by chemical-vapor infiltration (CVI). Densities approaching 90% are achieved.[13][14]

Such composites are characterized by low density, generally good thermal stability, and corrosion resistance. Still their theoretical strength is far from being achieved because of the non-ductile behavior of the matrix which results in pronounced notch sensitivity. This may be partially

alleviated by suitable intermediate coatings between fiber and matrix which allow a certain degree of load transfer to the fiber with resulting improved mechanical properties. However, exposure to high temperature (i.e., >1000°C) causes diffusion and chemical bonding across the interface and brittle failure is still dominant. A great deal of experimental work is under way to improve the mechanical properties of these composites.

Metal-Ceramic Composites. Metals such as aluminum, titanium, copper and the intermetallic titanium aluminide, which are reinforced with silicon-carbide fibers or whiskers show an appreciable increase in mechanical properties particularly at elevated temperatures. These composites are being considered for advanced aerospace structures.[15]

Applications. To this date, most applications of ceramic and metal composites are still in the development stage and their production is usually limited to prototypes. These applications are found in high-cost, high-performance aerospace components such as missile guidance fins, hypersonic fuselage skins, inner flaps and rocket nozzles.[16]

Filters. If a ceramic composite, such as SiC fibers with a SiC matrix, is left only partially densified, it can be used as a filter for high-temperature filtering systems with high collection efficiency as required in direct coal-fired gas and steam turbines or in diesel engine exhaust.[17]

3.0 GENERAL INDUSTRIAL APPLICATIONS: MACHINERY AND EQUIPMENT

Applications of refractory carbides and nitrides are found extensively in machinery and equipment for protection against wear, erosion and chemical attack. Both bulk materials (WC, Si_3N_4, B_4C) and coatings (TiC, TiN) are used.

The most important bulk material is tungsten carbide sintered with a metallic binder which is usually cobalt. It is known as *cemented carbide* or *hard metal* (see Ch. 6, Sec. 8.0). Many combinations of carbides and binders are possible and it is estimated that 20,000 tons of these materials are produced annually throughout the world. An unusual and beneficial feature of WC is that it maintains its high hardness value at high temperature (see Ch. 6, Sec. 8.0)

3.1 Machinery

Existing production applications in wear, erosion and corrosion protection are shown in Table 16.2.

Table 16.2: Wear, Erosion, and Corrosion Applications of Refractory Carbides and Nitrides

Metal Forming (Non-Cutting):

Tube and wire drawing dies (TiN)
Stamping, chamfering and coining tools (TiC)
Drawing punches and dies (TiN)
Deep drawing dies (TiC)
Sequential drawing dies (Cr_7C_3)
Dressing sticks for grinding wheels (B_4C)

Ceramic and Plastic Processing:

Molding tools and dies for glass-filled plastics (Ti(C,N))
Extrusion dies for ceramic molding (TiC)
Kneading components for plastic mixing (TiC)

Chemical and General Processing Industries:

Pump and valve parts for corrosive liquids (SiC)
Valve liners (SiC)
Positive orifice chokes (SiC)
Packing sleeves, feed screws (TiC)
Thermocouple wells (SiC)
Heating elements (SiC)
Abrasive-slurry transport (WC)
Sandblasting nozzles (TiC, B_4C)
Textile-processing rolls and shafts (TiC, WC)
Paper-processing rolls and shafts (TiC)
Solder handling in printed-circuit processing (TiC, TiN)

Machine Elements:

Gear components (TiN)
Stainless-steel spray-gun nozzles (TiC)
Components for abrasive processing (TiC)
Wear plates (SiC)

Metal Coatings:

NbC and TaC for the protection of Nb and Ta metals

These materials are produced in monolithic form or as coatings. The coatings are generally applied by CVD on ceramic substrates and by sputtering, electron-beam evaporation, or ion-beam assisted deposition on steel substrates.

3.2 Decorative Applications

Coatings of refractory carbides and nitrides are used extensively in decorative applications on jewelry, eyeglasses, and similar products in attractive colors such as gold (TiN) and metallic grey or charcoal (CrN, TaN). They provide a surface that is hard and wear resistant, sweat resistant and, in the case of gold, less costly. They are usually applied by cathode sputtering and less frequently by CVD.

3.3 Abrasives

Silicon carbide and alumina still dominate the abrasive industry at the present time. However their performance in the grinding of superalloys, ceramics, reinforced plastics, and other hard materials is generally unsatisfactory. This has led to the development of new abrasives such as synthetic diamond and cubic boron nitride. Cubic boron nitride was first synthesized in 1957 and has been available commercially since the 1970's. Although not as hard as diamond, c-BN does not react with carbide formers such as Fe, Co. Ni, Al, Ta, and B at $\approx$1000°C (while diamond does). However, it reacts with aluminum at 1050°C, with Fe and Ni alloys containing Al above 1250°C, and with water and water-soluble oils.[18]

4.0 CUTTING AND GRINDING TOOLS

Cutting and grinding tools are a special case of wear and corrosion applications. Cutting tools have a sharp edge for the purpose of shaving and generating a material chip. This edge must remain sharp for the tool to perform properly. Grinding tools are different in that they have an abrasive-coated surface which generates a powder as opposed to the chip of a cutting tool.

The three requirements of a cutting or grinding tool material are hardness, toughness, and chemical stability. The refractory carbides and

nitrides meet these requirements and play an essential part in the tool industry. They are used in both bulk and coating forms.

4.1 Bulk Tungsten-Carbide Tools

A major tool material is tungsten-carbide cobalt (the so-called "cemented carbide") reviewed in Sec. 3.0 of this chapter (see also Ch. 6, Sec. 8.0). The great majority of tungsten-carbide tools are now coated with TiC, TiN, and/or Ti(CN), usually in a multilayer combination providing a considerable increase in tool life.[19] These coatings are usually applied by thermal CVD. However, a deposition temperature which is too high may lead to binder diffusion and the formation of a detrimental tertiary carbide Co_6W_6C, called the *eta phase*, at the WC/matrix interfaces. This causes loss of strength and adhesion failure of the coating.

