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THORIUM DIOXIDE:
PROPERTIES AND
NUCLEAR APPLICATIONS

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THORIUM DIOXIDE: PROPERTIES AND NUCLEAR APPLICATIONS

Edited by
J. BELLE and R. M. BERMAN

Naval Reactors Office
United States Department of Energy

NAVAL REACTORS HANDBOOKS

Liquid Metals Handbook.

First edition: Edited by R. N. Lyon, 1950.

Second edition: Edited by R. N. Lyon, 1952.

Third edition: (Sodium-NaK Supplement) Edited by C. B. Jackson. First printing June 1955; second printing (Revised), November 1955, Government Printing Office, Washington, D.C.

Metallurgy of Zirconium. Edited by B. Lustman and F. Kerze, Jr., 1955, McGraw-Hill Book Company, New York.

The Metal Beryllium. Edited by D.W. White and J. E. Burke, 1955, American Society for Metals, Cleveland.

Bibliography of Reactor Computer Codes, Report AECU-3078. Edited by R. S. Brodsky, 1955, Government Printing Office, Washington, D.C.

Reactor Shielding Design Manual. Edited by T. Rockwell III, 1956. (Published separately by Government Printing Office, McGraw-Hill Book Company, New York and D. Van Nostrand Company, Princeton, N.J.).

Corrosion and Wear Handbook for Water-cooled Reactors. Edited by D. J. DePaul, 1957 (Published separately by Government Printing Office and McGraw-Hill Book Company, New York).

Naval Reactors Physics Handbook. A. Radkowsky, Chairman of Editorial Board.

Volume I The Physics of Naval Reactors; Basic Techniques.
Edited by A. Radkowsky, 1964, Government Printing Office, Washington, D.C.

Volume II The Physics of Pressurized Water Reactors. Edited by S. Krasik, 1959 (Classified Edition only).

Volume III The Physics of Intermediate Spectrum Reactors. Edited by J. R. Stehn, 1958, Government Printing Office, Washington, D.C.

The Shippingport Pressurized Water Reactor. Naval Reactors Branch, Westinghouse Electric Corporation and Duquesne Light Company, 1958, Addison-Wesley Publishing Company, Reading, Mass.

The Metallurgy of Hafnium. Edited by D. E. Thomas and E. T. Hayes, Government Printing Office, Washington, D.C.

Uranium Dioxide: Properties and Nuclear Applications. Edited by J. Belle, 1961, Government Printing Office, Washington, D.C.

Neutron Absorber Materials for Reactor Control. Edited by W. K. Anderson and J. S. Theilacker, 1962, Government Printing Office, Washington, D.C.

Thorium Dioxide: Properties and Nuclear Applications. Edited by J. Belle and R. M. Berman, 1984, Government Printing Office, Washington, D.C.

FOREWORD

This is the sixth book on reactor materials published under sponsorship of the Naval Reactors Office of the United States Department of Energy, formerly the United States Atomic Energy Commission. This book presents a comprehensive compilation of the most significant properties of thorium dioxide, much like the book *Uranium Dioxide: Properties and Nuclear Applications* presented information on the fuel material used in the Shippingport Pressurized Water Reactor core.

Thorium dioxide is a fertile fuel material which was used in the Shippingport Light Water Breeder Reactor (LWBR) core. It is a ceramic form of thorium, an abundant material which has exceptional nuclear properties. Thorium-232, the stable and naturally occurring form of thorium, will transform to Uranium-233 upon absorbing a neutron in the reactor environment. Unlike Uranium-235 and Plutonium-239 which are not usable in thermal breeder reactors, Uranium-233 produces about 2.3 neutrons per thermal neutron absorbed making it possible to breed with thorium and Uranium-233 using conventional light water thermal reactor technology.

Thorium dioxide was tested extensively prior to its use in the LWBR core. Thorium dioxide also forms stable compounds when combined with uranium dioxide, thus allowing the fabrication of practical reactor fuel, as demonstrated in the LWBR. Irradiation testing has shown thorium dioxide-uranium dioxide to be highly resistant to corrosion in high temperature water and stable when exposed to neutron irradiation. Thorium dioxide-base fuel has a higher thermal conductivity than uranium dioxide-base fuel over most of the temperature range of interest and will release fewer fission products. This book provides a compilation of these properties. More detailed reports covering specific aspects of thorium dioxide-uranium dioxide have also been prepared throughout the development of the material and are referenced in this book as LWBR Development Program Technical Memoranda.

With fabrication of the Shippingport LWBR core nearing completion in 1976, the Advanced Water Breeder Applications (AWBA) program was established by Naval Reactors to develop and disseminate technical information which would assist U.S. industry in evaluating the LWBR concept for commercial-scale applications. AWBA Development Program Technical Memoranda are also referenced in this book.

The Shippingport LWBR core completed power operation on October 1, 1982. The core operated successfully for five years without refueling, giving a lifetime of 28,730 effective full power hours and peak local burnup of about 60,000 megawatt-days/metric ton without detectable fuel element failure. The core is being examined in detail to verify core performance including an evaluation of breeding characteristics and materials performance.

I extend my appreciation to the many persons who have given their expertise and efforts to the preparation of this book and, in particular, to Dr. J. Belle of the Bettis Atomic Power Laboratory for his technical contributions and stewardship in this endeavor.

Kinnaird R. McKee
*Director, Naval Nuclear
Propulsion Program*

August 1984

PREFACE

This book extends the study begun with publication in 1961 of *Uranium Dioxide: Properties and Nuclear Applications*. The earlier book organized information on uranium dioxide which had become available as a result of the rapid and extensive developments in nuclear reactor technology during the previous decade. A large part of that body of knowledge was obtained in the course of designing, building, and operating the Shippingport Pressurized Water Reactor (PWR). This work is a similar presentation of the technology developed in the process of investigating and utilizing thorium dioxide and thorium dioxide-uranium dioxide (thoria-urania) solid solutions as nuclear reactor fuel materials for the Shippingport Light Water Breeder Reactor (LWBR).

This book, like its predecessor, is a systematic and critical review of information on the properties and nuclear applications of a particular nuclear fuel material. In this volume, the material of concern is thoria, and the subject matter is restricted to this oxide and its solid solutions with urania. Although no attempt is made to update information on uranium dioxide, pertinent data on UO_2 are used and cited where that information is both relevant and necessary for a more complete understanding of thoria-base fuel materials. This work, it is hoped, will be as much a stimulus to further research on the thoria fuel system as was its predecessor for the urania fuel system.

The first chapter outlines applications of thorium dioxide in nuclear power reactors. The nuclear properties of thorium, as well as those of the isotopes ^{233}U and ^{233}Pa , are discussed in some detail in Chapter 2. Physical properties of ThO_2 and $\text{ThO}_2\text{-UO}_2$ are described in Chapter 3, and the various binary and ternary systems containing thoria are delineated in Chapter 4 on phase equilibria. Chapters 5, 6, and 7 deal, respectively, with thermodynamic and thermochemical properties, transport properties, and mechanical properties. Aspects of fabrication of ThO_2 and $\text{ThO}_2\text{-UO}_2$ fuels are treated in Chapter 8. Irradiation behavior and fuel performance of the thoria fuel system are

examined in Chapter 9. To complete the presentation of the thorium fuel cycle, reprocessing of $\text{ThO}_2\text{-UO}_2$ fuels is discussed in Chapter 10. Appendix A provides a ready reference to important properties of thorium dioxide.

Although the International System of Units, designated as SI, is used throughout, there are some data, primarily in graphs, expressed in the original units. For convenience, conversions between the SI and other unit systems are listed in Appendix B.

I wish to express my thanks to my coeditor, R. M. Berman, and to all chapter authors for their valuable contributions, and to J. Koffler for his help in editing all manuscripts for final publication. I also wish to thank Admiral H. G. Rickover for his initial sponsorship of this endeavor and H. F. Raab, Jr., R. H. Steele, and C. R. Thomas of the Naval Reactors Office of the United States Department of Energy, and R. A. Frederickson and J. A. Redfield of Bettis Atomic Power Laboratory, for their support and encouragement throughout the preparation of this book.

Jack Belle
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August 1984

CONTENTS

	Page
Chapter 1 APPLICATION OF THORIUM DIOXIDE IN NUCLEAR POWER REACTORS...	1
1.1 INTRODUCTION	1
1.2 HISTORY AND NONNUCLEAR APPLICATIONS	1
1.3 OCCURRENCE IN NATURE	3
1.4 THE THORIUM CYCLE: ADVANTAGES AND DISADVANTAGES	4
1.5 REACTOR EXPERIENCE WITH ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUELS	5
1.5.1 Elk River Reactor	5
1.5.2 Indian Point Reactor	7
1.5.3 High-temperature Gas-cooled Reactor	10
1.5.4 Light Water Breeder Reactor	13
1.6 OTHER REACTOR CONCEPTS	16
1.7 EFFECTS OF MATERIAL PROPERTIES ON FUEL PERFORMANCE	19
Chapter 2 NUCLEAR PROPERTIES OF THE THORIUM FUEL CYCLE	23
2.1 INTRODUCTION	23
2.2 THORIUM ISOTOPIC ABUNDANCE, NATURAL DECAY CHAINS, AND TRANSMUTATION CHAINS	25
2.2.1 Isotopic Abundance	25
2.2.2 Natural Decay Chains	26
2.2.3 Neutron-induced Transmutation Chains of Thorium	27
2.3 NEUTRON CAPTURE CROSS SECTION	30
2.3.1 Introduction	30
2.3.2 Thermal Capture Cross Section for ^{232}Th	34
2.3.3 Resonance Capture Cross Section	34
2.3.4 High Energy Neutron Capture: (n,γ) and $(n,2n)$ Reactions	37
2.3.5 Neutron Capture in Protactinium	40
2.3.6 Neutron Capture in ^{233}U	42
2.4 FISSION	43
2.4.1 Introduction	43
2.4.2 Fission Cross Section	45
2.4.3 Neutron Yield	45
2.4.4 Fission Product and Energy Yield	50
2.5 THORIUM NEUTRON SCATTERING CROSS SECTION	55
2.6 CROSS SECTIONS FOR THORIUM-GAMMA RAY REACTIONS	62
2.7 NUCLEAR PERFORMANCE OF THORIUM IN FISSION REACTORS	63
Chapter 3 PHYSICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	69
3.1 INTRODUCTION	69
3.2 PROPERTIES OF THE ThO_2 CRYSTAL LATTICE	71
3.2.1 Description of the Fluorite Structure	71
3.2.2 X-ray Diffraction Results	72
3.2.3 Theoretical Density	72
3.2.4 Neutron Diffraction Results	74
3.2.5 Lattice Thermal Vibration	75

Chapter 3	PHYSICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ —Continued	Page
3.3	BONDING IN THORIUM DIOXIDE	77
3.3.1	Atomic Radii	77
3.3.2	Electron Configuration	80
3.3.3	Lattice Energy	81
3.4	LATTICE DEFECTS IN ThO_2	82
3.4.1	Point Defects	83
3.4.2	Phase Transition	85
3.4.3	Dislocations or Line Defects	86
3.5	OPTICAL PROPERTIES OF CRYSTALLINE THORIA	86
3.5.1	Absorption Spectra	86
3.5.2	Fluorescence and Thermoluminescence	94
3.5.3	Optical Constants	96
3.6	THERMAL RADIATIVE PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	99
3.7	MAGNETIC PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	103
3.8	SUMMARY	113
Chapter 4	PHASE EQUILIBRIA	117
4.1	INTRODUCTION	117
4.2	THE THORIUM-OXYGEN SYSTEM	117
4.3	THE NATURE OF THORIUM DIOXIDE SOLID SOLUTIONS	122
4.3.1	Vegard's Law Behavior	122
4.3.2	Extent of Solid Solutions	125
4.3.3	Binary Phase Diagrams	126
4.4	THE THORIA-URANIA BINARY SYSTEM	128
4.4.1	Variation of Lattice Parameter with Composition	128
4.4.2	Calculation of Liquidus and Solidus	129
4.4.3	Thoria-Urania-Oxygen Pseudobinary	131
4.4.4	Cell Sizes in Cubic $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$	136
4.5	THE THORIA-PLUTONIA-OXYGEN SYSTEM	140
4.6	OTHER THORIUM DIOXIDE BINARY PHASE DIAGRAMS	143
4.6.1	The Thoria-Zirconia System	143
4.6.2	Thoria-Lanthanide Oxide Systems	146
4.6.3	The Thoria-Yttria System	150
4.6.4	The Thoria-Calcia System	153
4.7	BINARY COMPOUNDS OF THORIUM DIOXIDE	156
4.8	THORIUM DIOXIDE TERNARY SYSTEMS	158
4.9	SUMMARY	160
Chapter 5	THERMODYNAMIC AND THERMOCHEMICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	167
5.1	INTRODUCTION	167
5.2	THERMAL EXPANSION	167
5.2.1	Introduction	167
5.2.2	Thermal Expansion Data for ThO_2	169
5.2.3	Thermal Expansion Data for UO_2	173
5.2.4	Thermal Expansion of $\text{ThO}_2\text{-UO}_2$	175
5.2.5	Volume Expansion on Melting	175
5.3	DENSITIES OF $\text{ThO}_2\text{-UO}_2$ SOLID SOLUTIONS	180
5.4	CHANGE OF STATE	180
5.4.1	Melting Temperature	180
5.4.2	Heat of Fusion	182
5.4.3	Vapor Pressure	183
5.4.4	Boiling Point	187

Chapter 5	THERMODYNAMIC AND THERMOCHEMICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ —Continued	Page
5.5	ENTHALPY AND HEAT CAPACITY	188
5.5.1	Assessment of the Enthalpy and Heat Capacity Data for Uranium Dioxide	188
5.5.2	Measurements on ThO_2	192
5.5.3	Enthalpies and Heat Capacities of $\text{ThO}_2\text{-UO}_2$ Solid Solutions	198
5.5.4	Heat Capacity at Constant Volume	201
5.6	HEAT AND FREE ENERGY OF FORMATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	203
5.7	MISCELLANEOUS THERMOPHYSICAL PROPERTIES	207
5.7.1	Debye Temperature	207
5.7.2	Grüneisen Parameter	209
5.8	THERMODYNAMIC PROPERTIES OF HYPOSTOICHIOMETRIC THORIA	212
5.8.1	Oxygen Potential Measurements	212
5.8.2	Free Energy of Formation of ThO_{2-x}	213
5.8.3	High-temperature Vaporization of ThO_{2-x}	214
5.9	THERMODYNAMICS OF THE $\text{ThO}_2\text{-UO}_2\text{-O}$ SYSTEM	217
5.9.1	Oxygen Potentials and Activity Coefficients	218
5.9.2	Oxygen Potentials and Gibbs Free Energies of Formation	227
5.9.3	Oxygen Potentials and Vapor Pressures	227
5.10	CHEMICAL REACTIVITY	231
5.10.1	Thermal Stability in Air	231
5.10.2	Stability in High-Temperature Water	231
5.10.3	Compatibility Behavior	232
5.10.4	Dissolution Reactions	232
5.11	SURFACE PROPERTIES	232
5.11.1	Surface Energy	232
5.11.2	Adsorption of Gases and Liquids by Thorium Dioxide	234
5.12	SUMMARY	236
Chapter 6	TRANSPORT PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	243
6.1	INTRODUCTION	243
6.2	DIFFUSION PROCESSES IN ThO_2 AND $\text{ThO}_2\text{-UO}_2$	243
6.2.1	Introduction	243
6.2.2	Volume Diffusion	245
6.2.3	Short Circuit Diffusion	259
6.3	ELECTRICAL CONDUCTIVITY	264
6.3.1	Introduction	264
6.3.2	Defect Equilibria and Electrical Conductivity	264
6.3.3	Electrical Conduction in Pure and Doped ThO_2	270
6.3.4	Electrical Conductivities of $\text{ThO}_2\text{-UO}_2$ Solid Solutions	285
6.3.5	Ionic Conductivity and Diffusion	288
6.4	THERMAL CONDUCTIVITY OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	290
6.4.1	Introduction	290
6.4.2	Heat Transfer in Oxide Ceramics	292
6.4.3	Effect of Porosity on Thermal Conductivity	296
6.4.4	Consensus of Thermal Conductivity Data for UO_2	298
6.4.5	Thermal Conductivity Data for ThO_2 and $\text{ThO}_2\text{-UO}_2$	302
6.5	SUMMARY	312
Chapter 7	MECHANICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	319
7.1	INTRODUCTION	319

Chapter 7	MECHANICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ —Continued	Page
7.2	ANISOTROPY	319
7.3	TEMPORARY DEFORMATION	321
7.3.1	Elastic Properties	321
7.3.2	Effect of Microstructure	325
7.3.3	Effect of Temperature	328
7.3.4	Effect of Composition	329
7.4	PERMANENT DEFORMATION	330
7.4.1	Slip	331
7.4.2	Plastic Deformation	331
7.4.3	Creep Deformation	333
7.4.4	Effect of Composition	337
7.4.5	Hot Pressing	340
7.5	FRACTURE	344
7.6	HARDNESS	344
7.6.1	Effect of Temperature	345
7.6.2	Effects of Composition and Porosity	347
7.7	RUPTURE	350
7.8	THERMAL SHOCK	355
7.9	SUMMARY	357
Chapter 8	FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUELS	361
8.1	INTRODUCTION	361
8.2	TYPES OF FUEL ELEMENTS	361
8.2.1	Sol-Gel Microspheres	361
8.2.2	Vibratory-packed Fuel Elements	362
8.2.3	Metal-clad Pellets	362
8.3	SOURCE MATERIALS	363
8.4	POWDER PREPARATION METHODS	364
8.4.1	Pyrolysis of Thorium Oxalate	364
8.4.2	Pyrolysis of Other Thorium Compounds	368
8.4.3	Direct Decomposition of Thorium Nitrate	368
8.4.4	Preparation of UO_2 Powders	369
8.4.5	Preparation of $\text{ThO}_2\text{-UO}_2$ Powders by Coprecipitation	369
8.4.6	Preparation of $\text{ThO}_2\text{-UO}_2$ Powders by Mechanical Mixing Methods	371
8.5	PARTICLE PREPARATION PROCESSES	373
8.5.1	Sol-Gel Methods	373
8.5.2	Freeze-dry Process	375
8.5.3	Mechanical Methods	376
8.5.4	High Temperature Techniques	377
8.5.5	Large and Single-crystal Processes	377
8.6	CHARACTERIZATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FEED MATERIAL	378
8.6.1	Physical Characterization Data	378
8.6.2	Chemical Characterization Data	395
8.7	FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ PELLETS	397
8.7.1	Cold Pressing and Sintering	397
8.7.2	Other Methods	401
8.8	THERMODYNAMIC ASPECTS OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUEL FABRICA- TION	402
8.8.1	Pretreatment in Carbon Dioxide	402
8.8.2	Presintering and Sintering in Hydrogen	406