The main applications of coated tungsten carbide are tips and blanks, indexable inserts, milling tools, turning and boring tools, and circular saws.

4.2 TiN Coatings for Steel Tools

Titanium nitride is the material of choice for the coating of high-speed steel cutting tools. It is usually applied by physical vapor deposition (reactive sputtering or evaporation by electron-beam heating). These processes are preferred over CVD since the deposition temperature is below the autenitizing temperature of the steel and the tool is not dimensionally distorted.

4.3 Bulk Silicon-Nitride Tools

Monolithic silicon nitride is now used extensively as a cutting tool material.[12] The material is especially recommended for the high-speed machining of cast iron due to its excellent thermal stability, hardness, and wear resistance. When coated with TiN (by CVD), it is suitable for the machining of steel, since TiN provides further improvement in chemical resistance.[20]

5.0 ARMOR APPLICATIONS

The development of ceramic materials for armor since 1970 has been extensive.[21] In addition to alumina and titanium diboride, the most widely used ceramic materials are silicon carbide, boron carbide, and aluminum nitride, as monolithic plates and shapes, which are bonded to a fibrous laminate of fiberglass or Kevlar™. A typical impact sequence is shown in Fig. 16.2. On impact, the ceramic plate fractures the projectile core and absorbs a major part of the kinetic energy. The backing material absorbs the residual energy.[22]

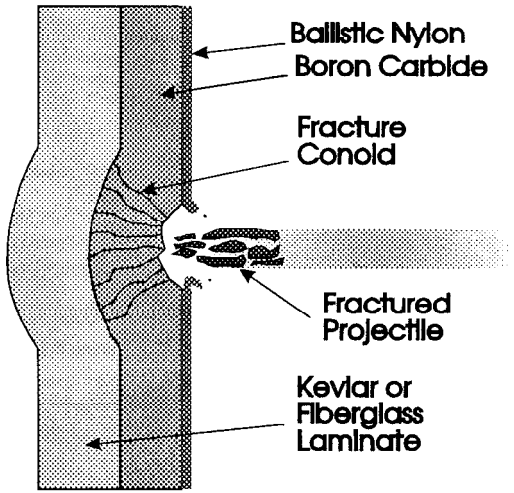


Figure 16.2: Schematic representation of armor impact.[40]

Most applications at this time are sponsored by the military. Boron carbide, with its low density (but higher cost), is used successfully in body armor and helicopter armor. Silicon carbide has been used in prototype quantities for land vehicles, but no large-scale production is planned at this stage.

6.0 NUCLEAR AND RADIATION APPLICATIONS

6.1 Nuclear Fission Applications

The composition of boron carbide is approximately 80 atomic percent boron. The material is often considered as a source of boron, without the high reactivity of the latter. Like boron, B_4C has a high neutron capture cross-section for thermal neutrons and a low secondary gamma radiation. As such, it provides an excellent neutron absorber and is used extensively to control the neutron flux in nuclear fission reactors, such as the boiling water, pressurized water, and fast breeding reactors. It is also used for the compact storage of spent fuel rods.[23]

Zirconium-carbide CVD coatings are used extensively on atomic fuel particles such as thoria and urania. These coatings are applied by thermal CVD in a fluidized bed reactor.[24]

6.2 Nuclear Fusion Applications

Refractory carbides, with their high chemical stability and low atomic number, are used in many experimental coatings for fusion devices. These materials must be able to withstand very severe thermal shock. The following applications have been reported:[25][26]

- TiC coating on graphite for limiters and neutral beam armor
- B_4C deposited by plasma CVD on graphite for wall armor protection

7.0 ELECTRONIC AND OPTICAL APPLICATIONS

Four materials play an increasingly important part in the design of advanced electronic and optical products: titanium nitride, silicon nitride, aluminum nitride, and silicon carbide. These materials have contributed to a sizeable extent to the dramatic progress of the semiconductor and optical industries in the last few years. The major applications are as follows.

7.1 Titanium Nitride Diffusion Barrier

A typical semiconductor device (found in the back-end of the line or the interconnects) consists of a layer of glass followed by a sputtered layer of titanium which is thermally treated to form a titanium silicide. Next a layer of titanium nitride is deposited on top of the silicide and on the sidewall of the contacts by sputtering or by MOCVD (Fig. 16.3).[1][27] This layer of TiN acts as a diffusion barrier and an adhesion promoter. It is followed by the main interconnect which is an aluminum-copper alloy, in turn followed by another layer of TiN which acts as adhesion and antireflecting layer.

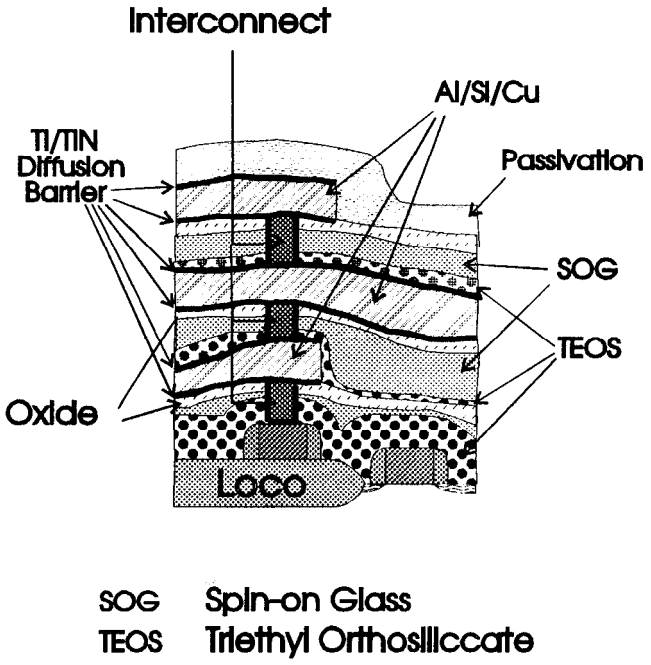


Figure 16.3: Cross–section of 0.5 μm triple–level integrated circuit (IC) with spin–on–glass planarization and Ti/TiN diffusion barrier.

7.2 Silicon Nitride Electrical Insulation

Silicon nitride (Si_3N_4) is an excellent electrical insulator which is increasingly replacing SiO_2 because, in contrast with SiO_2, it is an effective diffusion barrier, especially for sodium and water which are major sources of corrosion and instability in microelectronic devices.[1] As a result, it can perform two functions simultaneously: passivation and provision of a diffusion barrier. It is now used in the fabrication of integrated circuits in such areas as oxide insulation masking (to be removed during subsequent processing), local oxidation of silicon (known as LOCO), and as a dielectric between two layers of polysilicon for capacitors in analog cells. It is generally deposited by plasma CVD or by sputtering.

7.3 Silicon Carbide Semiconductor

The promising electronic properties of beta-silicon carbide are compared to those of other semiconductor materials in Table 8.3 of Ch. 8. A major advantage of this material is its high-temperature potential (>1000°C) which far surpasses that of other semiconductors. Beta-SiC should also be more effective than silicon or gallium arsenide particularly in microwave and millimeter-wave devices and in high-voltage power devices.[28] The development of SiC as a semiconductor is still in the laboratory state.

7.4 Aluminum Nitride Heat Sink

Aluminum nitride has outstanding thermal conductivity and is an electrical insulator and heat sink in competition with beryllium oxide and more recently polycrystalline diamond (see Ch. 13).

7.5 Thermoelectric Applications

With its wide gap in its forbidden band, low thermal conductivity, and high thermoelectric power, boron carbide is being investigated for high-temperature thermoelectric energy conversion (see Ch. 8, Sec. 5.0).

7.6 Optical Applications

The nitrides make excellent optical materials as a result of their large band gap energy which gives them a wide spectral range of transparency

from the ultraviolet to the infrared. Titanium nitride in particular is used on a large scale as a compound thin film with Si, SiO_2, SnO_2, and TiO_2. These films are deposited by atmospheric-pressure CVD in a continuous high-volume operation over flat glass for the production of low-emissivity glass (low-E) mostly for architectural use.[29][30]

REFERENCES

1. Singer, P., 1995: Looking Down the Road to Quarter-Micron Production, *Semiconductor International*, pp. 46–52 (Jan. 1995)
2. *R&D Magazine*, 19 (Sept. 1992)
3. Sims, C. T., Non-Metallic Materials for Gas-Turbine Engines, *Advanced Mat. and Processes*, pp. 32–39 (June 1991)
4. Lammerman, H., and Kienel, G., PVD Coatings for Aircraft Turbine Blades, *Advanced Mat. and Processes*, pp. 18–23 (Dec. 1991)
5. Longo, F., Thermal Spray Coatings Market, Trends, and Forecast, *Proc. Thermal Spray Conf.*, Gorham Advanced Mat. Inst., Gorham, ME (1992)
6. Rohde, S. L., *Sputter Deposition*, in *ASM Handbook, Vol. 5, Surface Engineering*, pp. 573–581, ASM Publ. (1994)
7. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes*, Noyes Publications, Park Ridge, NJ (1992)
8. Divakar, R., et al., Silicon Carbide in *Kirk Othmer, Encyclopedia of Chemical Technology*, John Wiley & Sons, New York (1991)
9. Pierson, H. O., Sheek, J. G, and Tuffias, R. H., Overcoating of Carbon-Carbon Composites, *Wright Research and Development Center*, WRDC-TR-89-4045, Wright Patterson AFB, OH (1989)
10. Savan, A., et al., Increased Performance of Bearings using TiC-Coated Balls, *Journal de Physique IV*, C7, 3:943–948 (Nov. 1993)
11. Walker, R. M., et al., Ceramic Coatings as Wear Inhibitors in Slow-Rolling Contacts, *Proc. Int. Conf. on Metal. Coatings and Thin Films*, San Diego, CA (Apr. 1993)
12. Silicon Nitride, Technical Brochure, Ceradyne Inc., Costa Mesa, CA (1994)
13. Veltri, R. D., Condit, D., and Galasso, F., Chemical Vapor Deposited SiC Matrix Composites, *J. Amer. Ceram. Soc.*, 72(3):478–480 (1989)
14. Foulds, W., LeCostaouec, J., Landry, C., and DiPietro, S., Tough Silicon Nitride Matrix Composites Using Textron Silicon Carbide Monofilaments, *Ceram. Eng. Sci. Proc.*, 10(9-10):1083–1099 (1989)