Chapter 8	FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUELS—Continued	Page
8.9	SINTERING OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	408
8.9.1	Introduction	408
8.9.2	Densification	411
8.9.3	Grain Growth	417
8.10	LWBR EXPERIENCE WITH FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	
	PELLETS	418
8.10.1	Powder Preparation Problems	418
8.10.2	Powder Processing Problems	419
8.10.3	Pellet Pressing Problems	420
8.10.4	Pellet Pretreatment Problems	421
8.10.5	Pellet Sintering Problems	422
8.10.6	Pellet Post-sintering Problems	424
8.11	SUMMARY	425
Chapter 9	IRRADIATION BEHAVIOR OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$	437
9.1	INTRODUCTION	437
9.2	RADIATION DAMAGE IN FLUORITE-TYPE LATTICES	439
9.2.1	Effect of Alpha Particles	439
9.2.2	In-Reactor Effects	440
9.3	STRUCTURE AND PROPERTY CHANGES	442
9.3.1	Microstructural Changes	442
9.3.2	Dimensional Stability	445
9.3.3	Property Changes	462
9.4	FISSION PRODUCT RELEASE AND CONTAINMENT	475
9.4.1	Fission Yields of ^{233}U and ^{235}U	475
9.4.2	Behavior of Solid Fission Products	479
9.4.3	Behavior of Volatile Fission Products	487
9.5	SUMMARY OF FUEL BEHAVIOR	502
Chapter 10	REPROCESSING OF $\text{ThO}_2\text{-UO}_2$ FUELS	509
10.1	INTRODUCTION	509
10.1.1	Nuclear Reactions of the Thorium Fuel Cycle	509
10.1.2	Effect of ^{232}U on Reprocessing Operations	511
10.2	HEAD-END PROCESSING OPERATIONS	512
10.2.1	Decanning	514
10.2.2	Decladding	514
10.2.3	Voloxidation	520
10.2.4	Fuel Dissolution for Aqueous Reprocessing	521
10.2.5	Auxiliary Reprocessing Operations	522
10.3	SEPARATION OPERATIONS	524
10.3.1	Solvent Extraction from Aqueous Solution	524
10.3.2	Nonaqueous Separation Processes	533
10.4	TREATMENT OF WASTES FROM REPROCESSING SPENT $\text{ThO}_2\text{-UO}_2$	
	FUEL	542
10.4.1	Characterization of Reprocessing Wastes	542
10.4.2	Treatment of Gaseous Reprocessing Wastes	544
10.4.3	Treatment of Liquid Reprocessing Wastes	545
10.4.4	Handling of Solid Reprocessing Wastes	548
10.5	SUMMARY	549
Appendix A	SUMMARY TABLE: PROPERTIES OF ThO_2	555
Appendix B	CONVERSION TABLE	559
Index		561

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Chapter 1

APPLICATION OF THORIUM DIOXIDE IN NUCLEAR POWER REACTORS

J. Belle and R. M. Berman

1.1 INTRODUCTION

The sole reason for using thorium in nuclear reactors is the fact that thorium can be converted by neutron capture into ^{233}U , an isotope of uranium that does not exist in nature. When a thermal neutron is absorbed by this isotope, the number of neutrons produced is sufficiently larger than 2.0 to permit breeding in a thermal nuclear reactor, as discussed in Chap. 2. No other fuel can be used for thermal breeding applications.

Since extensive reviews of the use of thorium dioxide in nuclear power reactors have been made in earlier publications (IAEA, 1966 and IAEA, 1979), no attempt is made to cover the same ground. After a brief review of the nonnuclear applications of thorium dioxide and its occurrence in nature, the following topics are summarized: (1) advantages and disadvantages of the thorium fuel cycle; (2) experience with ThO_2 -fueled reactors; (3) new reactor concepts using ThO_2 ; and (4) effects of material properties on fuel performance.

1.2 HISTORY AND NONNUCLEAR APPLICATIONS

Thorium was discovered by Berzelius in 1829 in a mineral which he named thorite for the Norse god of thunder, Thor. The mineral is nominally ThSiO_4 , and had been obtained from an island in Langesund Fjord in Norway. Berzelius obtained metallic thorium by reduction of anhydrous ThCl_4 using alkali metals. The radioactivity of thorium was reported by the Curies in 1898, in one of the early papers on radioactivity; it was also discovered simultaneously by Schmidt. A more complete history of thorium may be obtained in Gmelin (1955).

Thorium dioxide can be prepared by heating thorium metal, or a wide variety of other thorium compounds, in air. It occurs typically as a fine

white powder and is extremely refractory and resistant to chemical attack. It is a cubic, fluorite-type compound with a theoretical density of 10 Mg/m³ (see Chap. 3).

In 1886, Welsbach discovered that ThO₂-CeO₂ solid solutions, with approximately 1 mole percent ceria, have a highly abnormal emissivity spectrum in the visible range. When heated in a gas flame to 1200-1600 K, they display a brilliant white incandescence, slightly tinged with yellow, instead of the normal red-orange color. This property is utilized in the Welsbach Gas Mantle, an open-weave cotton tube saturated with thorium-cerium nitrate solution and dried. When this is suspended in the flame of a gas lamp, the cotton is burned away, leaving a fragile shell of thoria-ceria solid solution. The incandescence of this material transforms the energy of the flame to usable light with a high degree of efficiency. The Welsbach Gas Mantle enjoyed considerable commercial success. It was not until World War I that Edison's incandescent filament bulbs were recognized as being clearly superior. The development of the Welsbach Gas Mantle was largely responsible for most of the prenuclear research on thorium dioxide.

Aside from the gas mantle, the only significant nonnuclear use of thoria is in certain critical research applications where its extremely refractory nature is required. In a tungsten resistance furnace designed to operate above 2500 K, for example, the tungsten tube that serves both as a muffle and a heating element is surrounded by loosely packed, low-density sintered bodies of thoria which fill the space between the tungsten and the outer shell of the furnace. The U.S. Bureau of Mines (1981) estimated that American consumption in 1981 was 39 tons, including 14 tons for refractories, 9 tons for gas mantles, 3 tons as hardeners of magnesium-thorium alloys, and 3 tons for thoriated tungsten welding rods.

Thoria has also been used as an oxygen ion-conducting solid electrolyte in galvanic cells. In this application thoria generally is doped with an alkaline earth oxide or a rare earth oxide.

Although thoria has been used as an additive to the standard cobalt Fischer-Tropsch catalyst in the synthesis of hydrocarbons, it appears that thoria may itself be a suitable economic catalyst, according to some reported experimental work by Colmenares and McLean (1981). These workers showed that thoria can catalyze the synthesis of either methane or mixtures of saturated and unsaturated hydrocarbons (C₁ to C₆) from mixtures of CO and H₂. Thoria overcomes one limiting factor affecting the economic use of all current Fischer-Tropsch catalysts, namely, the poisoning effect of sulfur. Since ThO₂ does not react with sulfur under the conditions of the Fischer-Tropsch reaction, it does not lose its catalytic activity. Moreover, with use of ThO₂ as the catalyst, it may not be necessary to reduce the sulfur content of gas mixtures to the parts per billion range, as is required for all currently used catalysts.

1.3 OCCURRENCE IN NATURE

According to the U.S. Bureau of Mines (1975), thorium occurs in the earth's crust to the extent of 5.8 ppm, as compared to 1.7 ppm for uranium; there is therefore approximately 3.4 times as much thorium as uranium. These concentrations must be increased by factors on the order of 1000 for mining to be economically feasible.

Natural thorium consists of essentially one isotope, ^{232}Th , with only trace quantities of other much more radioactive thorium isotopes. In particular, an equilibrium concentration of ^{228}Th is produced by alpha decay of ^{232}Th (half life is 1.4×10^{10} years) followed by beta decay of the short-lived intermediate nuclides ^{228}Ra and ^{228}Ac . The isotope ^{228}Th , whose half life is 1.9 years, is the precursor of a chain of alpha, beta, and gamma emitting nuclides, which produce most of the radiation emitted by natural thorium.

There are comparatively few minerals for which thorium occurs as an essential constituent, and all of them are also compounds of oxygen. Also, in no recorded case in the geological or mineralogical literature is the thorium pure, in the sense that it is the only cation occupying that particular place in the crystal structure. All thorium minerals are solid solutions, in which uranium, yttrium, and lanthanides may proxy for the thorium, usually to the extent of several mole percent.

The most important minerals with thorium as an essential constituent are thorite, ideally ThSiO_4 , and thorianite, ideally ThO_2 . Thorite has a rare polymorph, Huttonite, also ThSiO_4 . These minerals occur in pegmatites, a type of igneous rock that represents the last residuum of a molten body to solidify. Pegmatites therefore contain materials that were not present in sufficient concentrations to crystallize as separate phases during earlier stages of the cooling. However, pegmatites are, generally speaking, too small for commercial mining. Thorium minerals have been reported from such bodies in Scandinavia, the Canadian Shield, Sri Lanka, the Malagasy Republic, and the western United States.

Where thorium bodies such as these are exposed to erosion at the surface of the earth and weathered, some thorianite and thorite survive; occurrences have been reported in stream gravels. For the most part, however, thorium is lost to the ocean in aqueous solution. In this regard, its behavior differs somewhat from that of uranium. Thorium, unlike uranium, is not oxidized above the +4 state; there are therefore no analogues to the "secondary" U^{+6} and uranyl minerals that may be found where uranium deposits are exposed to the atmosphere. (In the normal course of events, such uranium is also lost in aqueous solution to the oceans.) Some secondary thorium minerals have been reported, such as the ill-defined "thorogummite". However, these may be considered secondary uranium minerals, with the thorium physically entrained in a nonessential role.

Thorium occurs in solid solution replacing zirconium in the mineral zircon, nominally ZrSiO_4 , and replacing cerium in monazite, nominally CePO_4 . Concentrations of thorium can reach several weight percent of these minerals. Zircon and monazite are resistant to erosion; therefore they can be gathered, by natural processes, from a very large volume of eroded rock. They can be further concentrated as a result of water transport, since they have higher densities than most of the constituents of sands and gravels. Further concentrations can be carried out by means of gravity, using water suspensions.

Commercial thorium deposits consist largely of monazite sands. These deposits are widespread, and limitation of supply is not a factor in the utilization of thorium. Monazite sand deposits occur in the Piedmont regions of the Carolinas, in central Florida, in Brazil, and in Malaysia. Probably the largest deposits are the beach sands of the state of Kerala, in extreme southern India. All current production of thorium is as a by-product; the sole American producer obtains the material as a result of zircon sand processing in central Florida.

1.4 THE THORIUM CYCLE: ADVANTAGES AND DISADVANTAGES

The development of thorium-base fuels has been motivated by the superior nuclear properties of the thorium fuel cycle when applied in thermal reactors. The development of the uranium fuel cycle preceded that of thorium because of the natural occurrence of a fissile isotope in natural uranium, ^{235}U , which was capable of sustaining a nuclear chain reaction. Once the utilization of uranium dioxide nuclear fuels had been established, development of the isostructural compound, thorium dioxide, followed logically. This fuel would be the basis of a reactor design using the thorium cycle. The isotope ^{232}Th , rather than ^{238}U , would be the fertile material, and the isotope ^{233}U would be the principal fissile actinide product, playing the role that is assigned to ^{239}Pu in the uranium cycle.

Thorium dioxide is known to be one of the most refractory and chemically nonreactive solid substances available. Many advantages of this material over uranium dioxide are known. Its melting point is higher—indeed, among the highest measured. It is not subject to oxidation beyond stoichiometric ThO_2 . At comparable temperatures, over most of the expected operating range, its thermal conductivity is higher than that of UO_2 .

However, disadvantages of the thorium cycle were also known for some time. The thorium cycle produces more fission gas per fission, although experience has shown that thorium dioxide is superior to uranium dioxide

in retaining these gases. The recycling of thoria-base fuels, or the "spiking" of initial-load fuels with ^{233}U , is more difficult because the ^{233}U always contains ^{232}U as a contaminant. This isotope decays to 1.9-year half life ^{228}Th , which produces strong gamma and alpha emitters in its decay chain. All handling of such materials must be done under remote conditions, with containment. A further disadvantage was simply that the information on ThO_2 and $\text{ThO}_2\text{-UO}_2$ was much less complete than that on UO_2 .

A series of studies, reviewed in Chap. 2, indicated that it should be possible to build a thorium-cycle breeder, moderated by light water and utilizing much of the technology developed for pressurized water reactors. Among the possibilities discussed was that of retrofitting existing light water reactors with thorium-cycle replacement cores. The Shippingport (Pa.) plant was indeed retrofitted in this way, with the LWBR core. The fuel technology developed and utilized for this task is the principal subject of the present work.

1.5 REACTOR EXPERIENCE WITH ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUELS

The Elk River (Minn.) Reactor, the Indian Point No. 1 (N.Y.) Reactor, the HTGR (High-temperature Gas-cooled Reactor), and the LWBR (Light Water Breeder Reactor) are among the reactor designs featuring nuclear fuel composed largely of thorium dioxide.

1.5.1 Elk River Reactor

The Elk River Reactor was a small demonstration BWR (Boiling Water Reactor) with a rating of 58 MW(th). Its fuel consisted of right circular cylinders of $\text{ThO}_2\text{-UO}_2$, 1.035 cm in diameter and 1.27 cm long. Two compositions were used; 20 of the 148 fuel elements contained ThO_2 -5.27 mole percent UO_2 , and the remainder contained ThO_2 -4.36 mole percent UO_2 , with the uranium enriched to approximately 92 percent ^{235}U in total U. Densities of approximately 94 percent of theoretical were obtained by the addition of 0.4 weight percent CaO or TiO_2 , replacing an equivalent amount of thoria, before sintering. Boron (600 ppm) was also added as a burnable poison. The stack of fuel pellets in a rod was approximately 152.4 cm long. Cladding was 304 stainless steel, 0.051 cm thick. Nominal outside diameter of the rods was 1.148 cm.

The core was arranged as shown in the cross-sectional diagram in Fig. 1.1 (Audi et al, 1964). The elements marked "X" contained no fuel, those marked "S" contained the fuel with 5.27 mole percent UO_2 . However, these fuel elements contained central pins of boron steel, which acted

Figure 1.1. Horizontal Cross Sections through the Elk River Reactor: (a) Core, (b) Quadrant, (c) Typical Module (Courtesy, Allis-Chalmers Corporation).

as shims such that the reactivity of these bundles was the same as for ThO_2 -4.36 mole percent UO_2 bundles. Figure 1.1 also shows the cruciform control rods between the fuel bundles.

A prototype fuel element was irradiated to 0.24×10^{20} fissions/ cm^3 or 0.24 fission units (see Chap. 9). Postirradiation examination showed no dimensional changes, no thermal effects, and little cracking (Neimark, 1961).

The reactor attained criticality in November 1962, and was operated until final shutdown on January 31, 1968, producing 1.27 million MWhr(th) of power (United Power Association, 1974). The primary coolant system developed extensive stress-corrosion cracking, which led to the reactor's decommissioning and eventual dismantling in 1971-1975. Detailed dimensional change and metallographic studies of the actual reactor fuel (rather than the prototype) are apparently not available. However, the reactor fuel appears to have functioned satisfactorily, and did not contribute to Elk River's difficulties.

Two fuel rods of the Elk River Reactor were shipped to the Bettis Laboratory for postirradiation evaluation. Two unirradiated backup rods were also available for comparison. Average depletion for the two irradiated rods was 2.13 fission units. Neutron radiographs showed very little pellet cracking; only a few of the pellets in each rod were cracked, and these had only single cracks. Dimensional changes of the fuel stack in the axial direction were about 0.25 cm in one rod, and 1.5 cm in the other, in the nominal length of 152 cm. The rods were punctured, and a measurement was made of the fission-generated krypton and xenon gas released. It was, for the two rods, 0.14 and 0.20 percent of the amount generated. It was further noted that the homogenization of the ThO_2 - UO_2 fuel of the Elk River Reactor was poorer, by an order of magnitude, than the results being obtained in 1973 during the development work for the Light Water Breeder Reactor.

1.5.2 Indian Point Reactor

Indian Point Reactor No. 1 was a pressurized water reactor (PWR) with a rating of 270 MW(e). The fuel consisted of sintered right circular cylinders of ThO_2 and ThO_2 - UO_2 , 0.66 cm in diameter and 1.9 cm long. Nominal density was 94.5 percent of theoretical. The core was divided into three separate concentric zones, as shown in Fig. 1.2. Cross sections of the fuel rod assemblies are shown in Fig. 1.3; each of three zones had an individual loading plan for the various compositions used. Some of the rods on the periphery of the assemblies had lower concentrations of UO_2 than those in the interior; and assemblies on the periphery of the core had lower concentrations of UO_2 than those in the interior. The six compositions used

Figure 1.2. Cross Section of Indian Point Reactor No. 1, Core 1.
(Courtesy, International Atomic Energy Agency, Vienna)

ranged from pure ThO_2 to ThO_2 -9.1 mole percent UO_2 . The uranium was enriched to 93 mole percent ^{235}U in total uranium. Compositions are given in the caption of Fig. 1.3.

The ThO_2 - UO_2 fuel was used only for the first core of Indian Point No. 1. After three years of operation, this core was replaced by a core of different design, containing only UO_2 fuel. Core 1 had operated satisfactorily, at least in regard to its ThO_2 base fuel. However, to continue with ThO_2 - UO_2 fuel, it was necessary to use highly enriched uranium, which resulted in a considerable increase in cost. Also, reprocessing technology was not available. For these reasons and others, subsequent cores at Indian Point used UO_2 fuel.

Baroch et al (1969) and Kerr et al (1980) reported on the examination of several Indian Point No. 1 Core 1 fuel rods after their removal from the core. Maximum burnup achieved for these rods was 8 fission units (8×10^{20} fissions/cm³ of fuel). Photomicrographic montages showed an equiaxed grain structure throughout, with some intragranular porosity remaining even at the center of the rods. Gas release was 1 to 2 percent,

Figure 1.3. Cross Section of the Fuel Assembly of Indian Point: No. 1, Core 1, Showing the Distribution of Fuel Composition in Each of the Three Zones. Th:U Ratios are as Follows: A-33, B-23, C-17, D-12, E-10. Rods Labeled "F" are Comparable to Those Labeled "A", Except that the Middle Third of their Axial Lengths Contains Pellets of Pure ThO_2 . (Courtesy, International Atomic Energy Agency, Vienna)

consistent with a maximum fuel temperature of about 1900 K. Some bowing and ovality changes were noted, but generally the rods could be characterized as having exceptionally good dimensional stability. Baroch et al also noted that gamma scans detected misplaced pellets, i.e., pellets of the wrong composition for the regions in which they were located. However, there were no reports of problems due to the higher-than-intended power peaking which could have occurred as a result of misplaced fuel pellets. The references also showed a photograph of a pellet, intact after removal from the cladding. Other photographs showed some chipping of edges and cracks in the outer diameter of the pellet.