15. Continuous Silicon Carbide Metal Matrix Composites, Technical Brochure, Textron Specialty Materials, Lowell, MA (1994)
16. Ho, C. Y., and El-Rahaiby, S. K., Assessment of the Status of Ceramic Matrix Composites Technology in the U.S. and Abroad, *Ceram. Eng. Sci. Proc.*, 16th An. Conf. on Comp. Part 1, pp. 3-17, (Sept-Oct. 1992)
17. Stinton, D. P., and Lowden, R. A., Fabrication of Fiber-Reinforced Hot-Gas Filters by CVD Techniques, *Ceram. Eng. Sci. Proc.*, 9(9-10):1233–1244 (1988)
18. Gardinier, C., Physical Properties of Superabrasives, *Ceramic Bull.*, 67(6):1006–1009 (1988)
19. Clavel, A. L., Tool Coatings for the Metal-Working Industry, in *Thin Films 91*, Gorham Advanced Materials Inst., Gorham, ME (1991)
20. Rebenne, H. E., and Bhat, D. G., Effect of Diffusion Interface on Adhesion and Machining Performance of TiN-Coated Silicon-Nitride Cutting Tools, *Proc. Third Int. Conf. on Surface Modification Technologies*, Neuchatel, Switzerland (Aug. 1989)
21. Viechincki, D. J., Slavin, M. J., and Kliman, M. I., Development and Current Status of Armor Ceramics, *Ceramic Bull.*, 70(6) (1991)
22. Ceramic Armor, Technical Brochure, Ceradyne Inc., Costa Mesa, CA (1994)
23. ESK Engineering Ceramics, Technical Brochure, Wacker Chemicals, New Canaan, CT (1993)
24. Ogawa, T., and Ikawa, K., High-Temperature Heating Experiments on Unirradiated ZrC-Coated Fuel Particles, *J. Nucl. Mater.*, 99(1):85–93 (July 1981)
25. Mullendore, A. W., Whitley, J. B., Pierson, H. O., and Mattox, D. M., Mechanical Properties of Chemical Vapor Deposited Coatings for Fusion Reactor Application, *J. Vac. Sci. Technol.*, 18(3):1049–1053 (Apr. 1981)
26. Smith, M. F., and Whitley, J. B., Coatings in Magnetic Fusion Devices, *J. Vac. Sci. Technol. A*, 4(6):3038-3045 (Nov–Dec 1986)
27. Roberts, B., Harrus, A., and Jackson, R., Interconnect Metallization for Future Device Generations, *Solid State Technology*, pp. 69–77 (Feb. 1995)
28. Davis, R. F., Silicon Carbide and Diamond Semiconductor Thin Films, *Am. Ceram. Soc. Bull.*, 72(6) (1993)
29. Gerhardinger, P. F., Flat-Glass Developments Reflect New Applications, *Photonic Spectra*, pp. 104–105 (Jan. 1995)
30. Allen, T. H., et al., Enhanced Optical Thin-Film Materials, *Photonic Spectra*, pp. 103–109 (March 1991)

Appendix

Conversion Guide

Units in this book conform to the SI system (Système International d'Unités). They are listed in the following tables with the relevant conversion factors.

Table A.1: Base and Derived SI Units

Physical Quantity	Name	Symbol
	Base Units	
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric Current	ampere	A
Thermodynamic Temperature	kelvin	K
Amount of Substance	mole	mol
	Derived Units	
Frequency	hertz	Hz
Energy	joule	J
Force	newton	N
Power	watt	W
Pressure	pascal	Pa
Electric Potential Difference	volt	V
Electric Resistance	ohm	Ω

Table A.2: Decimal Multiples and Submultiples

Prefix	Symbol	Multiple
Giga	G	10^9
Mega	M	10^6
Kilo	k	10^3
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	μ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}

Table A.3: Conversion of Units to SI and Related Units

From	To	Multiply by
	Length	
in	m	2.54×10^{-2}
ft	m	0.3048
angstrom	m	10^{-8}
angstrom	nm	10^{-1}
	Area	
sq. in	m^2	6.4516×10^{-4}
sq. in	cm^2	6.4516
sq. ft	m^2	9.2903×10^{-2}
	Volume	
cu. in	m^3	1.63871×10^{-5}
cu. ft	m^3	2.83168×10^{-2}
liter	m^3	10^{-3}
gal. (US)	m^3	3.785×10^{-3}

Table A.3: *(Cont'd)*

From	To	Multiply by
	Mass and Mass per Volume	
lb	kg	0.453 592
g/cm^3	$kg\ m^{-3}$	10^3
lb/ft^3	$kg\ m^{-3}$	1.601×10^1
lb/in^3	$kg\ m^{-3}$	$2.767\ 99 \times 10^4$
lb/in^3	$g\ cm^{-3}$	$2.767\ 99 \times 10^1$
	Energy	
btu	J	1.054 35
cal	J	4.1868
eV	J	$1.602\ 10 \times 10^{-19}$
kW h	J	3.6×10^6
	Force	
kgf	N	9.806 65
lbf	N	4.448 22
	Power	
hp	W	7.457×10^2
btu/h	W	$2.928\ 75 \times 10^{-1}$
	Pressure	
mm Hg	Pa	$1.333\ 22 \times 10^2$
atm	Pa	1.01325×10^5
in. Hg (32°F)	Pa	$3.386\ 38 \times 10^3$
$N\ m^{-2}$	Pa	1
	Stress (force per unit area)	
kg/mm^2	MPa	9.806 65
lb/in^2 (psi)	MPa	$6.894\ 75 \times 10^{-3}$

Table A.3: *(Cont'd)*

From	To	Multiply by
	Specific Heat (heat capacity)	
btu/lb °F	J kg^{-1} K	$4.186\,80 \times 10^3$
cal/g °C	J kg^{-1} K	$4.186\,60 \times 10^3$
	Temperature	
°F	°C	5/9 (°F – 32)
	Thermal Conductivity	
J m^{-1} s^{-1} °C	W m–1 K	1
cal/cm·sec·°C	W m–1 K	4.185×10^2
Btu/ft·h.°F	W m^{-1} K	1.730 73
Btu·in/s·ft^2·°F	W m–1 K	$5.192\,20 \times 10^2$
	Thermal Expansion	
in/in·°C	m m^{-1} K	1
in/in·°F	m m^{-1} K	1.8