1.5.3 High-temperature Gas-cooled Reactor

The High-temperature Gas-cooled Reactor (HTGR) design was originated to explore the potential for higher temperature operation, and therefore higher efficiency, than is achieved in pressurized water reactors. The coolant in the HTGR is helium, typically at a temperature of 1050 K; it passes through a heat exchanger and produces steam at 811 K. Comparable temperatures for a PWR are 616 K and 560 K, respectively.

A demonstration reactor of the HTGR type, rated at 40 MW(e) net, was operated by the Philadelphia Electric Company from March 3, 1966, to October 31, 1974, at Peach Bottom, Pa. (Everett and Kohler, 1978). At the end of that period, its second core having successfully completed its entire design lifetime, the decision was made to decommission the plant. The benefits to be derived from further operation were judged insufficient to justify the large expenses that would be incurred in satisfying the requirement for a permanent license. A commercial plant of the HTGR type, rated at 330 MW(e) net, has been operated since 1976 at Fort St. Vrain, Colorado, by the Public Service Co. of Colorado. A vertical cross section of this reactor, showing the placement of the core and associated equipment in the prestressed concrete reactor vessel (PCRVR), is shown in Fig. 1.4 (Habush and Walker, 1974).

The fuel of the HTGR consists of two types of microspheres, randomly intermixed and distributed in a carbon matrix that serves as the moderator. These two types are termed fissile and fertile (see Chap. 2). In the fissile microspheres, the kernels consist of uranium carbide highly enriched in ^{235}U ; in the fertile microspheres, the kernels consist of high-density thorium (99 percent of theoretical) produced by the sol-gel process described in Chap. 8. In the first core of the Peach Bottom Reactor, these microspheres had, as a coating, a single layer of high-density pyrolytic carbon which was, in turn, in contact with the carbonaceous matrix (the

Figure 1.4. Cutaway View of the Fort St. Vrain HTGR (Courtesy, Nuclear Engineering and Design).

so-called BISO fuel elements). The fuel swelled during operation, cracking the pyrolytic carbon coatings and causing the release of an unacceptable amount of fission gases. (No information is available on the extent to which the thoria spheres, specifically, contributed to this phenomenon.) The first core was removed after half its design lifetime (450 of the 900 effective full power days, EFPD), and Core 2, containing the so-called TRISO fuel elements, was substituted. In these, the microsphere kernels, 400 μm in diameter, were coated by two pyrolytic carbon layers: the first, a low-density layer 55 μm thick with a density of 1.2 Mg/m^3 , served to accommodate the swelling; the second, a high-density layer 76 μm thick with a density of 1.97 Mg/m^3 , served to contain the fission gases. The total exterior diameter of the microspheres, as coated, was 662 μm .

These microspheres were distributed through a mixture of pitch (i.e., long-chain hydrocarbons) and graphite, to the extent of 40 percent of its total volume. The resulting mixture was placed in graphite sleeves which served as cladding. In Core 2 of the Peach Bottom Reactor No. 1, these sleeves had an outside diameter of 8.89 cm, a thickness of 0.96 cm, and a length of 3.66 m. Finally, the mixture of pitch and graphite was carbonized by a heat treatment. Most of the fuel elements (702) for this core had a graphite/thorium/uranium atom ratio of 1727/5.44/1.0, and 102 of the fuel elements had a ratio of 3087/22.7/1.0. The 102 high-thoria, high-graphite fuel elements served as a blanket and reflector, and were arranged around the periphery of the core.

Fuel elements containing thoria spheres of the TRISO type were subjected to irradiation testing and attained burnups as high as 15 percent of the original thorium present, which would require about 34 fission units. Typical center temperatures were 1500-1700 K. Gas release, from the entire fuel element, was on the order of 0.1 percent of the amount generated (Homan et al, 1974). Metallographic examination of sections cut through fertile spheres showed uniform spherical gas bubbles about 2 μm in diameter. In some cases, the thoria kernels had migrated through the surrounding carbon coatings; they were up to 15 μm less than their original thickness on the high-temperature side of the thoria kernel. An equal thickness of carbon, in the form of columnar grains, had been deposited in the vacated region on the cold side of the kernel.

In the HTGR concept, it was proposed to recover and reprocess the fertile microspheres of one reactor generation to produce some of the fissile fuel for the next generation. To simulate this recycled material, Long et al (1974) irradiated fuel elements with microspheres of ThO_2 , 2-, 20- and 31-mole percent UO_2 , using uranium highly enriched in ^{235}U rather than ^{233}U , as it would be in actual recycled material. Postirradiation examinations showed results very similar to those described above for pure thoria kernels.

1.5.4 Light Water Breeder Reactor

A light water breeder core, using the thorium- ^{233}U cycle, was designed, built, and installed in the pressure vessel of the original Shippingport (Pa.) PWR as its last core before decommissioning. The design output of the LWBR was 60 MW(e) net, the same as for the first Shippingport core. The original design lifetime for the LWBR core was 15,000 Effective Full Power Hours (EFPH). However, after a history of successful operation, lifetime was extended, and the reactor was shut down on October 1, 1982, after achieving 28,730 EFPH. A detailed program for proof of breeding is being undertaken concurrently with the disassembly and examination of the core. The fissile inventory ratio (FIR) will be determined; this is the ratio of final to initial fissile atoms.

The fuel of LWBR consisted, initially, of ThO_2 and $\text{ThO}_2\text{-UO}_2$ solid solutions, in the form of high-density (greater than 96 percent of theoretical) sintered pellets. The fuel in the core was zoned, both radially and axially (Figs. 1.5 and 1.6). There was a 2.66 m fueled length of each rod. The interior three seed-blanket modules were designed to permit use in a large light water breeder reactor plant (see Brennan et al, 1982). To provide the theoretical environment of a large core, the three interior modules were surrounded by nine larger modules with outer portions containing more highly loaded power flattening (p.f.) blanket zones. To reduce neutron leakage from the relatively small Shippingport reactor to that of a large LWBR, reflector modules containing pure thorium surrounded the 12 seed-blanket modules. The 12 hexagonal blanket modules forming the interior of the core (some of which are partially in the power-flattening blanket region) each contained identical interior hexagonal bundles of rods with the seed compositions and dimensions. Reactivity control was achieved by raising or lowering these seed bundles as a uniform bank relative to the surrounding blanket modules (Fig. 1.7). There were no poison control rods or burnable poisons, since it was necessary to keep neutron-absorbing materials in this breeder core to a minimum.

The ends of the pellets contained dishes, i.e., depressions corresponding to spherical segments 0.23 to 0.36 mm deep, occupying most of the end. Beyond the periphery of the dish, there was a small flat annular surface termed the land, or shoulder, which was normally in contact with a similar surface on the next pellet in the rod. The dish was omitted from the top of the uppermost pellets, to provide a bearing surface for a plenum spring (Fig. 1.8).

The function of these dishes was to minimize in-pile increases in fuel rod length. The pellets were also chamfered, to aid loading into the rod, and tapered, to minimize the formation of bamboo-like ridges on the exterior

Figure 1.5. Modules and Fuel Regions of LWBR.

of the cladding during irradiation. Detailed dimensions for each of these features, on each of the pellet types, are given by Connors et al (1979), together with specifications of the Zircaloy-4 cladding, which varied in thickness among the various types of rods from 0.56 mm (in the seed rods) to 1.07 mm (for reflector rods).

The breeder design required a very close spacing of the rods, and it was therefore particularly important that in-pile expansion of length did not lead to excessive bowing, which would constrict the coolant channels. In this design, the rods were held by a spring grid, and length changes were accommodated by sliding under the springs. The rods were held in position by hexagonal honeycomb grids of AM-350, a semi-austenitic precipitation hardened stainless steel (see Fig. 1.9).

The LWBR was shut down for the final time on October 1, 1982. In five years of operation, it accumulated 28,730 effective full power hours, for a

Figure 1.6. Movable Fuel Control and Axial Fuel Zoning in LWBR.

65 percent capacity factor (including semiannual shutdowns for technology testing) in this first-of-a-kind reactor. No fuel failures were observed. Reactivity and other nuclear parameters measured throughout life agreed well with predictions and indicated that the breeding of new fissile material may have exceeded predictions. Maximum burnup in the LWBR fuel was approximately 15 fission units or approximately 60,000 MWD/MT.

Figure 1.7. Control of LWBR by Vertical Movement of Seed Modules.

1.6 OTHER REACTOR CONCEPTS

In a survey of the status and prospects for thermal breeders, the International Atomic Energy Agency (1979) briefly described some concepts of

Figure 1.8. Typical LWBR Blanket Fuel Rod. Dimensions are in Inches.

thoria-fueled reactors other than those discussed in Sect. 1.5. These concepts, together with their generally recognized abbreviations, are as follows: the Canadian Deuterium Uranium (CANDU) type reactor with

Figure 1.9. Use in LWR of Grids Incorporating Flat Springs to Hold Fuel Rods in Position, While Permitting Axial Movement. Dimensions are in Inches.

thoria-base fuel (CANDU-Th); the Molten Salt Breeder Reactor (MSBR); and the Heavy Water Suspension Reactor (HWSR). All are intended to be near-breeder or breeder designs. Provision is made whereby initial loadings using ^{235}U would be replaced by ^{233}U formed from ^{232}Th as operation proceeded.

As a further development of LWBR technology, a series of reactor designs called, collectively, AWBA (Advanced Water Breeder Applications) was formulated. Among these concepts was one calling for a general scale-up of the LWBR design (Johnson, 1982); one involving control by movable thorium "finger" rods (Webb, 1982); and another called the Advanced Movable Fuel Breeder (Schneider, 1982), using smaller, more highly loaded blanket assemblies and less Zircaloy in the core than LWBR. These concepts require use of a prebreeder to produce the ^{233}U for the breeder and also include innovations such as the use of Zircaloy instead of AM-350 grids (Horwood et al, 1981, and Horwood, 1982) and of large-diameter blanket and reflector rods.

Other new design approaches included a study of the possibility of using duplex pellets, with an annular design. The central portion of these pellets would consist of high-density thorium during the initial loading, and the periphery would contain UO_2 enriched in ^{235}U (in the prebreeder) or ThO_2 - $^{233}\text{UO}_2$ (in the reprocessed fuel). Such a design would make possible a chemical separation of the generated ^{233}U fuel in ThO_2 - UO_2 from the initial ^{238}U - ^{235}U fuel.

Simplifications of the fabrication process, as described in Chap. 8, were also contemplated. However, further development of the AWBA concepts has been suspended. This work and the related work by the Knolls Atomic Power Laboratory (Merriman and Detwyler, 1983) are summarized in the Bettis Atomic Power Laboratory report (Vogel, 1982).

1.7 EFFECTS OF MATERIAL PROPERTIES ON FUEL PERFORMANCE

The nuclear properties of a material must be the first consideration in the selection of a suitable nuclear fuel. Principal properties are those bearing on neutron economy: absorption and fission cross sections, the reactions and products that result, neutron production and the energy released. These are properties of a specific nuclide, such as ^{232}Th and its product during breeding, ^{233}U . To assess these properties in the performance of the bulk fuel, use must be made of a density value, or frequency of occurrence per unit volume, of the specific nuclide.

Once it has been established that the desired nuclear reaction is feasible in a candidate fuel material, the effect of other material properties on reactor performance must be considered. For the reactor to perform its function of producing usable energy, the energy must be removed. Thermal conductivity as high as possible, throughout the temperature range of operations and working life of the reactor, would be very desirable. The selection of a ceramic fuel represents a compromise. Though it is known that thermal conductivities comparable to those of metals cannot be expected, chemical and dimensional stability at high temperature is obtained.

Since the thermal conductivity of a ceramic fuel is not high, it is necessary to generate relatively high temperatures at the centers of ceramic fuel elements. A high melting point enables more energy to be extracted, other things being equal. In all cases, the fuel must remain well below the melting point in normal operation; but a higher melting point results in a higher permissible operating temperature.

The dimensional stability of the fuel under conditions of high temperature and high burnup is of primary importance in determining the usable lifetime. This dimensional stability is compromised by swelling, which constricts the coolant channels, and may lead to rupture of the metal cladding and escape of highly radioactive fission products into the coolant. The various other factors leading to the degradation of fuel performance as reactor life proceeds—the exhaustion of fissionable material, the accumulation of nonfissionable products, the accumulation of radiation effects on associated nonfuel materials—are all of secondary importance in comparison to dimensional instability of the fuel elements.

The main cause of fuel element swelling is the accumulation of two fission product atoms for each atom fissioned. This is exacerbated by the fact that some of the fission products are gases. The ability of a ceramic fuel to retain and accommodate fission gases is therefore of primary importance in determining core lifetime.

The chemical properties of a fuel are also important considerations. A fuel should be able to resist the wholesale change in its properties, or the destruction of its mechanical integrity, that might take place if it is exposed to superheated coolant water through a cladding failure. On the other hand, certain chemical reactions are desirable. The incorporation of other materials in solid solution may be deliberately undertaken by the manufacturer in order to alter the properties to those needed for the reactor design. Also, it is generally advantageous for some of the products of the nuclear reaction to be accommodated in solid solution in the fuel, rather than accumulating as separate phases.

The physical properties of the fuel material are primarily of interest in ensuring its integrity during the manufacturing process. They must nevertheless be considered in assessments of the integrity of the core under operating conditions, or the conditions of hypothetical accidents.

It is not possible to fabricate typical refractory ceramics to 100 percent of their theoretical density. Methods of controlling the porosity of the final product must therefore be considered. The role of this initial porosity as sites for fission gas, as well as its effects on thermal conductivity and mechanical strength, is a significant factor in the design.

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Chapter 2

NUCLEAR PROPERTIES OF THE THORIUM FUEL CYCLE

M. Natelson

2.1 INTRODUCTION

Interest in thorium as a fuel material for nuclear power reactors arises from its ability to be transmuted into the fissile, non-naturally occurring isotope of uranium, ^{233}U , which has excellent nuclear properties. The abundant isotope of thorium, ^{232}Th , itself not fissile, captures a neutron and undergoes a series of nuclear decay processes leading to ^{233}U . Because of this property, thorium is referred to as a fertile material. The only other abundant, naturally occurring fertile isotope is ^{238}U , which makes up about 99.3 percent of natural uranium.

As a fertile material, thorium forms part of a nuclear fuel cycle. The properties of fissile ^{233}U make it possible for nuclear reactors fueled with Th and ^{233}U to convert significant amounts of Th to ^{233}U . Both thermal and fast reactors can be designed in which ^{233}U production is large enough to ensure a fissile fuel supply for a given reactor, i.e., *breeding* is possible with this fuel cycle.

In thermal reactors, neutrons are slowed down, i.e., moderated to energies at which fission readily occurs in fissile fuels. The moderating materials commonly used in such reactors are light water, heavy water, and graphite. In fast reactors, little moderation takes place; the energy of fission is removed by a liquid metal (a sodium-potassium alloy, for example) or by helium gas, neither of which produces significant neutron moderation. The nuclear fuel cycle utilizing ^{238}U is particularly well suited to fast reactors. In this cycle, the fissile materials are the isotopes of plutonium, ^{239}Pu and ^{241}Pu . For high energy neutrons ($E > 50 \text{ keV}$) both of these isotopes produce on the average well over two neutrons for each neutron absorbed. This ratio of neutron production to neutron absorption of a fissile fuel is conventionally called *eta* (η). It characterizes the breeding potential of a fissile isotope. In a breeder reactor, one neutron per neutron absorbed in

fissile fuel must be produced to keep the chain reaction going. A second neutron must be produced to transmute a fertile atom to a replacement for the fissile atom that has been transformed. Finally, some excess is needed to make up for neutron losses through leakage out of the reactor and absorption by other materials in the reactor. Thus, the requirement for breeding is that η must be greater than 2. In Fig. 2.1, η is plotted for the fissile isotopes ^{233}U , ^{235}U , and ^{239}Pu versus neutron energy, for the range of neutron energies found in nuclear reactors.

The great potential for the Th- ^{233}U fuel cycle lies in the fact that η for ^{233}U is large enough throughout the neutron energy range in which most fissions are induced in thermal reactors to make these reactors breed or to have very high conversion ratios, i.e., to be near-breeders. As can be seen in Fig. 2.1, the corresponding η for plutonium and ^{235}U cannot provide comparable performance in thermal reactors. Near-breeding or breeding in thermal reactors means that high utilization of nuclear fuel can be achieved in reactor systems of proven technology. Even with the successful technical development and commercialization of fast reactors, it may well be that the most economical way to utilize thorium and uranium resources is with an appropriate mix of thermal and fast reactors.

In this chapter, those nuclear properties that are of particular importance for the application of thorium and ^{233}U in fission-reactor fuel cycles are emphasized. The values presented for various parameters are best estimates, representing the current judgment of the Bettis

Figure 2.1. Neutron Yield per Neutron Absorbed, η , versus Neutron Energy for ^{233}U , ^{235}U , and ^{239}Pu .

Atomic Power Laboratory physics staff and confirmed by the successful operation and testing of the Shippingport LWBR core. The values derived from experimental data are the work of many researchers throughout the world, and, when used, are acknowledged in the references. However, discussion of the rationale for selecting one estimate over others is beyond the scope of this book.

Much of the data presented here can be found in the computer files issued by the National Nuclear Data Center at Brookhaven National Laboratory. The center coordinates evaluation efforts at various installations and periodically issues inclusive sets of nuclear data. The files are designated ENDF/B followed by a roman numeral, which is the version number. The latest is ENDF/B-V (Kinsey, 1979). For each isotope there are principal evaluators; these are used for reference purposes. In the file itself a detailed list is given of the evaluators for specific types of data.

The nuclear data are presented as follows. In Sect. 2.2, the isotopic abundance, natural decay chains, and neutron-induced transmutation chains of thorium are discussed. In Sect. 2.3, neutron capture cross sections are given for ^{232}Th , ^{233}U , and a key isotope in the thorium transmutation chain, ^{233}Pa . Section 2.4 deals with the neutron-induced fission process in thorium and ^{233}U , Sect. 2.5 with neutron scattering, and Sect. 2.6 with gamma ray-induced reactions. A final section is included in which nuclear characteristics of thorium and ^{233}U are compared with those of the key isotopes in the uranium fuel cycle, ^{238}U , ^{235}U , ^{239}Pu , and ^{241}Pu . To facilitate the comparison required, nuclear data for ^{238}U , ^{235}U , ^{239}Pu , and ^{241}Pu are presented in the appropriate sections.

2.2 THORIUM ISOTOPIC ABUNDANCE, NATURAL DECAY CHAINS, AND TRANSMUTATION CHAINS

2.2.1 Isotopic Abundance

In the earth, thorium exists effectively as a single isotope, $^{232}_{90}\text{Th}$. Its atomic number, $Z = 90$, is the number of positive elementary charges carried by its nucleus, i.e., the number of protons in the nucleus. Its mass number, $A = 232$, is the number of nucleons (protons + neutrons) in the nucleus. The atomic mass is 232.038054 atomic mass units in the Carbon-12 system.