Index

A

Abrasion coatings 298
Abrasive 138
Abrasives 319
Acceptor 120
Acetonitrile 283
Acetylides 15
Acheson process 138, 151
Acoustic wave devices 245
Actinide carbides 15
Actinides 3, 161
Activated reactive evaporation 295
Adiabatic temperature 254
Aerospace 3, 312, 317
Aircraft 314
Al-N
  phase diagram 237
Alkali metals 161
Alkaline-earth metals 161
Alkoxides 256
Allotropes 212
AlN 252, 295
Aluminum 211, 237
Aluminum carbide 15
Aluminum nitride 2, 161, 185, 209, 216–218, 223, 229, 231, 237, 243, 245, 257, 288, 322, 324
  production 161
Aluminum powder 254
Ammonia 161
Ammonium-oxo complex 253
Anisotropy 214, 233, 234
Antireflection coating 287
Applications 1, 110, 116, 142, 195, 249, 276, 309
  boron carbide 152
  electronic 289
  grinding 250
  large-volume 311
  machining and grinding 237
  polishing 250
  production 318
  silicon carbide 152
  structural 289
  wear 287
ARE 295
Argon 287, 296
Atom
  volume per 29, 31
Atomic bonding 15, 41, 210
Atomic characteristics 9
Atomic fuel particles 74
Atomic number 165
Atomic radii ratio 36, 169
Atomic radius 11, 12, 119, 159, 210
Atomic spacing 39, 215
  of SiC 123, 132
Atomic structure 51, 119

Autenitizing temperature 320
Automotive 3, 312

B

B_2O_3 253
B_4C 132, 270
Ball bearings 311, 316
Band structure 42, 44, 48, 175
Bandgap 148
  energy 324
  indirect 147
Barium nitride 161
bcc structure 39, 172
Bending test 66
Benzene 286
Beryllium carbide 14, 15
Beryllium nitride 161
Beryllium oxide 324
Blast nozzle 310
Boat form 217
Body-centered cubic 31
Boiling point 292
Bond dissociation 12
Bond energy 61, 85, 122, 123, 132, 176, 215, 218, 220
Bond formation 12, 24
Bond length 213, 215, 220
Bond strength 43
  of βSiC 127
Bonding 12, 22, 42, 46, 51, 119, 132, 174, 179, 210, 214, 220, 227
  boron carbide 132
  electronic 159
  silicon carbide 122
Bonding characteristics 9
Bonding effect 167
Bonding energy 42, 290
Bonding orbitals 175
Bonding schemes 42
Bonding system 41
Borazene 256
Borides 3, 56, 144
Boron 2, 120, 128, 147, 211
Boron carbide 14, 118, 128, 131, 132, 137, 142, 149, 150, 151, 286, 321, 322, 324
  production process 152
Boron-carbon phase diagram 134
Boron icosahedra 130
Boron nitride 150, 161, 209, 212, 213, 216, 223, 224, 231, 232, 233, 243, 244, 291
Boron-nitrogen phase diagram 212, 234
Breeding reactors 322
Brillouin zone 148
Brittle 149
Brittle fracture 231
Brittleness 65, 314
βSiC 147
Bulk processes 250

C

C-Mo phase diagram 110
C-Ta phase diagram 97
C-Ti phase diagram 72
Calcium carbide 15
Carbide formation 11, 12
Carbide formers 237
Carbides 8, 9, 58, 68, 120, 144, 248
  formation of 9
  of Group VI 101
  and nitrides 3
  titanium 1
  tungsten 1
Carbon 120, 147
Carbon allotropes 212
Carbon vacancies 59
Carbon-atom orbitals 21
Carbon-atom vacancies 50
Carbon-carbon 15, 315
Carbon-silicon
  phase diagram 127
Carbonitrides 3, 266
Carborundum 1, 137
Carbosilane 256
Carburization of molybdenum oxide 112
Cemented
  carbides 107, 115, 195, 317, 320
Ceramic composites 316
Ceramic industry 2
Ceramic materials 321
Ceramics 65, 313
Chair form 217
Char yield 256
Chemical precursors 279

Chemical processing industry 302
Chemical properties 68
Chemical resistance 107, 110, 192, 232, 291, 320
Chemical-vapor infiltration 316
Chemically resistant 232
Chlorides
  of refractory metals 284
Chlorosilanes 256
Chromium 15, 100, 110, 164
Chromium carbide 15, 36, 101, 107, 284, 302
Classification 8
Close packing 27
Close-packed interstitial carbide 36
Close-packed layers 123
Close-packed structure 39, 171
Closed-shell structure 131
Coating failure 280
Coatings 249, 276, 279
Cobalt 15
Cobalt binder 302
Cobalt nitride 161
Colors 319
Comminution 253
Composites 276, 317
Conduction 64
Conductivity 58, 85, 146, 147, 149, 184, 226, 235, 237
Conductors 62, 87, 104, 187
Contaminant gases 296
Contamination 280
Conversion factors 327
Coordination
  number 29, 31, 122, 171, 172
Corrosion resistant 200, 236
Cost 311
Covalence 25
Covalent bond energy 123, 132
Covalent bonding 46, 175
Covalent bonds 12, 13, 25, 122, 167, 214, 220
Covalent carbides 8, 9, 10, 12, 14, 118, 119, 137, 144–146
  mechanical properties 149
Covalent materials 2
Covalent nitrides 156, 158, 161, 209, 223, 224, 226, 227, 232, 244
Covalent radius 120
Cr_3C_2 101, 110
Cracking 65
Cracks 280
Creep rate 229
CrO_2Cl_2 252
Crucible 239
Cryogenic pumps 296
Crystal orientation 190
Crystal structure 210
Crystalline forms 212
Crystalline structure 119
Crystals 15
CTE 280
Cubic boron nitride 123, 150, 212, 216, 235
  production 161
Cutting tools 2, 72, 107, 116, 156, 200, 277, 281, 295, 297, 319, 320
Cutting-tool materials 282
CVD 253, 264, 268, 278, 279, 284, 287
CVD-SiC fibers 266, 269
CVI 316

D

D-block elements 26
D-gun 300
Decomposition 145
Decorative applications 319
Decorative coatings 205, 295, 298
Defect structures 49
Delamination 280
Delocalized electrons 14
Density 56, 57, 83, 102, 182, 291
  of βSiC 127
Density of metals 40
Density of states 42, 175
Density of the interstitial mononitrides 174
Deposition rate 290
Deposition reactions 284
Deposition temperature 283, 289
Detonation gun 300
Diamond 123, 324
Diborane 287
Diboride 321

Dichlorosilane 289
Dielectric 62, 232, 245
Diesel engines 302, 313
Diethyl aluminum azide 289
Diffusion barriers 195, 200, 287, 289, 297, 311, 323, 324
Diode sputtering 297
Dissociation energy 214
Divalent 22
Doped diamond 147
Ductile-brittle transition 88, 106, 189
Ductile-to-brittle 66, 150, 231

E

Early transition metals 172
Early-transition elements 164
ECR 290
EDM 259
Electrical conductors 104
Electrical discharge machining 259
Electrical insulator 324
Electrical properties 187
Electron beam 292
Electron conduction 64
Electron wave function 20
Electronegativity 8, 9, 10, 14, 15, 46, 119, 157, 158, 179, 210, 214
Electronic bonding 159
Electronic configuration 119, 175, 210
Electronic devices 245
Electronic energy spectra 48
Electronic industry 237
Electronic shell
  filling 26
Electronic structure 18
  of nitrides 165
Electronics 3
Electrostatic attraction 12, 123
Energy of formation 292
Engines 313
Enthalpy 58, 83, 102
Entropy 58
Equipment 317
  high temperature 300
Evaporation 292, 293
Exothermic 254, 284
Expansion 185
  thermal 61, 85, 104, 147, 227

F

Face-centered cubic close-packed 28
Failure mechanism 65, 189
fcc structure 37, 171
Fermi level 48
Fiberglass 321
Fibers 249, 262, 264, 269, 279
Fifth period 26
Forbidden-energy gap 147
Fourth period 26
Fracture mechanism 88, 106
Fracture toughness 65, 259
Friction 316
Fuel rods 322
Furnaces 2
Fusion devices 322

G

Gallium arsenide 148, 244, 324
Gas turbines 240
Gas-turbine components 302
Glow characteristics 147
Glow discharge 295
Glow plugs 257
Graded-composition coatings 281
Graphite 282
Graphite-like structure 209
Green fibers 265
Grinding 253
Grinding tools 72, 156, 319
Ground state 20, 21, 61
Group III 161
Group IIIb 161
Group IV 33, 34, 39, 40, 44, 46, 47, 55, 58, 62, 66, 68, 164, 172, 178, 179, 181, 182, 190
  mechanical properties 64, 65
Group IV nitrides 177
Group V 33, 34, 39, 40, 42, 44, 46, 61, 66, 68, 81, 82, 164, 172, 178, 181, 182, 190
Group V carbides 104
Group V nitrides 177

Group VI 33, 34, 36, 40, 42, 44, 46, 100, 101, 164, 172, 178
Group VI carbides 104, 106
Group VI nitrides 158
Group VII 161
Group VIII 161
Groups IV 42

H

Hafnium 55, 164, 181
Hafnium carbide 76, 78, 284
Hafnium chloride 284
Hafnium nitride 198, 288
Hägg's structures 17
Hall constant 87, 105
Hall effect 64
Hard coatings 295
Hard metal 115, 317
Hardest carbide 106
Hardness 66, 88, 106, 142, 150, 189, 190, 232, 235, 277, 291
Hazardous 279
hcp structure 172
Heat of formation 44, 58, 178, 280
Heat sinks 237
Hex 31
Hex structure 172
Hexagonal boron nitride 212
Hexagonal close-packed 28
Hexagonal structure 31, 36
Hf-C system 77
Hf-N phase diagram 199
Hf-N systems 172
HfN 190, 252
HfN coatings 200
High temperature equipment 300
High-voltage power devices 148
Hipping 258
Host metals 41
Host metal atoms 17
Hot isostatic pressing 258
HPZ 266
HVOF 300
Hybrid atomic orbitals 22
Hybrid circuits 297
Hybridization 120, 167, 211
Hydridopolysilazane polymer 266
Hydrocarbons 15, 284
Hydrogen 15, 280
Hydrolysis 161
Hyperstoichiometric compositions 182

I

IBAD 298
Icosahedron 128
Industrial applications 309
Industrial materials 137, 156, 161, 163, 195, 223, 259, 286, 289
Industrial use 302
Infrared 325
Insulation 237
Insulators 62, 147, 214, 227, 289, 324
Integrated circuits 324
Interatomic spacing 61
Intermediate carbides 9, 36
Intermetallic bonds 175
Interstital mononitrides 176
Interstitial carbides 8, 9, 10, 12, 14, 17, 18, 25, 26, 37, 41, 48, 49, 56, 82, 101, 118
Interstitial materials 2
Interstitial mononitrides 175
Interstitial nitrides 56, 156, 158, 159, 163, 168, 169, 181, 187, 288
Interstitial sites 34, 169
Interstitial structure 34
Ion beam assisted deposition 298
Ion plating 292, 298
Ionic bond energy 123, 132
Ionic bonding 46, 175, 179
Ionic bonds 12, 122
Ionic radius 48
Iron 15
Iron nitride 161
Isoelectronic 212
Isomorphism 194, 195, 200, 204, 205
Isotypical structures 91, 200

J

Jewelry 205, 295, 319

K

K shell 19
Kevlar 321

L

L shell 20
Lanthanide carbides 15
Lanthanides 3, 161
Late-transition metals 161
Lattice constants 124, 132
Lattice parameters 49, 133, 182
  of AlN 218
  of βSiC 127
Lattice substitution 280
LED 2
Liquid-phase sintering 257
Low-E 325
Lubricants 232, 244
Lubricating 195
Lubrication 316