Two other isotopes of thorium are found in nature in trace amounts. The isotope $^{228}_{90}\text{Th}$ (Radiothorium, RaTh) is a decay product (daughter) of $^{232}_{90}\text{Th}$ and thus is found in trace quantities in all thorium ore deposits. Its half life is 1.913 a (years). The assumption that $^{228}_{90}\text{Th}$ is in secular equilibrium with $^{232}_{90}\text{Th}$ leads to a concentration of 0.000137 appm for this isotope (atoms of $^{228}_{90}\text{Th}$ per million atoms of $^{232}_{90}\text{Th}$).

The second isotope, $^{230}_{90}\text{Th}$ (Ionium, Io) is a decay product of $^{238}_{92}\text{U}$. Since thorium is sometimes found mixed with uranium ores, refined thorium from such ores will contain trace amounts of $^{230}_{90}\text{Th}$. Its half life is 7.54×10^4 years; in secular equilibrium with $^{238}_{92}\text{U}$, the $^{230}_{90}\text{Th}$ concentration is 16.4 appm. For ores with high uranium content, specifically arothorite ores from the Eliot Lake region of Ontario, Canada (Kirk and Othmer, 1963), the $^{230}_{90}\text{Th}$ concentration can be as high as 77 appm.

2.2.2 Natural Decay Chains

All nuclei with mass numbers greater than 209 are radioactive. Those found in nature can be grouped into three chains or series in which each member of a given series is the product of radioactive decay of another member of the series. Each series is named for the isotope that has the longest half life, i.e., the isotope that is at the head of the series. The mass numbers of all the members of a given series can be expressed as a simple linear function of an integer. Thus, for members of the *thorium* series, $A = 4n$; for the *uranium* series, $A = 4n + 2$; and for the *actinium** series, $A = 4n + 3$. The members of the thorium series are shown in Table 2.1 along with their half lives, types of decay, and decay-particle energies. The uranium series is given in Table 2.2.

As noted in Sect. 2.2.1, $^{228}_{90}\text{Th}$ is a member of the thorium series (a daughter of $^{232}_{90}\text{Th}$). The isotope $^{230}_{90}\text{Th}$ is a member of the uranium series (a daughter of $^{238}_{92}\text{U}$). Additional isotopes of thorium, $^{231}_{90}\text{Th}$ and $^{234}_{90}\text{Th}$, appear, respectively, in the actinium and uranium series. Their half lives, however, are so short (25.52 hours and 24.10 days, respectively) that their natural abundances are negligible.

The thorium natural-decay series is of particular importance because two of the daughters of thorium, $^{208}_{81}\text{Tl}$ (Thallium 208) and $^{212}_{83}\text{Bi}$ (Bismuth 212) produce the major gamma radiation emission associated with thorium-based nuclear fuel systems. The decay scheme for $^{212}_{83}\text{Bi}$, a precursor of $^{208}_{81}\text{Tl}$, is shown in Fig. 2.2. The high energy gamma rays associated with the beta decay of $^{208}_{81}\text{Tl}$ and $^{212}_{83}\text{Bi}$ provide the major portion of radiation doses received in handling thorium or, as is discussed in Sect. 2.2.3, in handling uranium generated in a thorium-uranium fuel cycle.

*Actually $^{235}_{92}\text{U}$ is the longest-lived isotope in this series. It was not discovered until after other members of the series had been identified.

TABLE 2.1—THE THORIUM SERIES, NATURALLY OCCURRING PORTION*

Nuclide	Historical Name	Type of Decay [†]	$t_{1/2}$ Half Life [‡]	Maximum Energy of Decay Particle (MeV)
$^{232}_{90}\text{Th}$	Thorium	α	1.40×10^{10} a	4.01
$^{228}_{88}\text{Ra}$	Mesothorium I	β^-	5.75 a	0.039
$^{228}_{89}\text{Ac}$	Mesothorium II	β^-	6.13 h	2.08
$^{228}_{90}\text{Th}$	Radiothorium	α	1.913 a	5.4233
$^{224}_{88}\text{Ra}$	Thorium X	α	3.66 d	5.8656
$^{220}_{86}\text{Rn}$	Emanation	α	55.6 s	6.2883
	Thoron			
$^{216}_{84}\text{Po}$	Thorium A	α	0.15 s	6.779
$^{212}_{82}\text{Pb}$	Thorium B	β^-	10.64 h	0.569
$^{212}_{83}\text{Bi}$	Thorium C	α (35.9%) β^- (64.1%)	60.6 m	6.0901 α 2.251 β^-
$^{212}_{84}\text{Po}$	Thorium C'	α	0.298 μs	8.7844
$^{208}_{81}\text{Tl}$	Thorium C''	β^-	3.053 m	1.796
$^{208}_{82}\text{Pb}$	Thorium D		-- Stable --	

*From Walker et al (1983).

[†]In β^- decay, a high energy electron is emitted; this changes Z by +1 unit and leaves A unchanged.In α decay, an alpha particle is emitted; this changes Z by -2 units and A by -4 units.[‡]a = years, d = days, h = hours, m = minutes, s = seconds, μs = 10^{-6} second.

2.2.3 Neutron-Induced Transmutation Chains of Thorium

The transmutation process from fertile thorium to fissile uranium is initiated by neutron radiative capture in $^{232}_{90}\text{Th}$ followed by two beta decays yielding a $^{233}_{92}\text{U}$ nucleus. A schematic diagram of the process is given in Fig. 2.3. Note that neutron capture by the intermediate nucleus $^{233}_{90}\text{Th}$ or $^{233}_{91}\text{Pa}$ can interrupt the production of $^{233}_{92}\text{U}$. Beta decay following such captures will lead to $^{234}_{92}\text{U}$, which after consecutive neutron captures becomes $^{235}_{92}\text{U}$ and $^{236}_{92}\text{U}$. Of course, in this case it takes three neutrons to transform a thorium atom into fissile uranium $^{235}_{92}\text{U}$, rather than a single neutron as in $^{233}_{92}\text{U}$ production. As is discussed further in Sect. 2.2.7, the question of neutron economy is central to achieving high utilization of nuclear fuels.

TABLE 2.2—THE URANIUM SERIES, NATURALLY OCCURRING PORTION*

Nuclide	Historical Name	Type of Decay†	$t_{1/2}$ Half Life‡	Maximum Energy of Decay Particle (MeV)
$^{238}_{92}\text{U}$	Uranium I	α	4.468×10^9 a	4.196
$^{234}_{90}\text{Th}$	Uranium X ₁	β^-	24.10 d	0.195
$^{234}_{91}\text{Pa}^m$	Uranium X ₂	β^-	1.17 m	2.29
$^{234}_{91}\text{Pa}$	Uranium Z	β^-	6.70 h	1.13
$^{234}_{92}\text{U}$	Uranium II	α	2.45×10^5 a	4.775
$^{230}_{90}\text{Th}$	Ionium	α	7.54×10^4 a	4.688
$^{226}_{88}\text{Ra}$	Radium	α	1600 a	4.7845
$^{222}_{86}\text{Rn}$	Emanation	α	3.8235 d	5.4897
	Radon			
$^{218}_{84}\text{Po}$	Radium A	α (99.98%)	3.11 m	6.0026 α
		β^- (0.02%)		0.25 β^-
$^{214}_{82}\text{Pb}$	Radium B	β^-	26.8 m	1.02
$^{218}_{85}\text{At}$	Astatine	α	~ 2 s	6.694
$^{214}_{83}\text{Bi}$	Radium C	α (0.02%)	19.8 m	5.512 α
		β^- (99.98%)		3.27 β^-
$^{214}_{84}\text{Po}$	Radium C'	α	163.7 μs	7.6871
$^{210}_{81}\text{Tl}$	Radium C''	β^-	1.30 m	2.3
$^{210}_{82}\text{Pb}$	Radium D	β^-	22.3 a	0.061
$^{210}_{83}\text{Bi}$	Radium E	α (0.00013%)	5.01 d	4.686 α
		β^- ($\sim 100\%$)		1.161 β^-
$^{210}_{84}\text{Po}$	Radium F	α	138.38 d	5.3045
$^{206}_{81}\text{Tl}$	Radium E''	β^-	4.20 m	1.530
$^{206}_{82}\text{Pb}$	Radium G		-- Stable --	

*From Walker et al (1983).

†In β^- decay, a high energy electron is emitted; this changes Z by +1 unit and leaves A unchanged.In α decay, an alpha particle is emitted; this changes Z by -2 units and A by -4 units.‡a = years, d = days, h = hours, m = minutes, s = seconds, μs = 10^{-6} second.

A second transmutation chain, which is important to thorium fuel systems, is initiated by an (n,2n) reaction* in $^{232}_{90}\text{Th}$, leading to the production of $^{232}_{92}\text{U}$. This chain is illustrated by a schematic diagram in Fig. 2.4. The isotope $^{232}_{92}\text{U}$ has a half life of 72 years for alpha decay to $^{228}_{90}\text{Th}$, a member of the thorium natural decay series (see Table 2.1). Uranium produced in nuclear reactors utilizing thorium will contain some $^{232}_{92}\text{U}$. After chemical separation from thorium, its daughters, and fission products, this uranium will become increasingly more radioactive (in terms of high energy gamma emissions) as the daughters of thorium, $^{208}_{81}\text{Tl}$ and $^{212}_{83}\text{Bi}$, build up.

*In an (n,2n) reaction, a neutron with kinetic energy above some minimum threshold value is absorbed by a nucleus, which immediately gives off two neutrons of substantially lower energy.

Figure 2.2. Decay Scheme for Bismuth 212.

Activity of these isotopes will peak after approximately 10.3 years and subsequently decay with the half life of ^{232}U . This is illustrated in Fig. 2.5, a plot of disintegrations per second of ^{208}Tl per initial atom of ^{232}U versus time. It is the presence of ^{232}U that requires remote fabrication for the production of fuel elements utilizing recycled uranium in a thorium-uranium fuel cycle.

While the $(n,2n)$ reaction in ^{232}Th is the dominant mode of ^{232}U production in the Light Water Breeder Reactor (LWBR), there are other reactions that produce ^{232}U . A (γ,n) reaction* in ^{232}Th will result in ^{231}Th just as does an $(n,2n)$ reaction (see Fig. 2.4). As is discussed in detail in Sect. 2.6, the gamma energy required for this reaction is high (>6 MeV). Because there are few such gamma rays in nuclear reactors and the probability for the reaction is small, this process is a minor contributor to the formation of ^{232}U . Finally, if the thorium used in a nuclear reactor contains ^{230}Th (ionium), ^{231}Th can be created through neutron capture in ^{230}Th (see Fig. 2.4). As noted in

*In a (γ,n) reaction a gamma ray with energy above some minimum value is absorbed by a nucleus which immediately gives off a neutron of substantially lower energy. This is the inverse reaction of neutron radiative capture (n,γ) .

Figure 2.3. Principal Reactions in Conversion of $^{232}_{90}\text{Th}$ to Uranium by Neutron Capture and Radioactive Decay.

Sect. 2.2.1, $^{230}_{90}\text{Th}$ is only present in thorium obtained from ores containing natural uranium. Even for the highest concentration quoted in Sect. 2.2.1, $^{230}_{90}\text{Th}$ would not be a large contributor to the generation of $^{232}_{92}\text{Th}$ in, for example, a typical LWBR.

2.3 NEUTRON CAPTURE CROSS SECTION

2.3.1 Introduction

Neutron capture is the nuclear reaction of primary importance for thorium as it is used in a fuel cycle. The probability of a given neutron interaction taking place is characterized by a parameter, with dimensions of area, called the cross section. A commonly used unit for cross section is the *barn*, which is equal to 10^{-24} cm^2 . Data are presented (in Sects. 2.3.2, 2.3.3, and 2.3.4) for the cross section for neutron capture in thorium as a function of neutron kinetic energy, E . For comparison purposes, similar data are presented for the $^{238}_{92}\text{U}$ neutron capture cross section. In Sects. 2.3.5 and 2.3.6 data are presented for neutron

Figure 2.4. Generation of ^{232}U in a Thorium-Fueled Nuclear Reactor.

capture in ^{233}Pa and ^{233}U , respectively. The term *capture** cross section refers here specifically to (n,γ) reactions in which a neutron combines with the target nucleus and a gamma ray (or rays) is emitted from the resultant nucleus.

Cross sections for reactions initiated by neutrons are categorized by neutron energy range. Starting near zero energy, one can define a thermal range, $0 < E < 0.625$ eV. Neutrons within this range are normally in near-thermal equilibrium with their host medium. In a nuclear reactor the thermal neutron distribution in energy can be described approximately by a Maxwell-Boltzmann distribution whose effective temperature is somewhat higher than the moderator temperature. Above this range is the slowing-down range in which neutrons lose energy in scattering collisions.

*Often the word absorption is used interchangeably with capture to describe reactions in nuclides that do not readily fission. However, conventionally the term absorption cross section is associated with the sum of the cross sections for capture (n,γ) , fission, and other possible reactions in which the incident neutron is eliminated, for example, reactions in which charged particles are produced: (n,p) or (n,α) reactions.

Figure 2.5. Disintegration Rate of ^{208}Tl per Initial Atom of ^{232}U as a Function of Time.

For many materials, particularly heavy nuclides such as ^{232}Th and ^{233}U , cross section profiles (versus energy) exhibit a series of high, narrow peaks called resonances. These can extend from the thermal range up to about 50 keV. The widths and spacing of these resonances depend very much on the atomic mass number; resonances become narrower and more densely spaced with increasing mass number, A . For a given nuclide, the resonances become wider and more closely spaced at higher energies, until they eventually overlap.

Resonances occur at those neutron energies for which reactions with target nuclei lead to compound nuclei (with $A = A_{\text{target}} + 1$) that are in well-defined, i.e., relatively long-lived, excited energy states. Cross sections become very large for those neutron energies which provide approximately the energy needed to achieve a particular compound-nucleus excited state. For still higher neutron energies,

compound nuclei, if formed, are in higher energy, more closely spaced excited states. Each excited state has an energy uncertainty, or energy width ΔE , associated with it; thus, when the excited states are closely spaced, their widths overlap and cross sections do not show distinct resonance behavior.

Since the resonance cross section structure is a nuclear phenomenon and has no direct connection with the kinematics of neutron thermalization, it is possible for a resonance to fall in the thermal energy range. In fact, the train of resonances extends below zero neutron energy, as bound nuclear levels, and these can affect the shape of the cross section at thermal and low-eV energies, particularly when a level falls just below zero eV, as happens in ^{232}Th . When there are no resonances close to the thermal range, the shape of the thermal capture cross section is inversely proportional to neutron velocity.

Above a certain energy it becomes impractical to resolve individual resonances experimentally. Hence, they must be treated statistically over a so-called *unresolved resonance range*. For ^{232}Th and ^{238}U , resonances are well resolved up to approximately 4 keV, and the unresolved resonance range extends up to approximately 50 keV. At sufficiently high energies (above the unresolved resonance range) cross section fine structure usually dies away and becomes unimportant for thermal reactor behavior.

The major reason for detailed consideration of cross section resonances is the *self-shielding* that occurs in large samples of material, i.e., strong absorption by the nuclei on the periphery of a region depletes the neutron population so that the reaction rate is reduced in the center of the region. This effect is particularly important within the narrow energy bands of a resonance where the cross section is very highly peaked. As is discussed in Sect. 2.3.3, proper treatment of resonance self-shielding is very important in nuclear reactor calculations. A set of cross sections must yield correct reaction rates for both dilute and self-shielded systems.

Neutron resonance cross sections exhibit an important temperature dependence which stems from the so-called *Doppler effect*. The cross section is a function of energy alone when viewed in the center-of-mass coordinate system of the neutron and a target nucleus. This remains true in the laboratory coordinate system when the target nuclei are assumed to be at rest (zero kelvin). In calculations performed for real systems, however, cross sections must be averaged over momenta of target nuclei; they are thus characterized by both neutron energy in the laboratory system and by target temperature. The dependence on target temperature is particularly important for resonance cross sections. The effect of averaging over the thermal agitation of target nuclei is to broaden the resonances and to lower their peaks. This so-called *Doppler broadening* causes an increase in

neutron absorption rate with increased temperature when the density of target nuclei and the cross section are high enough to cause significant self-shielding.

2.3.2 Thermal Capture Cross Section for ^{232}Th

The capture cross section for ^{232}Th in the thermal neutron energy range is shown in Fig. 2.6; for comparison, the capture cross section for ^{238}U is also included. Note that the values of the cross section at 0.0253 eV are explicitly given. This energy, which corresponds to a neutron speed of 2200 m/s, is the peak of the Maxwell-Boltzmann distribution at 293 K. Thermal capture cross sections are conventionally characterized by the 2200 m/s value. When the energy dependence of a capture cross section is inversely proportional to the neutron velocity (i.e., $1/v$), the reaction rate ($\text{No./cm}^3 \cdot \text{s}$) initiated by thermal neutrons is precisely given by the product of the target atomic density, the 2200 m/s cross section, the neutron density (integrated over the thermal energy range), and the thermal neutron velocity, 2200 m/s. Thorium capture, however, does not have a $1/v$ cross section. This can be seen from the plot of a unit $1/v$ cross section in Fig. 2.6. Capture cross sections for target nuclei, in which (n,γ) reactions dominate and for which both positive and negative energy resonances are far from the thermal range (0 to 0.625 eV), display $1/v$ energy dependence in the thermal range. The isotope ^{232}Th does not have a $1/v$ dependence because of the existence of negative energy resonances, i.e., the compound nucleus ^{233}Th has an excited state or states with energies below that of the total rest mass energy of ^{232}Th plus a neutron.

Figure 2.6 also shows that ^{238}U does not have a $1/v$ energy dependence for its capture cross section. The significant comparison to make, however, is that between the magnitudes of the ^{232}Th and ^{238}U cross sections. The impact on reactor design of the larger ^{232}Th thermal cross section is discussed in Sect. 2.7.

2.3.3 Resonance Capture Cross Section

The ^{232}Th capture cross section in the resolved resonance energy range is presented in Fig. 2.7. This plot is constructed from parameters provided in the ENDF/B-IV evaluation (Wittkopf et al, 1975). It is shown here to illustrate the general properties of heavy fertile element resonance capture. A target temperature of 293 K was used in generating the plot; however, given the scales involved, there is no difference between this and a zero kelvin plot.

Figure 2.6. Thermal Capture Cross Section for ^{232}Th , ^{238}U , and Unit $1/v$ Cross Section.

To use the large mass of data needed to describe a cross section in the resonance energy range in practical nuclear reactor calculations, the data must be stored in computer files and manipulated with special programs to provide effective cross sections over heterogeneous spatial regions and energy ranges that are large compared to a typical resonance width. The exception to this calculational approach is the Monte Carlo technique where full spatial detail of a reactor system can be retained and the full description of cross section energy dependence can be used.

In the unresolved energy range, between 4 and 50 keV, distributions of resonance widths and spacings can be used to generate nuclear data. Parameters for these distributions are provided in ENDF/B-V (Kinsey, 1979) for the first three angular momentum states of the $(n, ^{232}\text{Th})$ system. Unresolved energy range nuclear data are needed to represent adequately neutron flux depression in fuel elements.