M

M-C 42
M-C bond strength 43
M-C bonds 48, 66, 88, 106
M-M 39, 42, 48
M-M bond strength 43
M-M spacing 41, 174
M-N bonding 189
M_2C 81
M_2N 172, 173
Machinery 317
Magnetic susceptibity 63
Magnetron sputtering 297
Manganese 15
Manganese nitride 161
MBE 295
MC 81
MC structure 39
Mean-free path 297
Mechanical properties
  of covalent nitrides 228
  of Group IV 64
  of Group V 88
  of Group VI 106
Mechnaical properties 188
Melting point 2, 9, 15, 42, 44, 56, 57, 83, 102, 145, 158, 164, 176, 182, 224
Metal carbides 64
Metal halide 252, 284, 288
Metal-atom vacancies 164
Metal-carbon bond 47
Metal-carbon bonding 41
Metal-ceramic composites 317
Metal-to-metal atomic spacing 39, 172
Metallic bonding 48, 175
Metallic bonds 12, 14
Metals 3
Meteorites 248
Methane 282, 284
Methanides 15
Methyl silane 286
Methyl trichlorosilane 253, 286
Microwave activation 290
Microwave devices 148
Military 321
Millimeter-wave devices 148
MN 173
Mo-C 107
β-Mo_2C 112
Mo_2C 101
Mobility 148
MOCVD 280, 282, 289, 291
Modulus 229
Molded shapes 137
Molecular beam epitaxy 295
Molybdenum 100, 164, 282
Molybdenum carbide 107, 110
Molybdenum oxide 112
Monocarbide NbC 95
Monocarbide phases 81
Monocarbides 36, 39, 41, 47, 68, 91
Monolithic 321
Monolithic components 279
Monolithic processes 250
Monolithics 319
Mononitrides 68, 171, 173, 177, 182
Mutual solubility 68

N

NaCl 81, 173, 218
Na_xSO_y 314
Nb-N phase diagram 204
NbC 95
NbN 182, 190, 252
NbN/TiN 190

Needle structure 259
Neon 20
Neutron absorber 322
Neutron absorption 151
Nextel 265
NH_4VO_3 253
Nicalon 265, 266
Nickel 15
Nickel nitride 161
Niobium 81, 164, 181
Niobium carbide 92, 284
Niobium nitride 202, 288
Nitride powders 254
Nitrides 56, 144, 156, 163, 169, 181, 187, 210, 223, 227, 244, 248
  atomic characteristics 158
  covalent 161
  formation 158, 159
  refractory 156
  structure of 159
Nitrogen 156, 165
  radius of atom 169
Nitrogen atom 168
Nitrogen compounds 166
Nitrogen content 171
Nitrogen pressure 182
Nitrogen-to-metal ratio 164
Nuclear applications 151
Nuclear fission power plants 74
Nuclear fission reactors 322
Nuclear industry 142

O

Octahedral sites 36, 169, 173
Octahedron 35
Optical products 322
Optics 3
Orbital state 120
Orbitals 20, 21
Organic solvents 236
Osbornite 248
Oxidation 315
Oxides 3
Oxy-fuel 300
Oxygen 51, 164, 280
Oxyhalide 252

P

Packing of atoms 27
Passivation 311, 324
Peritectic reaction temperature 127
Phase diagram 72
Phenacite-type structure 219
Phonon-assisted hopping 148
Phonons 59
Phosphides 3
Phosphorus 161
Physical vapor deposition 320
Pi bond 214
Piezoelectric 245
Planetary 292
Plasma 295
Plasma reactor 282, 290
Plasma spray 300
Plasma torch 254, 300
Plasma-based ion plating 298
Plutonium nitride 161
Poisoning 297
Polar optical phonons 59
Polarons 148
Polycarbosilane 265, 266
Polycrystalline materials 64
Polydimethyl silane 256
Polymorphs 123, 212
Polysilanes 256
Polytypes 123
Powder production 254
Powders 137, 249, 250, 253, 257, 279
  submicron 116
Precious metals 161
Precipitation 291
Precursor material 256
Precursors 264, 279, 282
Preform 259
Pressing 257, 258
Propane 282, 284, 286
Propene 284
Puckered layers 214, 218, 219
Puckered rings 219
PVD 278, 279, 291
Pyrolysis 289
Pyrolytic boron nitride 234

Q

Quantum numbers 19
Quaternary systems 68

R

Radiation damage 297
Radii ratio 169, 173
Radio-frequency plasma torch 254
Radioactive 151
Ramsdell notation 123
Rare-earth elements 3
Reaction sintering 258
Reaction temperatures 282
Reactive evaporation 292, 293
Reactive ion plating 298
Reactive sputtering 297
Refractory 2, 9, 158
Refractory carbide powders 250
Refractory carbides 118, 248, 254
Refractory compounds 224
Refractory covalent nitrides 223
Refractory nitride powders 252
Refractory
  nitrides 156, 163, 209, 248, 254
Refractory transition-metal nitrides 181
Resistivity 63, 87, 104, 187
RF sputtering 297
Rhombohedral ororthorhombic
  structures 172
Rhombohedron 130
Rotors for turbochargers 312
Rupture strength 66

S

Salinic carbides 15
Salinic nitrides 161
Salt-like carbides 9, 13, 15
Salt-like nitrides 158, 161
Sawdust 151
Seebeck coefficient 149
Self-diffusion of nitrogen 259
Semiconductor 148, 211, 295, 311, 322
Semiconductor applications 297
Semiconductor devices 2, 195,
  289, 323
Semiconductor properties 147
Semiconductors 3, 156
Shapes 249, 257
  complex 258
SHS 254
SI system 327
Si-N
  phase diagram 240
Si_3N_4 297
Sialons 219, 243
αSiC 123
βSiC 123
βSiC to αSiC 127
SiC 286, 295, 317
  thermal decomposition 145
SiC crystal 121
SiC whisker 272
Sigma bond 24, 214
Sigma orbital 24
Silane 256, 286
Silazanes 256
Silicides 3
Silicon 2, 120, 147, 161, 211
Silicon carbide 14, 118, 121, 122,
  124, 137, 151, 216, 229,
  248, 315, 322, 324
Silicon carbide fibers 262
Silicon dioxide 315
Silicon halides 253
Silicon nitride 161, 209, 216, 219,
  220, 221, 223, 225, 229,
  231, 239, 245, 259, 289,
  290, 311, 314, 316, 320,
  322, 324
  production 161
Silicon nitride blast nozzle 310
Silicon oxynitride 219
Silicon tetrachloride 289
Silyl amine 256
Sintering 257
Sintering additives 161, 258
Sintering agents 259
Sintering process 259
Sixth period 26
Sodium chloride 13
Sol-gel 116, 264, 265
Sol-gel process 256
Solid lubricant 316
Solid solutions 3, 91, 200
Solubility 68, 191
  of WC 107

Soluble 194, 195, 199, 204, 205
Solvents 236
sp^3 bond 24
sp^3 configuration 120
sp^3 hybrid 22
sp^3 orbital 22
Specific heat 58, 84, 146, 226
Sphalerite 123, 214
Spinnerets 264
Spray coatings 278
Sputtering 292, 295, 296, 297
  reactive 297
Stacking structure 124
Standard entropy 44
Steam turbines 302
Steel 282
Steel alloys 112
Steel balls 312, 316
Strength 67, 149, 229, 231, 267
  of WC 106
Stress 280
Structural characteristics 8
Structural parts 257
Submicron powder 116
Subshells 20
Substoichiometric compositions 182
Substrates 282
Superconducting coating 205
Superconductivity 188
Supersaturation 253
Surface properties 277
Switching 172

T

Ta-N phase diagram 205
TaC 95, 98
TaN 190, 252, 297
Tantalum 81, 164, 181
Tantalum carbide 95, 284
  production 98
Tantalum nitride 288
TDEAT 287
TDMAT 287
Temperatures
  deposition 289
  reaction 282
Tensile properties 66
Ternary carbides 107
  systems 68
Ternary carbides and nitrides 191
Ternary systems 314
Tetragonal orbital state 120
Tetrahedral sites 35, 169
Tetrahedron 34
Tetramethylsilane 253
Textile machinery 2
Thermal
    conductivity 85, 146, 184, 226
Thermal conductors 104
Thermal expansion 61, 85, 147, 185, 227, 280
Thermal functions 58
Thermal properties 57, 83, 102, 146, 176, 183
  of covalent nitrides 225
Thermal spray 250, 279, 300
Thermal-barrier coating 314
Thermal-decomposition temperature 259
Thermoelectric power 149
Thin film process 295
Thin films 137, 147, 278, 292, 325
Thoria 74
Thorium nitride 161
Ti-C 48
Ti-N phase diagram 194
Ti(C,N) 68
Ti(CN) 281
$Ti_{0.6}Hf_{0.4}C$ 68
TiB_2 270
TiC 41, 46, 270, 282, 298
TiC_xN_y 298
TiN 171, 175, 179, 187, 190, 195, 252, 293, 295, 297, 298
Titanium 55, 164, 181, 224
Titanium alkoxide 266
Titanium carbide 49, 55, 68, 280, 316
Titanium carbonitride 1, 194, 282
Titanium compounds 144
Titanium nitride 163, 181, 193, 205, 248, 259, 277, 287, 320, 322, 325
Titanium silicide 323
Titanium tetrachloride 282, 287
Toluene 282, 284
Tool coating industries 295

Tool steel 195, 283
Toughness 277
Toxic 279
Transformation of bSiC to aSiC 127
Transition elements 25, 26
Transition metal carbides 64, 66
Transition metal nitrides 172, 178, 181
Transition metals 15, 118
  early 169
Transition temperature 66
Trigonal prisms 36, 120, 172
Triode sputtering 297
Tungsten 100, 164
Tungsten carbide 36, 101, 104, 113, 115, 116, 256, 282, 300, 302, 314, 317
Tungsten carbide cobalt 320
Tungsten mononitride 172
Tungsten titanium carbide 107
Turbines 2, 302, 314
Turbochargers 311, 312
Tyranno 265, 266

U

Ultraviolet 325
Unit cell volume 133
Units 327
Urania 74
Uranium nitride 161

V

V-C phase diagram 91
V-N phase diagram 200
V_2O_3 253
Vacancies 48
Vacancy ordering 164
Vacuum-based ion plating 298
Valence concentration 48
Valence electrons 22, 26
Valence state 10
Van der Waal's bond 214
Vanadium 81, 92, 164, 181
Vanadium nitride 200
VC 68, 92
VN 190, 192, 252
VN/TiN 190

W

W-C 107
Wave function 20
  sign 22
WC 101, 104, 107
WC structure 31
Wear coatings 298
Wear resistance 68, 72, 110
Wear resistant coatings 195
Wear surfaces 156
Whiskers 249, 264, 271
Wurtzite 124, 212, 218

X

X-ray lithography 244

Y

Young's modulus 150

Z

Z number 165
Zinc sulfide 123, 124
Zincblende 123, 212, 214, 217, 218
Zirconia 314
Zirconium 55, 164, 181
Zirconium carbide 73, 284, 322
Zirconium nitride 195, 197, 288
Zr-C phase diagram 74
Zr-N phase diagram 195
Zr-N systems 172
ZrC 41
ZrN 190, 252