Figure 2.7. Resonance Capture Cross Section for ^{232}Th .

The resonance capture cross section is characterized in an integral sense by the infinitely dilute resonance integral, I_x . This quantity is the integral over energy of the capture cross section weighted inversely by the energy*. For resolved resonances over the energy range 0.5 to 4000 eV, the infinitely dilute resonance integrals for ^{232}Th and ^{238}U are:

	<u>Calculated</u>	<u>Measured</u>
$I_x (^{232}\text{Th})$	85.6 b	85 ± 3 b
$I_x (^{238}\text{U})$	277.5 b	275 ± 5 b

The calculations are from the ENDF/B-IV evaluations (Wittkopf et al, 1975; Paik, 1975). The measured values (Mughabghab and Garber, 1973) are provided to demonstrate the adequacy of the data sets in estimating these important quantities. In any nuclear reactor system in which thorium or uranium 238 is used as a fertile fuel, resonance capture plays a major role in the conversion process. However, as mentioned in Sect. 2.3.1, resonance cross sections used to calculate reaction rates in practical reactor systems must be able to represent the effect of self-shielding. An integral quantity which characterizes this performance is the heterogeneous resonance integral, I . This quantity depends on target temperature and macroscopic geometric configuration. It is defined to be the number of captures per target atom in the resonance energy range when the neutron flux at the top of the range is equal to $1/E$ and is uniform in space. Comparisons of representative calculations and measurements of this quantity for isolated rods (of ThO_2 and $^{238}\text{UO}_2$) in water are given in Figs. 2.8 and 2.9. The resonance integrals are plotted versus the square root of the surface-to-mass ratio of the target material. Comparisons are made for two different target temperatures.

2.3.4 High Energy Neutron Capture: (n, γ) and (n,2n) Reactions

High energy here refers to the high end of the energy spectra of neutrons in a nuclear reactor in which fissions initiated by thermal neutrons predominate. The capture cross sections for ^{232}Th and ^{238}U in the high energy range (from 100 keV to 10 MeV) are presented in Fig. 2.10. The data are from the ENDF/B-V evaluations (Bhat, 1977a, and Pennington et al, 1979).

* $1/E$ is the energy dependence of the neutron flux in most moderators (e.g., water, heavy water, graphite, sodium) for energies above the thermal range and below the energies at which neutrons are introduced.

Figure 2.8. ^{232}Th Resonance Integral (ThO_2 Fuel, Isolated Rod).

The cross section for the $(n,2n)$ reaction in ^{232}Th is given in Fig. 2.11. As noted in Sect. 2.2.3, this reaction is important in that it initiates the transmutation chain leading to the production of ^{232}U in thorium-fueled nuclear reactors. It is a threshold reaction; the incoming neutron must have some minimum kinetic energy before the reaction can take place in order to conserve both energy and momentum. The energy balance must include the rest mass energies of the inputs and outputs of the reaction.

The energy distribution of neutrons emitted in the $(n,2n)$ reaction depends on the energy of the initiating neutron. Figure 2.12 shows

Figure 2.9. ^{238}U Resonance Integral (UO_2 Fuel, Isolated Rod).

the distribution for initial neutron energies in the range 7.79 to 10.0 MeV. This range is characteristic of reactions that take place in a fission reactor. In ENDF/B files (Bhat, 1977a; Pennington et al, 1979), a full matrix for initial and final energies is given. For fission reactor calculation, it is adequate to assume that the angular distribution of the emitted neutrons is isotropic.

Figure 2.10. High Energy Capture Cross Sections for ^{232}Th and ^{238}U .

Finally, note from Fig. 2.10 that ^{232}Th capture cross sections are larger than the ^{238}U cross sections. This was also the case for the thermal range. The consequences of this fact relative to nuclear reactor design are discussed in Sect. 2.7.

2.3.5 Neutron Capture in Protactinium

As noted in Sect. 2.2.3, the radioactive isotope ^{233}Pa plays a key role in the transmutation chain in which ^{233}U is formed. Neutron capture by a ^{233}Pa atom removes it from the direct chain leading to a ^{233}U atom. Since the isotope ^{233}Pa has a β -decay half life of 27 days, there is a significant population of ^{233}Pa atoms in an operating nuclear reactor utilizing a thorium-uranium fuel cycle. In the LWBR at Shippingport, the atom population of ^{233}Pa was approximately 2 percent of the ^{233}U population under full power equilibrium operating conditions. Thus, proper accounting for neutron capture in ^{233}Pa is important in the designing of such a reactor to optimize breeding.

The capture cross section for ^{233}Pa is shown in Fig. 2.13 for the full range of neutron energies of interest in the nuclear reactors. The data

Figure 2.11. ^{232}Th (n,2n) Cross Section versus Energy.

are from the ENDF/B-V evaluation for which the 0.0253 eV cross section, $\sigma_0 = 4.46$ b, and the infinitely dilute resonance integral, $I_\infty = 855.4$ b. The corresponding isotope in the uranium-plutonium fuel cycle is ^{239}Np . However, its half life for β decay into ^{239}Pu is only 2.35 d; thus its population in a ^{238}U -Pu fuel cycle reactor is small. Therefore, knowledge of the neutron capture characteristics of ^{239}Np is not nearly as important as is that for ^{233}Pa in a Th- ^{233}U fuel cycle reactor.

Figure 2.12. Energy Spectrum of Neutrons Produced in an (n,2n) Reaction in ^{232}Th (Initial Energy Range = 7.79 to 10.0 MeV).

2.3.6 Neutron Capture in ^{233}U

The performance of a fissile isotope in a nuclear reactor is governed not only by its propensity to fission but also by the probability that in capturing a neutron it does not fission. The parameter eta (η), defined in Sect. 2.1 as the ratio of neutron production to loss for a fissile isotope, is dependent on the neutron capture cross section, $\sigma_c(E)$. For neutron energy E ,

$$\eta(E) \equiv \frac{\nu(E)\sigma_f(E)}{\sigma_f(E) + \sigma_c(E)}$$

where

$\nu(E)$ = the total number of neutrons produced per fission induced by a neutron with energy E ,

$\sigma_f(E)$ = the microscopic fission cross section.

The capture cross section for ^{233}U is shown in Fig. 2.14 along with those of the other important fissile isotopes, ^{235}U , ^{239}Pu , and ^{241}Pu . The 0.0253 eV cross section values and the infinitely dilute resonance integrals, I_∞ , are also given.

Figure 2.13. Neutron Capture Cross Section for Protactinium.

2.4 FISSION

2.4.1 Introduction

All heavy elements ($A > 90$) are energetically unstable to division into approximately equal parts. The binding energy* per nucleon (B/A) of the product nuclei is greater than that of the parent nuclei. There is, however, a nuclear potential which prevents naturally occurring heavy elements from spontaneously decaying by fission. To induce fission of a given nucleus it must be sufficiently excited to overcome this nuclear potential. For several heavy nuclei containing even numbers of neutrons and protons (^{234}U , ^{236}U , ^{240}Pu , and ^{242}Pu) the excitation required for spontaneous fission can be provided by forming these nuclei through neutron absorption by their odd $A - Z$ even Z isotopic neighbors (^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu , respectively) even when the neutron contributes zero kinetic energy to the excitation process. This is due to the quantum mechanical pairing of nucleons in a nucleus which in an even-even case makes for a large binding energy for the last neutron (B_n)† added to the nucleus as compared to that for its odd-even isotopic neighbor. Note that $B_n = 5.295$ MeV for ^{235}U and $B_n = 6.5451$ MeV for ^{236}U . Thus, when an odd-even nucleus absorbs a zero energy neutron the resultant even-even nucleus is highly excited relative to its normal ground state.

*The binding energy (B) of a nucleus is the work required to disassemble a nucleus of mass M into its constituents, i.e., $B = ZM_H + (A - Z)M_n - M$ where M_H is the mass of a hydrogen atom and M_n is the mass of a neutron. Conventionally, all masses are expressed in energy units.

† $B_n = A^{-1}M_Z + M_n - AM_Z$ is the work required to remove one neutron from a nucleus of mass AM_Z .

Figure 2.14. Neutron Capture Cross Sections for Fissile Isotopes ^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu .

On the other hand, when ^{232}Th ($B_n = 6.4364$ MeV) absorbs a zero energy neutron, the resultant odd-even nucleus ^{233}Th

($B_n = 4.7864$ MeV) will not be sufficiently excited to fission. As is seen from the ^{232}Th cross section for fission, considerable additional energy must be supplied through neutron kinetic energy to initiate a fission reaction. The same is true for ^{238}U .

In the following sections, data are presented for the thorium and ^{233}U fission cross sections, and the neutron, fission product, and energy yields. Comparisons are made with corresponding data for ^{238}U , ^{235}U , ^{239}Pu , and ^{241}Pu .

2.4.2 Fission Cross Section

The ENDF/B-IV evaluations of the ^{232}Th and ^{238}U fission cross sections are presented in Fig. 2.15 (Wittkopf et al, 1975; Paik, 1975). As noted above, both cross sections are characteristic of threshold reactions*. The ^{238}U cross sections, however, have non-zero values at lower energies than ^{232}Th . In addition, its magnitude at 2 MeV ($\sim$ the average energy at which fission neutrons are born) is about 4.5 times greater than that for ^{232}Th . In Sect. 2.7, the impact of the relative magnitude these cross sections have on nuclear reactor design is discussed.

Fission cross sections for ^{233}U and the other important fissile isotopes ^{235}U , ^{239}Pu , and ^{241}Pu are presented in Fig. 2.16. The data are from the ENDF/B-V evaluations (Stewart et al, 1978; Bhat, 1977b; Kujawski and Stewart, 1976; Weston et al, 1977).

2.4.3 Neutron Yield

In a fission reaction, the bulk of the neutrons produced are released instantaneously with reaction initiation. A small fraction of the neutrons is released subsequently through neutron decay of various fission products. The former are conventionally referred to as prompt neutrons, the latter as delayed neutrons. Those fission product nuclei whose decay produces delayed neutrons are called delayed neutron precursors. One hundred and two precursors have been identified to date. In nuclear reactor calculations six effective precursor groups are used to describe delayed neutron behavior. Data are presented here for these six groups.

The number of neutrons produced in a fission reaction depends on the energy of the neutron initiating the reaction. For thorium and

*Nuclear reactions are quantum mechanical phenomena, and thus there is some small but finite probability for fission below the threshold energy. The 2200 m/s cross sections for subthreshold fission of ^{232}Th and ^{238}U are 0.054 mb and 0.0053 mb, respectively. The energy dependence of these cross sections is thought to be $1/v$. Subthreshold fission is of negligible importance in reactor design.

Figure 2.15. Fission Cross Sections for ^{232}Th and ^{238}U versus Energy.

Figure 2.16. Fission Cross Sections for Fissile Isotopes (^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu) versus Energy.

^{238}U the dependence for prompt neutron production can be represented as linear in energy. As the delayed neutron fraction is so small the linear relationship also holds for the total neutron yield. Results based on the ENDF/B-IV evaluation (Wittkopf et al, 1975; Paik, 1975) are given in Fig. 2.17 for total neutrons produced per fission, $\bar{\nu}_T$, versus the energy of the reaction-initiating neutron. The energy dependence of total delayed neutron yield, $\bar{\nu}_d$, is thought to be constant up to approximately 4 MeV and then to drop down to a second constant level by about 7 MeV. Evaluated data for $\bar{\nu}_d$ and the relative abundances and decay constants for the six delayed groups for both ^{238}U

Figure 2.17. Total Neutron Yield from Fission of ^{232}Th and ^{238}U as a Function of the Energy of the Neutron Initiating the Fission Reaction.

and ^{232}Th are presented in Table 2.3 (Bhat, 1977a; Pennington et al, 1979). Table 2.4 contains the delayed neutron data for ^{233}U and the other fissile isotopes: ^{235}U , ^{239}Pu , and ^{241}Pu . The dependence of the total neutron yields on the energy of the fission-inducing neutron is plotted in Fig. 2.18 for each of the fissile isotopes.

The final characteristic of interest for neutrons produced in fission reactions is their energy distribution upon emission. The energy spectra for prompt neutrons are given in Fig. 2.19 for ^{232}Th and ^{238}U . In Fig. 2.20 the spectra for each effective delayed neutron group are presented for ^{232}Th . The corresponding delayed neutron spectra for ^{238}U are given in Fig. 2.21. Prompt spectra for ^{233}U and the other fissile isotopes are presented in Fig. 2.22. Delayed neutron spectra for ^{233}U are given in Fig. 2.23. Comparison of Figs. 2.20, 2.21, and 2.23 reveals that the spectrum for a given delayed neutron group does not vary dramatically for different isotopes. This is not surprising, since the spectrum for each delayed group is a weighted average of the emission spectra of collections of the same delayed neutron precursors. The emission spectra for fission neutrons appear to have little

TABLE 2.3—DELAYED NEUTRON DATA FOR ^{232}Th AND ^{238}U

^{232}Th			^{238}U	
E(Mev)*	$\bar{\nu}_d$		E(Mev)	$\bar{\nu}_d$
1.2	0.0527		1.0	0.0460
4.0	0.0527		4.0	0.0460
7.0	0.0300		9.0	0.0260
13.0	0.0300		20.0	0.0260
20.0	0.0300			

^{232}Th			^{238}U	
Delayed Group	Decay Constant λ_i, s^{-1}	Relative Abundance γ_i	Decay Constant λ_i, s^{-1}	Relative Abundance γ_i
1	0.01237	0.034	0.01323	0.013
2	0.03340	0.150	0.03212	0.137
3	0.1210	0.155	0.1390	0.162
4	0.3210	0.446	0.3590	0.388
5	1.210	0.172	1.410	0.225
6	3.290	0.043	4.030	0.075

*The energy of the neutron initiating fission.

TABLE 2.4—DELAYED NEUTRON DATA FOR ^{233}U , ^{235}U , ^{239}Pu , ^{241}Pu

E(MeV)	$\bar{\nu}_d$			
	^{233}U	^{235}U	^{239}Pu	^{241}Pu
0-4	0.0074	0.0167	0.00645	0.0162
7	0.0047	0.0090	0.0043	0.0084

Delayed Group	^{233}U		^{235}U		^{239}Pu		^{241}Pu	
	Decay Constant	Relative Abundance						
	λ_i, s^{-1}	γ_i	λ_i, s^{-1}	γ_i	λ_i, s^{-1}	γ_i	λ_i, s^{-1}	γ_i
1	0.01258	0.086	0.01272	0.038	0.0129	0.038	0.0128	0.010
2	0.03342	0.274	0.03174	0.213	0.0311	0.280	0.0299	0.229
3	0.131	0.227	0.116	0.188	0.134	0.216	0.124	0.173
4	0.303	0.317	0.311	0.407	0.332	0.328	0.352	0.390
5	1.27	0.073	1.4	0.128	1.26	0.103	1.61	0.182
6	3.14	0.023	3.87	0.026	3.21	0.035	3.47	0.016

dependence on the energy of the neutron initiating the fission reaction. The spectra presented here are for initiating energies typical of fission nuclear reactors (<3 MeV); they are from the ENDF/B-V evaluations.

2.4.4 Fission Product and Energy Yield

The energy released in a fission reaction consists of the kinetic energy of fission products and neutrons, the energy of prompt and delayed gamma rays, the energy of beta particles given off in the decay of fission products, and the unrecoverable energy of neutrinos* emitted in conjunction with fission product beta decay. The total energy yield and its component parts are given in Table 2.5 for ^{232}Th , ^{238}U , ^{235}U , ^{233}U , ^{239}Pu , and ^{241}Pu (Kinsey, 1979). Note that, in the computation of energy production in a nuclear reactor, the total energy release figures in Table 2.5 are not used. The contribution from neutrinos is subtracted, and the nuclear energy release per fission from (n,γ) reactions, in the form of gamma ray energy, is added. The (n,γ) contribution is reactor dependent. The gamma energy released

*The neutrino is a massless neutral particle emitted in the β -decay of radioactive fission products. Its mean free path from birth to first collision is much larger than the dimensions of a nuclear reactor. Therefore, its energy will not be deposited in the reactor where it could contribute to the useful work output of the system.

Figure 2.18. Total Neutron Yield from Fission of the Fissile Isotopes (^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu) as a Function of the Energy of the Neutron Initiating the Fission Reaction.

is a function of the materials present in a given reactor and the fraction of the neutron population captured in the various materials.

Nuclei of heavy elements, such as ^{232}Th , contain more neutrons than protons (142 versus 90 for ^{232}Th). As the mass of a nucleus increases so does the number of neutrons required for nuclear stability. These additional neutrons supply the nuclear (attractive) forces needed to overcome the repulsive forces generated with the increase in the proton number.

The fragments produced on fission are particularly rich in neutrons. It is this neutron excess which leads to beta decay and neutron decay among the products of the fission process. Isotopes in both their ground and excited states can be produced directly in the fission

Figure 2.19. Energy Spectra of Prompt Neutrons Produced in ^{232}Th and ^{238}U Fission.

process. The total number of these direct products is approximately 800. Evaluated data for the fractional yields and subsequent decay chains for these isotopes and their excited states are contained in large computer files (England et al, 1976). These files are designed for use in programs for determining (1) decay heat levels in nuclear fuel,

Figure 2.20. Energy Spectra for the Six Groupings of Delayed Neutrons Produced in ^{232}Th Fission.

(2) effective* neutron capture cross sections for fission products, and (3) radiation levels associated with irradiated nuclear fuel. The distribution of direct yield fission product atomic masses for thorium fission is given in Fig. 2.24 (Kinsey, 1979). The figure illustrates the dependence of the mass distribution on the energy of the neutron initiating the fission event. The double humped nature of the mass distribution curve is characteristic of all fissioning nuclei. For comparison, similar

*In reactor calculations of power distribution, in which depletion of fissile isotopes is considered, certain fission products involved in decay chains that include one or more significant neutron absorbers are treated explicitly. The remaining fission products are lumped into a single pseudo-nuclide with an effective capture cross section.

Figure 2.21. Energy Spectra for the Six Groupings of Delayed Neutrons Produced in ^{238}U Fission.

curves for ^{233}U are provided in Fig. 2.25 (Kinsey, 1979). In Table 2.6, the fractional yields are given for the fission product isotopes of greatest importance in reactor neutron balance calculations (England et al, 1976).

The isotopes ^{135}Xe , with its large thermal neutron capture cross section, and ^{135}I , the direct precursor to ^{135}Xe , are of particular importance in determining reactor transient behavior. The next two isotopes in the table are precursors to the promethium-samarium fission product chain. The populations of the large neutron absorbers in this chain, ^{147}Pm , ^{149}Sm and ^{151}Sm in a given nuclear reactor, depend on the neutron flux energy distribution and reactor power (flux level). Their sensitivity to power history is, however, much less than that of ^{135}Xe . These isotopes plus ^{135}Xe represent a significant fraction of total neutron absorption by fission products in power reactors. At midcycle in the LWBR at Shippingport, they accounted for

Figure 2.22. Energy Spectra of Prompt Neutrons Produced in ^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu . ($P_f(E')$ $\equiv$ probability per unit energy.)

approximately 56 percent of total fission product absorption (Hecker, 1979). The last five isotopes in Table 2.6 yield, through beta decay, five additional isotopes that account for significant neutron absorption in light water moderated nuclear reactors (Wilson and England, 1979). These isotopes are indicated in parentheses following their precursors.

2.5 THORIUM NEUTRON SCATTERING CROSS SECTION

Scattering interactions between neutrons and nuclei can be divided into two classes: *elastic*, if energy is transferred to the internal degrees of freedom of the nucleus; *inelastic*, if not. Inelastic scattering reactions leave the nucleus in an excited state from which it subsequently decays by gamma emission. Neutron energies for which inelastic scattering is important begin in the unresolved resonance range described in Sect. 2.3. The reaction continues to be significant

Figure 2.23. Energy Spectra for the Six Groupings of Delayed Neutrons Produced in ^{233}U Fission.

TABLE 2.5—ENERGY YIELD FROM FISSION REACTIONS*

Energy Source	Fissile or Fertile Isotope†					
	²³² Th	²³⁸ U	²³⁵ U	²³³ U	²³⁹ Pu	²⁴¹ Pu
Fission Fragment Kinetic Energy	162.1 ± 1.5	170.0 ± 0.66	169.6 ± 0.7	168.7 ± 0.7	175.9 ± 0.1	175.5 ± 1.1
Prompt Neutron Kinetic Energy	4.7 ± 0.12	5.51 ± 0.1	4.79 ± 0.07	4.9 ± 0.1	5.9 ± 0.1	5.99 ± 0.13
Delayed Neutron Kinetic Energy	0.024 ± 0.004	0.021 ± 0.003	0.0071 ± 0.0007	0.0014 ± 0.0005	0.001 ± 0.0005	0.0074 ± 0.0015
Prompt γ rays	6.15 ± 1.75	6.28 ± 0.8	6.96 ± 0.7	7.59 ± 0.71	7.74 ± 0.45	7.86 ± 1.8
Delayed γ rays	8.01 ± 0.2	8.04 ± 0.08	6.26 ± 0.05	4.99 ± 0.04	5.16 ± 0.1	6.33 ± 0.07
β particles	8.28 ± 0.21	8.25 ± 0.08	6.43 ± 0.05	5.13 ± 0.04	5.3 ± 0.1	6.51 ± 0.04
Neutrino Energy	11.1 ± 0.3	11.14 ± 0.11	8.68 ± 0.06	6.91 ± 0.05	7.15 ± 0.11	8.78 ± 0.09
Total Energy Yield	200.3 ± 0.5	209.3 ± 0.3	202.7 ± 0.1	198.2 ± 0.1	207.2 ± 0.3	211.0 ± 0.3

*From Kinsey (1979) in units of MeV.

†The energy of the neutron initiating the fission is in the thermal range for ²³⁵U, ²³³U, ²³⁹Pu, and ²⁴¹Pu. For ²³²Th and ²³⁸U, the energy yields are due to fissions initiated by neutrons with a spectrum of energies typical of a light water moderated nuclear reactor.

for still higher energies, as can be seen in Fig. 2.26, which is a plot of the ENDF/B-V evaluation (Bhat, 1977a) of the ^{232}Th inelastic neutron scattering cross section. The elastic neutron scattering cross section for ^{232}Th is plotted in Fig. 2.27; this is also the ENDF/B-V evaluation (Pennington et al, 1979). As can be seen in Fig. 2.27, there is resonance elastic scattering. There is also what is called potential elastic scattering, in which the nuclear structure of the target plays no role. There is constructive and destructive interference between potential and resonance elastic scattering mechanisms. This is reflected in the shape of the total elastic cross section just below and above resonance energies. Note in Fig. 2.27 the dip in the cross section below resonance energies and the elevated cross section immediately above resonance energies.

Neutron scattering events in nuclear reactors are important in that they change neutron energies and directions. For elastic scattering, the change in neutron energy can be determined from simple kinematics. For massive nuclei such as ^{232}Th , this change in neutron energy is very small and is not very important in determining the overall energy moderation of neutrons in a nuclear reactor. Even these small energy changes are, however, of some significance in

Figure 2.24. Fission Product Yield for ^{232}Th .

determining effective self-shielded capture cross sections in the resonance energy range. The changing of neutron direction in resonance elastic scattering is also important in determining self-shielded capture cross sections.

Up to approximately 5 keV elastic neutron scattering from thorium is isotropic in the center-of-mass coordinate system. For a neutron- ^{232}Th nucleus system the laboratory and center-of-mass coordinate systems are practically identical. Thus neutrons scattering from thorium will come off isotropically in the laboratory coordinate system (the system in which reactor calculations are performed). Above 5 keV, elastically scattered neutrons have a distribution weighted towards the forward direction, i.e., the direction in which the incident neutrons are traveling.

In inelastic scattering events, neutrons come off nearly isotropically. Final neutron energies are much lower than for corresponding elastic scattering events as a significant fraction of the initial neutron energy is imparted to the target nucleus. An example of the probability distribution for final energies for ^{232}Th is given in Fig. 2.28. In this case, the initial neutron energy was taken to be that for the maximum of the inelastic cross section (approximately 2.5 MeV). ENDF/B cross section files contain these probability distributions over the complete

Figure 2.25. Fission Product Yield for ^{233}U .

TABLE 2.6—DIRECT YIELD FRACTIONS (X100) FOR ISOTOPES IN THE MORE IMPORTANT FISSION PRODUCT CHAINS

Fission Product	Fissile or Fertile Isotope*				
	^{232}Th	^{238}U	^{235}U	^{233}U	^{239}Pu
^{135}I	5.238	6.548	6.349	4.860	6.303
^{135}Xe	0.0403	0.0150	0.255	1.337	1.152
^{147}Nd	3.08	2.711	2.271	1.775	2.073
^{149}Pm	0.825	1.765	1.089	0.769	1.261
^{99}Mo (^{99}Tc)	2.965	6.247	6.127	4.957	6.144
^{103}Ru (^{103}Rh)	0.164	6.336	3.137	1.707	6.991
^{131}I (^{131}Xe)	1.481	2.982	2.473	2.352	3.093
^{133}I (^{133}Cs)	3.858	6.356	6.787	5.974	6.923
^{143}Ce (^{143}Nd)	6.619	4.834	5.972	5.881	4.561

*The energy of the neutron initiating the fission is in the thermal range for ^{235}U , ^{233}U , and ^{239}Pu . For ^{232}Th and ^{238}U , the yields are due to fissions initiated by neutrons with a spectrum of energies typical of light water moderated nuclear reactors.

Figure 2.26. Neutron Inelastic Scattering Cross Section for ^{232}Th .

energy range for inelastic scattering. For systems containing significant amounts of thorium and in which few light nuclei are present, thorium inelastic scattering can have a significant influence on the

Figure 2.27. Neutron Elastic Scattering Cross Section for ^{232}Th .

energy distribution of neutrons. Examples might be the blanket of liquid metal fast breeder reactors or fission-fusion hybrid devices.

The scattering cross sections for ^{233}U are very similar to those for ^{232}Th . The elastic and inelastic cross sections for ^{233}U are plotted in Fig. 2.29 (Stewart et al, 1978). In reactor systems using the thorium- ^{233}U fuel cycle or when thorium is a blanket material (as noted above) ^{233}U neutron scattering is not an important reaction. Fuel elements in all these cases will contain mostly thorium. In the LWBR at Shippingport, for example, the highest concentration of ^{233}U was 5.2 weight percent. Thus the effect of neutron scattering in the fuel on resonance shielding is dominated by thorium.

Finally, it should be noted that, for low neutron energies, when the wave lengths of neutrons are of the same order of magnitude as the spacing between nuclei, diffraction effects modify elastic scattering cross sections. This phenomenon depends on the properties of the particular lattice in which nuclei are found. For ThO_2 and thorium (α -form), which are both face-centered-cubic structures, the lattice parameters at 298 K are, respectively, 0.55975 nm (see Chap. 3) and 0.50861 nm (Norman et al, 1967). Neutron wavelengths of the magnitude of these dimensions correspond to kinetic energies of 0.0026

and 0.00316 eV. Modifications of the thorium elastic scattering cross section for such energies are of negligible importance for nuclear reactor systems, and thus are not discussed further.

2.6 CROSS SECTIONS FOR THORIUM-GAMMA RAY REACTIONS

The final class of nuclear data for thorium, important in its application to power generation, is that which governs the interaction of gamma rays with thorium. Cross sections for the various reactions are required to determine the distribution of gamma rays within reactor systems. This distribution governs the energy deposition rate within the system due to fission and neutron capture generated gammas and provides source distributions for shielding calculations. Certain of the reactions can influence the neutron population in a reactor system. In Fig. 2.30, the cross sections for (γ, n) , $(\gamma, 2n)$, and $(\gamma, \text{fission})$ reactions are given (Caldwell et al, 1980). Data for neutron yields from the photofission reaction $(\gamma, \text{fission})$ are presented in Table 2.7 (Caldwell et al, 1975.) Note that all of the reactions have energy thresholds. In fission reactors, the populations of gammas with energies above those thresholds are small, and the reactions are, therefore, not very important. It should also be pointed out that the (γ, n) and $(\gamma, 2n)$ reactions in thorium can initiate the chains leading to ^{232}U (see Sect. 2.2.3). Again, given the small population of gammas

Figure 2.28. Energy Spectrum of Neutrons Inelastically Scattered from ^{232}Th (Initial Neutron Energy = 2.5 Mev).

with the required high energies and the small (γ, n) cross sections, these reactions provide only a small contribution to ^{232}U production in fission reactors.

All reactions discussed thus far (Fig. 2.30) involve interaction with the thorium nucleus. Those reactions which predominate in determining the gamma distribution in reactor systems involve interaction with (1) atomic electrons and (2) the electric fields associated with atomic nuclei and electrons. In the former interaction, there is both the Compton effect, an inelastic scattering of gammas (γ, γ') , and the photoelectric effect, in which gammas are absorbed and atomic electrons are emitted (γ, e^-) . In the latter interaction, the reaction is pair production where a gamma is absorbed and an electron-positron pair is produced (γ, e^-e^+) . Cross sections for these reactions in thorium are presented in Fig. 2.31 (Bhat, 1977a). For further discussion of these reactions, including the Klein-Nishina formula which gives the final energy and angular distribution of Compton scattered gammas, see Evans (1955).

2.7 NUCLEAR PERFORMANCE OF THORIUM IN FISSION REACTORS

As noted in the introduction to this chapter, interest in thorium as a contributor to the world's useful energy supply is based on its

Figure 2.29. Inelastic (above) and Elastic (below) Neutron Scattering Cross Sections for ^{233}U .

transmutability into the fissile isotope ^{233}U . The ease with which this property can be utilized depends on the impact of the nuclear characteristics of thorium on the various reactor systems in which it might be placed.* This is discussed briefly in this section. As a point of reference in this discussion, the properties of ^{238}U are used for comparison.

Initial fissile loading required for criticality is affected first by the fact that there is no naturally occurring fissile isotope of thorium. When ^{238}U is to be used as the fertile isotope, there is always some ^{235}U present. Even if tails from a diffusion plant are used, 0.2 weight percent ^{235}U will most likely be present. Second, the fast fission cross section for ^{232}Th has a higher energy threshold than that for ^{238}U ; and when it is nonzero, it has a smaller magnitude than that for ^{238}U (see Fig. 2.15). Third, the number of neutrons produced per fission in ^{232}Th is less than that produced per fission in ^{238}U (see Fig. 2.17). Fourth, the capture cross section for ^{232}Th is greater than that for ^{238}U for much of the energy range of interest in nuclear reactors. Note Fig. 2.6 for the thermal range and Fig. 2.10 for the fast range. It is true that resonance capture cross sections are greater for ^{238}U than for ^{232}Th (see Figs. 2.8 and 2.9). However, for the energy distributions of neutrons present in common reactor types (light water reactors, heavy water-moderated reactors, gas-cooled thermal reactors, and liquid metal fast reactors), the fraction of neutrons captured in fertile material is greater for ^{232}Th than for ^{238}U when systems are compared for equal fissile loading and equal fertile loading. In total, these effects all lead to a higher fissile material loading requirement for initial criticality for a given reactor system and fissile fuel when thorium is used than is the case for an otherwise comparable system using ^{238}U .

The reduction with depletion of the neutron multiplication of most nuclear reactors when utilizing thorium is less rapid than for comparable systems using ^{238}U . This is due to the superior neutron production properties of ^{233}U as compared to ^{239}Pu and ^{241}Pu in all but fast reactor systems (see Fig. 2.1). Thus, on the basis of nuclear performance, the interval between refuelings for comparable thermal reactor systems can be longer when thorium is the fertile fuel. Of course, for a given reactor system, fuel element integrity may be the limiting factor in the depletion levels that can be achieved.

Finally, several nuclear properties of thorium affect the dynamic behavior of nuclear reactor systems. First, the transmutation chain for the conversion of thorium to ^{233}U (see Fig. 2.3) includes ^{233}Pa , which has a significant neutron capture cross section, particularly its resonance cross section ($I_x = 895 \text{ b}$), and a 27-day half life for radioactive decay to ^{233}U . Thus, ^{233}Pa acts as a power history dependent

*It also depends on being able to fabricate thorium into suitable fuel elements and after irradiation to separate chemically the resultant uranium.

Figure 2.30. Photon-Nucleus Reaction Cross Sections for Thorium.

TABLE 2.7—PROMPT AND DELAYED NEUTRON YIELDS FROM PHOTOFISSION OF $^{232}\text{Th}^*$

Energy (MeV)	$\bar{\nu}_p$	$\bar{\nu}_d^\dagger$
6.44	1.96 ± 0.11	0.0310 ± 0.0028
7.02	1.89 ± 0.11	0.0306 ± 0.0031
7.10	1.89 ± 0.11	0.0267 ± 0.0021
8.06	2.08 ± 0.11	0.0259 ± 0.0031

*Caldwell et al (1975).

†Total delayed neutron yield.

Figure 2.31. Thorium Cross Sections for Compton Scattering (γ, γ'), for the Photoelectric Effect (γ, e^-), and for Pair Production (γ, e^-e^+).

neutron poison in a thorium-fueled nuclear reactor. There is no isotope with comparable properties present in a ^{238}U fuel system. In the $^{238}\text{U} \rightarrow ^{239}\text{Pu}$ transmutation chain, ^{239}Np lies in the same position relative to ^{238}U as does ^{233}Pa relative to ^{232}Th . However, ^{239}Np has a much shorter half life (2.35 days) and smaller neutron capture cross sections: $I_x = 476$ b, $\sigma_{2200} = 45$ b (Joanou, 1961). Because of its shorter half life and moderate capture cross section, ^{239}Np does not act as a significant neutron poison.

The second nuclear property is the sensitivity of thorium resonance cross sections to temperature under self-shielded conditions, i.e., the thorium Doppler effect. Even though the effective resonance integral for a given temperature and lattice of fuel rods is greater for ^{238}U -base

fuel than for thorium-base fuel, the change in the integral per degree is greater for thorium (see Figs. 2.8 and 2.9). Thus, for comparable reactor systems, one with a thorium-base fuel will have a larger negative feedback on neutron multiplication with increased fuel temperature (Doppler coefficient) than will a ^{238}U -fueled reactor (see Shapiro et al, 1977, for results for a typical pressurized water reactor).

The third nuclear property is the direct yield of ^{135}Xe in thorium fission. As can be seen in Table 2.6, the direct yield of ^{135}Xe from thorium fission is greater than that from ^{238}U fission. This is true to an even greater extent for ^{233}U fission as compared to ^{235}U fission. A larger direct yield of ^{135}Xe relative to the direct yield of ^{135}I , the precursor to ^{135}Xe , means an increase in reactor stability to xenon-induced power oscillations. Thus, for comparable reactor configurations, a ^{232}Th - ^{233}U fuel system will have a greater stability relative to xenon-induced power oscillations than will a ^{238}U - ^{235}U fuel system. The stability is also enhanced by the larger Doppler coefficient for the ^{232}Th - ^{233}U fuel system.

The fourth nuclear property is the total delayed neutron yield, $\bar{\nu}_d$, of ^{232}Th . The delayed neutron fraction $\beta = \bar{\nu}_d/\bar{\nu}_T$ is an important parameter in describing the kinetic behavior of reactors which are close to prompt critical, i.e., their configuration is such that they could sustain a chain reaction on prompt neutron production alone. The total $\bar{\nu}_d$ for a reactor is the sum of the $\bar{\nu}_d$'s for each fissioning isotope, each weighted by the fraction of total fissions occurring in that isotope. For a ^{232}Th - ^{233}U fuel system, the large $\bar{\nu}_d$ for ^{232}Th (Table 2.3) compensates slightly for the low $\bar{\nu}_d$ of ^{233}U , 0.0074 for thermal fission as compared to 0.0167 for ^{235}U (Table 2.4). (See Hecker (1979) for discussion concerning the calculation of β for the LWBR at Shippingport.) The effective value of β for thorium- ^{233}U systems is about half that of ^{235}U -fueled reactors and about the same as for plutonium-fueled reactors. A small value of β means that the reactor is more responsive to reactivity changes, resulting in use of slower moving control elements than in ^{235}U -fueled reactors.

In conclusion, the nuclear properties of thorium and its bred fissile fuel, ^{233}U , are such that relatively abundant thorium can be a source of vast energy production. As demonstrated by the Light Water Breeder Reactor Program, this production can be achieved in nuclear reactors utilizing proven light water reactor technology.

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Chapter 3

PHYSICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

J. Belle and R. M. Berman

3.1 INTRODUCTION

The physical properties arising from the crystal and electronic structure of thorium dioxide are discussed in this chapter. In editorial organization, subsets of certain physical properties which could be treated in this chapter were deemed appropriate for discussion elsewhere. Thus, for example, thermal expansion is treated as a thermodynamic property in Chap. 5. Electrical conductivity is treated as a transport property in Chap. 6, though magnetic properties are discussed in Sect. 3.7 and thermal radiative properties in Sect. 3.6. Mechanical properties are discussed in Chap. 7.

The term *crystal structure*, as used here in its application to thorium dioxide, refers to the details of the arrangement of thorium and oxygen ions within a typical unit cell. The term *lattice* refers to the geometrical properties of that structure.

The thorium dioxide lattice has a cubic symmetry, and the properties of thoria are therefore isotropic, in the sense that three mutually perpendicular directions are interchangeable with regard to any property. Materials with lower symmetry are subject to various sorts of undesirable behavior under irradiation: dimensional instabilities due to anisotropic growth, phase changes to higher-symmetry configurations, and sometimes a complete destruction of the lattice (metamictization). Thoria is not subject to these phenomena.

The thorium dioxide structure is highly stable thermodynamically, in comparison to any other possible crystalline arrangement of the ions. As a result, there are no phase changes below the very high melting point, except for the *diffuse transition* (see Sect. 3.4.2 below and Chap. 5). Furthermore, the structure is one that can accommodate a considerable amount of solid solution substitution. Other

cations can therefore be introduced into the ThO_2 structure, changing the properties of the material in a controlled, systematic, and predictable way.

The crystal structure of ThO_2 , shown in Fig. 3.1, is very similar to that of UO_2 . By identifying the dark spheres as uranium atoms, Fig. 3.1 could represent UO_2 , in which case the cell edge at room temperature would be 2 percent smaller (0.54705 instead of 0.55975 nm). It follows that the properties of the materials arising out of the crystal structure should be very similar for the two substances.

The electronic structures of ThO_2 and UO_2 are also similar, except for one feature: the presence of 5f electrons in UO_2 . This major difference is responsible for profound differences in some physical proper-

FLUORITE STRUCTURE OF ThO_2
 DARK = Th
 LIGHT = O

Figure 3.1. Structure of the Unit Cell of Thorium Dioxide.

ties, notably magnetism, electrical conductivity, and color. Thus, thorium dioxide is diamagnetic, a colorless insulator and stoichiometric, whereas uranium dioxide is paramagnetic, a colored semiconductor and can be nonstoichiometric.

For many of the properties discussed in this chapter and others, it will be appropriate to compare the corresponding values for thoria and urania, and also the solid solutions between them. Not only are these substances of intrinsic interest, but the information available on one may serve to explain, verify, or permit estimates to be made of the data for the other.

3.2 PROPERTIES OF THE ThO_2 CRYSTAL LATTICE

3.2.1 Description of the Fluorite Structure

The only oxide of thorium with significant stability in the solid state is ThO_2 , thorium dioxide (thoria). The solid monoxide, ThO , is metastable (see Chap. 4). Below its melting point of 3640 K (see Chap. 5), ThO_2 occurs only as a cubic phase having the fluorite structure, which was first identified and described by Goldschmit and Thomassen (1923) for the mineral *fluorite* (CaF_2). An authoritative review of this work is available in Wyckoff (1963). Goldschmit and Thomassen (1923) also correctly identified ThO_2 and UO_2 as materials having this structure.

The fluorite structure is represented in Fig. 3.1. The pattern shown here is repeated indefinitely in three dimensions. Each thorium ion (dark sphere) is surrounded by eight oxygen ions (light spheres) at the corners of a cube of which the thorium ion is the center. Each oxygen ion is surrounded by a similar cube, but only four of the eight corners are occupied by thorium ions. The four thorium ions form a tetrahedron surrounding the oxygen ion. The thorium ions are therefore in 8-coordination (or have a coordination number of 8) and the oxygen ions are in 4-coordination; the fluorite structure is sometimes described as exhibiting "8-4" coordination.

Among the 32 crystallographic point groups, thoria is assigned to the one of highest symmetry, $4m\bar{3}m$, commonly abbreviated $m\bar{3}m$. This symmetry is identical to that of the cube; the symbols indicate that there are 4-, 3-, and 2-fold symmetry axes, mirror planes in which the 3-fold axes lie, and separate mirror planes in which the 4-fold axes lie. Each of the point groups corresponds to one or more of the 230 space groups, which specify the internal symmetry. The notation of the space group that includes thoria is formed by prefixing the letter F to the abbreviated point-group notation; the space-group notation is therefore $Fm\bar{3}m$. The letter F indicates that the structure, in

addition to satisfying the point group criteria, also falls into that class of substances having the face-centered-cubic lattice, one of the 14 Bravais lattices.

3.2.2 X-ray Diffraction Results

A face-centered-cubic structure, such as that shown in Fig. 3.1 produces observable diffraction peaks only for those sets of planes having Miller Indices, h , k , and l , that are either all even or all odd. The peaks observable with copper $K\alpha$ X-rays are listed in Table 3.1 together with newly calculated position and intensity data based on the wavelength and atomic scattering factor data of Wyckoff (1963). Table 3.1 also lists similar data for three other commonly used X-ray wavelengths.

In calculating the positions of Table 3.1, the edge of the unit cell of pure thorium at room temperature was taken as 0.55975 nm. This is a consensus value based on many measurements made on reactor-grade material at the Bettis Atomic Power Laboratory. A typical sample of pure, well-crystallized thorium, made by calcining thorium oxalate for example, gives a diffractogram of excellent quality, with exceptionally sharp, strong peaks at highly reproducible diffraction angles.

On the basis of this unit cell measurement, the distances between the centers of the ions shown in Fig. 3.1 may be calculated. The closest approach of the centers of two oxygen ions to each other is half the unit cell edge, or 0.27988 nm. The closest approach of thorium to oxygen ion centers is $\sqrt{3}/4$ times the cell edge, or 0.2424 nm. The closest approach of the centers of two thorium ions is $\sqrt{2}/2$ times the cell edge, or 0.3958 nm at room temperature.

3.2.3 Theoretical Density

The appropriate SI unit for density is the kg/m^3 . A more convenient unit is obtained by using a multiple of this basic unit, the Mg/m^3 , which is identical to the more familiar g/cm^3 .

For pure thorium dioxide, the volume of the unit cell is $(0.55975 \text{ nm})^3 = 1.75381 \times 10^{-22} \text{ cm}^3$. This volume contains 4 thorium and 8 oxygen ions which, together, have a mass, in atomic weight units, of $4(232.038) + 8(15.9994) = 1056.147$, which is equivalent to $1056.147 / (6.02252 \times 10^{23}) = 1.75366 \times 10^{-21} \text{ g}$. The density of pure thorium at 298 K may therefore be calculated as $(1.75366 \times 10^{-21}) / (1.75381 \times 10^{-22}) = 10.00 \text{ g/cm}^3 = 10.00 \text{ Mg/m}^3$. Similarly, the corresponding theoretical density for pure uranium dioxide is 10.96 Mg/m^3 . Note, however, that Fink et al (1981) cite the value of 10.97 Mg/m^3 for the density of UO_2 at 298.15 K (see Chap. 5).

TABLE 3.1—X-RAY DIFFRACTION ANGLES (BRAGG ANGLES, 2θ , DEGREES) AND
RELATIVE INTENSITIES FOR THE MOST COMMONLY USED WAVELENGTHS

h	k	l	Interplanar Distance, D (nm)	Cu $K\alpha$		Fe $K\alpha$		Cr $K\alpha$		Mo $K\alpha$	
				2 Theta	I	2 Theta	I	2 Theta	I	2 Theta	I
1	1	1	0.323172	27.58	100.00	34.86	100.00	41.50	100.00	12.60	100.00
2	0	0	0.279875	31.95	48.82	40.47	48.13	48.29	47.52	14.56	49.87
2	2	0	0.197902	45.81	42.56	58.57	40.34	70.69	39.53	20.65	47.09
3	1	1	0.168771	54.31	54.66	70.00	51.87	85.43	54.7	24.26	63.61
2	2	2	0.161586	56.94	16.58	73.61	15.88	90.23	17.5	25.36	19.58
4	0	0	0.139938	66.80	7.22	87.54	7.58	109.79	11.1	29.36	8.88
3	3	1	0.128415	73.72	24.54	97.84	29.59	126.13	59.6	32.06	30.46
4	2	0	0.125614	75.96	21.83	101.32	27.91	132.32	64.35	32.92	27.03
4	2	2	0.114258	84.78	18.18	115.82	31.26			36.17	21.65
5	1	1									
			0.107724	91.29	20.87	127.95	48.03			38.44	23.33
3	3	3									
4	4	0	0.098951	102.24	7.05	156.08	39.34			42.01	6.60
5	3	1	0.094615	109.00	28.91					44.03	23.25
6	0	0									
			0.093292	111.31	18.31					44.69	13.90
4	4	2									
6	2	0	0.088504	120.99	15.25						
5	3	3	0.085361	129.94	18.51					47.25	8.86
6	2	2	0.084385	131.79	18.92					49.10	8.41
4	4	4	0.080793	144.88	8.95					49.70	7.83
										52.08	2.32

In fluorite-type solid solutions, including thoria and its solid solutions, if the cell edge a (in nanometers) and molecular weight M are known, the theoretical density, in Mg/m^3 , may be calculated from the equation

$$D = 6.6423 \times 10^{-3} M/a^3 \quad \text{Eq. (3.1)}$$

The measured lattice constants of some $\text{ThO}_2\text{-UO}_2$ solid solutions and their calculated theoretical densities from the work of Cohen and Berman (1966) are shown in Table 3.2; this work is discussed further in Chap. 4.

TABLE 3.2—ROOM TEMPERATURE LATTICE CONSTANTS AND THEORETICAL DENSITIES OF $\text{ThO}_2\text{-UO}_2$ SOLID SOLUTIONS*

Composition (mole % UO_2)	Lattice Parameter ($\text{nm} \pm 0.00003 \text{ nm}$)	Theoretical Density (Mg/m^3)
0.0	0.55975	10.00
10.1	0.55846	10.09
20.2	0.55726	10.18
30.1	0.55590	10.28
40.3	0.55475	10.37
50.1	0.55355	10.46
60.1	0.55225	10.55
69.9	0.55098	10.65
80.1	0.54969	10.75
90.0	0.54841	10.85
100.0	0.54705	10.96

*Cohen and Berman (1966)

3.2.4 Neutron Diffraction Results

Willis (1963a, 1963b) studied both thoria and urania by neutron diffraction, a technique that has the advantage of being responsive to the positions of oxygen ions in the cell. The oxygen positions cannot readily be observed by X-ray diffraction because the scattering of X-rays by oxygen is very much less than by the heavy metallic ions. Willis (1963a) found that the structures did, indeed, closely approach the ideal fluorite configuration at low temperature. As the temperature is raised, the vibration of the oxygens about their ideal positions

becomes anharmonic due to the effect of the vacancy at the center of the unit cell. As a result, the mean positions of the oxygen ions are displaced some distance toward the center, such that the cell coordinates of an oxygen ion, instead of being (0.25, 0.25, 0.25), for example, become (0.25+d, 0.25+d, 0.25+d). (For other oxygen ions in the cell, the values 0.75 and 0.75-d can be substituted for any or all of the coordinates.) Measured values (Willis, 1963b) for this displacement,

in ThO₂ for various temperatures, are given in Table 3.3. Willis (1963b) reported that the value of d for UO₂ at 1273 K is slightly higher than that for ThO₂ at 1293 K: 0.016 ± 0.001 compared to 0.014 ± 0.001 .

Willis (1963a) gave a value of $0.995 \pm 0.009 \times 10^{-12}$ cm for the scattering amplitude for ²³²Th in neutron diffraction. This quantity is a measure of the intensity of the waves generated by the interaction of the thorium and the neutrons, and is used for calculating diffraction intensities. The work also included a determination of the Renninger peaks of the (200) reflection of a single crystal of thoria, i.e., the minor fluctuations in intensity observed in rotating a (200) surface in its own plane. The Renninger peaks are an expression of the fact that, from the point of view of the neutron beam, the density of ions defining the plane changes as the sample is rotated. The observed variations are shown in Fig. 3.2.

3.2.5 Lattice Thermal Vibration

Thermal motion of the atoms causes a degradation of the intensities of diffraction peaks with increasing angle. This is due to the fact that, at high temperature, the mass of the atom effectively sweeps out

TABLE 3.3—DISPLACEMENT, d, OF MEAN POSITION OF OXYGEN IONS IN THORIA AT VARIOUS TEMPERATURES ALONG UNIT CELL AXES, IN FRACTION OF AXIAL LENGTH

Temperature (K)	d	Standard Deviation
571	0.006	0.004
715	0.008	0.003
846	0.009	0.001
1054	0.012	0.001
1163	0.013	0.002
1293	0.014	0.001

For displacement toward center in nanometers, multiply by $\sqrt{3} \times 0.55975 = 0.9695$.

Figure 3.2. Dependence of Peak Intensity of (200) Reflection from ThO_2 on Azimuthal Orientation of (200) Plane. The Renninger Peaks are Labeled a, b, c, etc. (from Willis, 1963a).

and occupies a larger sphere than it would if it were at rest. This effect can be expressed by the Debye-Waller temperature factor B , which, theoretically, is equal to $8\pi^2 (= 78.96)$ times the mean square displacement of a particular atom from its ideal position, in a direction perpendicular to the plane being measured.

Willis (1963a, 1963b) determined these values separately for thorium and oxygen atoms in the thoria structure, at temperatures between 293 and 1293 K. Clausen et al (1983) extended these measurements on both ThO_2 and UO_2 beyond 1293 K to about 2400 K. The results for both investigations are listed in Table 3.4. The parameters at 293 K determined by Clausen et al (1983) are in good agreement with those of Willis (1963a, 1963b). Clausen et al (1983) reported that the oxygen Debye-Waller parameter B_o starts to rise rapidly above 2000 K, and that the anharmonicity is larger in UO_2 than in ThO_2 . Since the values apply to all the planes examined, the square roots of the values in Table 3.4 may be regarded as $8.89 (= \sqrt{78.96})$ times the mean amplitude of thermal vibrations, in nanometers. A distinction must here be made: Table 3.3 gives values for the displacement of mean positions with temperature, while Table 3.4 reflects the amplitudes of the vibrations about those mean positions.

TABLE 3.4—DEBYE-WALLER TEMPERATURE FACTORS
FOR THORIUM AND OXYGEN IONS, (nm)²

Temperature (K)	B _{Th}	B _O	References
293	20 ± 3	37 ± 4	Willis (1963a, b)
293	27.8 ± 3.1	38.3 ± 4.0	Clausen et al (1983)
410	26 ± 4	40 ± 5	Willis (1963a, b)
571	39 ± 4	72 ± 4	Willis (1963a, b)
715	55 ± 6	94 ± 7	Willis (1963a, b)
846	65 ± 3	109 ± 4	Willis (1963a, b)
1054	81 ± 6	138 ± 7	Willis (1963a, b)
1163	99 ± 7	145 ± 8	Willis (1963a, b)
1293	105 ± 6	168 ± 7	Willis (1963a, b)
1653	185 ± 4	292 ± 4	Clausen et al (1983)
1873	180 ± 4	304 ± 7	Clausen et al (1983)
2273	233 ± 3	393 ± 4	Clausen et al (1983)
2473	268 ± 5	455 ± 9	Clausen et al (1983)

Results of neutron diffraction measurements carried out to much higher temperatures (to 2930 K) on both ThO₂ and UO₂ were reported by Hutchings et al (1984). This work was a continuation of the earlier work reported by Clausen et al (1983) on efforts to obtain direct information on Frenkel defect formation in these oxides (see Sect. 3.4). The temperature variations of the Debye-Waller parameters for thorium and oxygen in ThO₂ and for uranium and oxygen in UO₂ are shown, respectively, in Fig. 3.3 and 3.4. (Presumably, the measurements reported by Clausen et al (1983) are included in these plots.) The lower-temperature data of Willis (1963b) are also shown in the figures. As Hutchings et al suggest, the Debye-Waller parameters for ThO₂ and UO₂ plotted as a function of homologous temperatures, i.e., versus T/T_m , show the data to fall close to common curves for oxygen and the cations (see Fig. 3.5).

3 BONDING IN THORIUM DIOXIDE

3.3.1 Atomic Radii

Shannon and Prewitt (1969) compiled an empirical set of "effective" ionic radii that agreed with measured interatomic distances for most oxides and fluorides. Included in this compilation are the radii for the divalent oxygen ion in 4-fold coordination (0.138 nm) and the tetravalent thorium and uranium ions in 8-fold coordination (0.106 and 0.100 nm, respectively). Shannon (1976) reported a revised value of 0.105 nm for Th⁴⁺. The sum of the cation and anion radii in the case of thorium dioxide is 0.244 or 0.243 nm, values which are in fair agreement with the value of 0.242 nm measured for the Th-O distance

Figure 3.3. Temperature Variation of Debye-Waller Temperature Factor B for Thorium and Oxygen, According to Hutchings et al (1984). Various Symbols are for Different Specimens; the Data of Willis (1963b) are Shown as Filled-in Circles.

in thorium. In the case of UO_2 , the values are 0.238 and 0.237 nm, respectively, for the sum of radii and the experimentally determined U-O distance in urania. These agreements suggest that the bonding is ionic in these oxides. On the other hand, the stability limit criterion for the ionic model of the fluorite structure, i.e., $R_{M+4}/R_{O-2} > 0.732(\sqrt{3} - 1)$, indicates that ThO_2 is stable but UO_2 is not. Indeed, according to this stability rule, all actinide dioxides except those of thorium and protactinium should be unstable.

Blank (1974) examined the problem by comparing the interatomic distances with values obtained for halides in which the bonding is certainly ionic. He concluded that the interatomic distances for fluorite-type MO_2 compounds are smaller than would be expected from the analogous fluorides. He gave the values for the Phillips

Figure 3.4. Temperature Variation of Debye-Waller Temperature Factor B for Uranium and Oxygen, According to Hutchings et al (1984). Various Symbols are for Different Specimens; the Data of Willis (1963b) are Shown as Filled-in Circles.

Ionicities (Phillips, 1970), i.e., fraction of ionic character in a typical nion-cation bond. For fluorite-type compounds of the general formula MF_2 , this fraction is stated to be >0.911 . For MO_2 compounds of the fluorite-type structure, the fraction is <0.91 , and the bonds therefore have a significant portion of covalent character. Thus, Blank (1975) argued that the conventional view of fluorite oxides as ionically bonded should be modified; some covalent character must be present because ionic bonding alone cannot explain the stability of the actinide dioxides. However, in the Discussion of Blank's paper (Blank, 1975), Catlow pointed out that the radius ratio rules are based on the hard sphere concept, a model not theoretically correct for these oxides, and therefore that violation of the stability rule does not prove the existence of large deviations from ionic bonding.

Figure 3.5. Variation of Debye-Waller Temperature Factors for Thorium, Uranium, and Oxygen with T/T_m . Data are from Hutchings et al (1984) and Willis (1963b).

3.3.2 Electron Configuration

The electron shells of the thorium atom consist of the stable configuration of radon (2 K electrons, 8 L electrons, 18 M electrons, 32 N electrons, 18 O electrons, 8 P electrons), plus two additional electrons in the P shell and two in the Q shell. The usual symbolic notation for this configuration is $(Rn)(6d^2)(7s^2)$; the final two electrons in the sixth (P) shell being in the d orbital, and the first two electrons in the seventh (Q) shell being in the s orbital. These final four electrons are stripped off when the thorium atom becomes a Th^{+4} ion. In contrast, the free-atom electronic configuration for uranium is $(5f^3)(6d^1)(7s^2)$. Veal and Lam (1974) showed, by means of X-ray photoemission spectroscopy, that the electronic structures of thoria and urania are similar, except for the presence of 5f electrons in uranium dioxide. These

low-binding-energy 5f electrons permit uranium to assume the U^{+5} and U^{+6} states, allow interstitial oxygen to enter the lattice, and produce dramatic differences in such physical properties as electrical conductivity, magnetism, and color. By contrast, all the thorium valence electrons are tied up in the thorium-oxygen bond in ThO_2 , and interstitial oxygen is excluded from the lattice.

Gubanov et al (1977) studied the problem of interaction of these electron shells with those of the eight surrounding oxygens in the crystal structure for thoria and urania; effectively, the entity considered was a $(\text{ThO}_8)^{-12}$ or $(\text{UO}_8)^{-12}$ ion. From the distribution of electron populations, he concluded, in the case of the $(\text{ThO}_8)^{-12}$ ion, that the net charge on the central thorium ion was not +4, as it would be for purely ionic bonding, but +2.47. A similar evaluation of the uranium-oxygen complex gave a value of +2.21 for the net charge on the uranium. The departure of these values from +4 represents a sharing of the electrons with the oxygens, and therefore a partially covalent character to the bonds.

3.3.3 Lattice Energy

The problem of the nature of the bonding has also been approached from the point of view of the lattice or cohesive energy. Thorium dioxide, like other crystalline materials, spontaneously forms itself into the orderly array of its crystal structure, rather than the pseudo-random arrangement of a liquid or glass, because the ordered crystalline form has a lower free energy at temperatures below the melting point. This decrease in free energy attributable to the ordering is termed the lattice energy, and is a direct reflection of the stability of the crystal structure.

The lattice energy is zero at the melting point; at that point, the free energies of the liquid arrangement of the ions and the crystalline arrangement are equal. The total energies are different due to the differences in entropy between the liquid and the crystalline states; this difference in energy is expressed as ΔH , the latent heat of crystallization, —the amount of heat released, per mole, on moving from the liquid to the crystalline form at the melting temperature. This is the starting point for the calculation of the lattice energies at lower temperatures.

To find the difference in energy appropriate to a lower temperature, it would be useful if the gap, ΔH , could be "corrected", first by adding the energy gained by moving a mole of the crystalline solid from the melting point to the desired temperature, and then by subtracting the amount of energy needed to perform a similar operation for the supercooled glass. This energy amounts to the difference between $\int C_p dT$ at the two temperatures. Tabulated values are available for the crystalline solid (see Chap. 5, Tables 5.6 and 5.8), but not for the glass,

TABLE 3.5—CALCULATIONS OF THE LATTICE ENERGY
(kJ/mol) OF ThO₂ BY THE BORN-HABER CYCLE

Symbol from Eq. (3.2)	Childs (1958)	Benson et al (1963)
ΔH_f	-1130	-1222
L	+640	+563.6
D	+490	+490.4
A	-711	-749
ΣI_i	+6339	+6322
U	-10021	-10096

since the material cannot be made. It is necessary, instead, to calculate indirectly what the enthalpy of formation would be for such an imaginary material, starting with the elemental components, which, by definition, have a value of zero.

This exercise is called the Born-Haber Cycle and is based on the Born model of a crystal having integral ionic charges. The calculation made for a temperature of 0 degrees K is as follows:

$$U = \Delta H_f - L - D + 2A - \Sigma I_i \quad \text{Eq. (3.2)}$$

where

- U = lattice energy
- ΔH_f = heat of formation of the crystalline solid
- L = heat of vaporization of the metal
- D = dissociation energy of O₂
- A = affinity of O atom for two electrons
- ΣI_i = sum of first four ionization potentials of the metal atom.

This calculation has been performed for thorium by Childs (1958) and by Benson et al (1963). Results of their calculations are shown in Table 3.5. Although slightly different values were used for various quantities in Eq. (3.2) and different theoretical approaches were taken, both authors found values for the lattice energy U that were close to -10000 kJ/mol (-2400 kcal/mol). Benson et al (1963) also calculated a value of -9929 kJ/mol for the cohesive energy using experimentally derived elasticity data. The reasonably good agreement between this value and the Born-Haber cycle calculation supports the assumption of ionic bonding for ThO₂.

3.4 LATTICE DEFECTS IN ThO₂

Crystalline solids contain various types of lattice or structural imperfections. One classification due to Van Bueren (1961) is based on

linear dimensions and, accordingly, divides these imperfections or defects into four groups: point defects, line defects, plane defects, and volume defects. Only the first two are lattice defects and are discussed in this section. Point defects include vacancies, which are empty lattice sites where atoms are missing, interstitials, which are atoms that occupy interstices between regular sites, chemical impurities, color centers, or some combination of these. Line defects are dislocations, i.e., displacements of the periodic structure in certain directions. Grain boundaries and external surfaces are examples of planar defects; voids and second-phase inclusions are representative of volume defects.

3.4.1 Point Defects

Crystalline point defects are present in thorium, as in all other crystalline materials, at an equilibrium concentration dependent on the temperature. The two main types of atomic point defects for a stoichiometric crystal are the Frenkel defect, which consists of equal concentrations of vacancies and interstitial ions for the same atom, and the Schottky defect, which consists of equivalent concentrations of cation and anion vacancies. The Frenkel defect is more probable for thorium by analogy to stoichiometric UO_2 , where the dominant point defects are anion Frenkel defects (O^{2-} vacancies and O^{2-} interstitials). This condition for the anion sublattice is referred to as anti-Frenkel disorder, the term Frenkel disorder being used to denote the analogous state of the cation sublattice where equal concentrations of cation vacancies and cation interstitials exist. Frenkel or anti-Frenkel disorder is generally favored in stoichiometric crystals if the sizes of cations and anions are appreciably different, whereas Schottky disorder occurs where the cations and anions are of comparable size.

Since formation of a Schottky defect will increase the volume of the crystal but will not affect the lattice constant, the concentration of Schottky defects can, in principle, be determined by comparing the expansion with temperature as measured both by dilatometry and by X-ray diffraction. The results for thorium discussed in Chap. 5 confirm the absence of Schottky defects in ThO_2 .

Point defects are also formed as a result of departure from stoichiometry. Hyperstoichiometric UO_{2+x} is formed by incorporating interstitial oxygen rather than by forming uranium vacancies. Similarly, hypostoichiometric UO_{2-x} has oxygen vacancies rather than uranium interstitials. Note, however, that the pressure dependency of the degree of hypostoichiometry in UO_{2-x} , as measured at 2073–2673 K by Tetenbaum and Hunt (1968), can be rationalized in terms of the presence of uranium interstitials, i.e., U_{1+y}O_2 . By analogy with UO_{2-x} , the defects in ThO_{2-x} should be oxygen vacancies rather than thorium interstitials.

In addition to the structural defects, crystals also contain electronic defects (electrons and holes). The electronic defects in ThO_2 are involved as a result of changes in stoichiometry and are responsible for the electrical conductivity of ThO_2 .

Colbourn and Mackrodt (1983) reported results of theoretical calculations for the energies of both atomic and electronic disorder in thoria. Not surprisingly, their calculations predict the predominance of anion Frenkel defects in ThO_2 . The theoretical value for the energy of formation of anion Frenkel defects in ThO_2 was calculated to be 6.01 eV (580 kJ/mol); this contrasts with the much higher energetic requirement (11.93 eV or 1151 kJ/mol) calculated for the formation of Schottky defects. The authors point out that their values are close to those for UO_2 reported previously by Catlow (1977), who made similar calculations. A value of 3.0 eV (289 kJ/mol) was calculated by Colbourn and Mackrodt (1983) for the energy of formation of anion vacancies or anion interstitials. They also calculated values for energy levels and electronic defects.

In principle, lattice disorder can be detected from neutron diffraction and scattering measurements at high temperatures, since these measurements provide information on both the time-averaged positions of the ions in the lattice and on their average thermal motion. The first attempt to determine disorder from such experiments was negative; there was no definite indication of Frenkel disorder in UO_2 up to about 2400 K (Clausen et al, 1983). In later investigations the same working group (Hutchings et al, 1984) reported the first direct evidence of Frenkel disorder in the oxygen sublattices of both ThO_2 and UO_2 from neutron scattering experiments at high temperatures. In the case of UO_2 , oxygen disorder occurs above about 2000 K and increases with increase in temperature. An activation energy of about 4.6 ± 0.5 eV for the formation of a Frenkel pair was obtained from the data. This value is smaller than the calculated value of 5.6 eV reported by Catlow (1977). In the case of ThO_2 , there appears to be a measurable amount of Frenkel disorder above about 2100 K, but the ThO_2 data are not sufficiently precise to obtain an accurate activation energy. Nevertheless, the authors suggest a homologous value of about 5.4 eV, by using the ratio of the melting temperatures, i.e.,

$$\frac{3640 \text{ K}}{3120 \text{ K}} \times 4.6 \text{ eV} = 5.4 \text{ eV}$$

Note that this value is also smaller than that calculated (6.01 eV) by Colbourn and Mackrodt (1983).

As thoria is heated above 2000 K in a nonoxidizing atmosphere, oxygen is lost; on cooling, the material is observed to be dark. If the oxygen loss is substantial, it can be measured by determining the weight gain on heating in air at temperatures below 1500 K, —an

operation that returns the material to stoichiometry, from ThO_{2-x} to ThO_2 , and restores its initial color. The delineation of the Th-O binary system, including the extent of hypostoichiometry obtainable at various temperatures, is discussed in Chaps. 4 and 5.

A vacancy is formed when oxygen is lost from the anionic lattice. To maintain overall electrical neutrality, it is necessary that one or more thorium ions assume a charge somewhat lower than normal. A similar type of defect (impurity defect) is created by introducing into the structure various foreign cations with an electronic charge less than Th^{+4} , such as Ca^{+2} or Y^{+3} (Naik et al, 1977; Maiti and Subbarao, 1976). The presence of these altermvalent impurities also leads to formation of anion vacancies.

Defects are also caused by irradiation. Neeley et al (1967) describe experiments in which single crystals of thoria were irradiated with 2 MeV electrons, 150 keV X-rays, and gamma rays from ^{60}Co . The electron-spin-resonance (ESR) spectra indicated that the optical absorption could be attributed to the trapping of single electrons in the vicinity of doubly charged oxygen vacancies in the ThO_2 lattice. This is the so-called F-center, responsible for the optical absorption.

Defects exist as single, isolated point defects at low concentrations, but at high concentrations defects can agglomerate into clusters. This is the case in hyperstoichiometric UO_{2+x} as revealed by neutron-diffraction measurements made on a single crystal of $\text{UO}_{2.12}$ at 1073 K by Willis (1964a, 1964b). Willis showed that on oxidation of UO_2 to UO_{2+x} , as a result of the introduction of interstitial oxygen ions, vacancies in oxygen sites are also created. Thus UO_{2+x} can be considered to be a solid solution which contains three types of oxygen atoms: O, O', and O". The O atoms occupy the regular fluorite sites of UO_2 , but some of these sites are empty in UO_{2+x} , i.e., there are vacancies. The O' and O" atoms occupy interstitial positions which are displaced by about 0.1 nm along the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, respectively. To account for the diffraction results, Willis (1964a, 1964b) postulated that the interstitial oxygen atoms are not distributed at random throughout the lattice but are together in clusters. In a later analysis of the same neutron-diffraction data, Willis (1978) proposed a new model, the so-called 2:2:2 configuration of oxygen defects, which permitted a better treatment of the anharmonic motion of the oxygen atoms. In this interpretation, the cluster contains two anion vacancies, two $\langle 110 \rangle$ interstitial oxygens, and two $\langle 111 \rangle$ interstitial oxygens.

3.4.2 Phase Transition

A change in the lattice that goes beyond the formation of a limited number of Frenkel defects is the so-called "diffuse" or "lambda" transition found for various nonoxides of the fluorite or antfluorite

structure (Dworkin and Bredig, 1968). This transition occurs at about $0.8 T_m$ (T_m is the melting point in K) and is characterized by large anomalies in enthalpy and heat capacity. Dworkin and Bredig (1968) suggested that the fluorite-type oxides, such as ThO_2 and UO_2 , should also show this transition. Indeed, Bredig (1972) interpreted the high-temperature enthalpy data for UO_2 as evidence for the existence of such a transition at 2670 K for this oxide, and predicted a similar transition for ThO_2 . Bredig viewed this order-disorder transition as a cooperative process resembling somewhat that of melting in which there is a change of the normal fluorite structure AB_2 to a disordered structure where the B atoms are randomly distributed over both the tetrahedrally and the octahedrally coordinated sites. Experimental evidence from enthalpy measurements for the existence of such transitions in ThO_2 and UO_2 and in their solid solutions is discussed in Chap. 5.

3.4.3 Dislocations or Line Defects

In a lattice defect, an ion moves from its ideal position to some other position, representing an energy minimum, where it can lodge and exist in a metastable state. The distance moved is a multiple of a unit distance between minima; this unit translation is called the Burgers Vector.

The translation is most likely to occur along the planes of highest ion density; these will also be the planes along which the dislocations will be most mobile. In the face-centered-cubic structure, this translation occurs along the (110) plane, and the shortest Burgers Vector corresponds to a distance of 0.3958 nm in the case of thoria. This is the value previously given as the closest approach of the centers of two thorium ions. Translations of one unit cell length (0.55975 nm) along the cubic plane may resolve themselves into two dislocations of the type described above, but there is no energy advantage in so doing. Dislocations in other possible directions, however, are less stable than the two described above, in the sense that the free energy of the system is lowered if they resolve or dissociate themselves into dislocations of the type described.

3.5 OPTICAL PROPERTIES OF CRYSTALLINE THORIA

3.5.1 Absorption Spectra

Details of the optical absorption spectra of ionic oxides, such as ThO_2 and UO_2 , are useful in revealing much about the oxide, such as electronic levels, lattice vibrations, and the behavior of lattice defects. Results of studies of the optical absorption spectra of thoria are discussed below.

Childs et al (1970, 1972) investigated the optical absorption spectrum of arc-melted single crystal thoria from its ultraviolet absorption edge, which they placed at 213 nm, through the visible range (400—700 nm), and into the near infrared, to 2700 nm. They distinguished 31 absorption peaks, which are listed, together with their assigned designations, in Table 3.6. Typical spectra obtained by Childs et al (1972) are shown in Fig. 3.6. In this particular material,

TABLE 3.6—OPTICAL ABSORPTION BANDS IN FUSED THORIA

Band	Energy (eV)	Half-width (eV)
α'	5.624(0.056)	0.251(0.087)
α	5.455(0.023)	0.347(0.048)
β	5.323(0.023)	0.281(0.046)
γ	5.190(0.041)	0.283(0.076)
δ	4.906(0.048)	0.267(0.094)
ϵ	4.485(0.028)	0.379(0.074)
ζ'	4.254(0.016)	0.304(0.044)
ζ	4.067(0.020)	0.320(0.049)
η'	3.856(0.017)	0.298(0.045)
η	3.638(0.021)	0.279(0.042)
θ'	3.445(0.031)	0.248(0.052)
θ	3.225(0.038)	0.225(0.068)
ι	3.056(0.033)	0.224(0.045)
κ	2.826(0.036)	0.248(0.073)
λ'	2.657(0.023)	0.223(0.081)
λ	2.475(0.033)	0.246(0.054)
μ	2.330(0.023)	0.239(0.038)
ν	2.202(0.026)	0.227(0.044)
ξ	2.095(0.030)	0.219(0.052)
$\omicron$	1.991(0.026)	0.224(0.043)
π'	1.834(0.038)	0.216(0.054)
π	1.701(0.030)	0.224(0.058)
ρ	1.525(0.035)	0.244(0.051)
σ	1.328(0.046)	0.233(0.047)
τ'	1.142(0.024)	0.193(0.054)
τ	0.975(0.019)	0.190(0.063)
ϕ	0.820(0.025)	0.179(0.045)
χ'	0.720(0.017)	0.155(0.027)
χ	0.626(0.013)	0.123(0.031)
ω'	0.571(0.016)	0.070(0.022)
ω	0.498(0.019)	0.087(0.026)

(Courtesy, American Ceramic Society)

1. Nomenclature is that assigned by Childs et al (1972).
2. Peaks have Gaussian profiles on a scale in which wavelengths are expressed as eV; to convert to nm, divide eV values into 1239.85, i.e., the alpha prime peak is at $1239.85/5.624 = 220.46$ nm.
3. Numbers in parentheses are standard deviations.

Figure 3.6. Typical Absorption Spectra for Pure ThO_2 (A) Annealed for 2 Hours in Air at 1400 C, (B) Annealed for 2 Hours in Ar (Ta Heating Element) at 1400 C, and (C) γ -irradiated to 10^6 r (from Childs et al, 1972; Courtesy, American Ceramic Society).

samples heated in an oxidizing atmosphere (two hours in air at 1673 K) showed a series of low-intensity, coalesced peaks. The same material, enclosed in tantalum foil and heated in a static atmosphere of purified argon at the same temperature and time, showed the second spectrum, with the α , β , and γ peaks much increased in intensity. The third spectrum was obtained from the same material after γ -irradiation with a ^{60}Co source to 10^6 r; the coalesced peaks of the first spectrum are more or less uniformly increased in intensity. Not all samples of thoria reacted in this way; some showed very little change on heating in a nonoxidizing atmosphere, or on γ -irradiation.

Childs et al (1972) expressed the opinion that probably all the observed absorption peaks could be ascribed to impurities in the ppm

range in their material. However, the only tentative correlations they could establish were Zn as the cause of the ϵ and θ' bands (4.485 and 3.445 eV; 276 and 360 nm), and Nd or Tb for the ι band (3.056 eV; 406 nm). Values were given in eV because the resolution of coalesced peaks into Gaussian profiles was performed on a spectrum presented in this manner. To convert to wavelength units, note that the product of the energy (in eV) and the wavelength (in nm) is equal to 1239.85.

Childs et al (1972) maintained that absorption bands such as the strong peaks of Fig. 3.6(B) had been mistaken for the absorption edge by previous investigators, who placed the absorption edge at approximately the high-wavelength margin of these peaks. These reported values were 3.9 eV by Weinreich and Danforth (1952); 3.5 eV by Bodine and Thiess (1955); 5.0 eV by Bates (1967); 4.1 eV by Neeley et al (1967); and 4.9 eV by Linares (1967). According to Childs et al (1972) the true absorption edge for thorium, i.e., the wavelength below which it has an opacity comparable to metals, is at 213 nm. This value of the wavelength corresponds to 5.82 eV for the energy gap between the valence band of electrons and the conduction band of electrons.

Linares (1967) investigated the optical transmission of single-crystal thorium in the near infrared. He found a nearly featureless spectrum, with a maximum transmission in the vicinity of 6000 nm. Beginning at a wavelength of 7000 nm, the transmission began to decline, reaching about 2 percent of the 6000 nm value through a 2 mm section at a wavelength of 9000 nm.

Bates (1967) obtained absorption spectra for both single-crystal and polycrystalline thorium. Results for the infrared region are shown in Fig. 3.7. The visible and ultraviolet ranges were also investigated; results were in general agreement with the later, more detailed work of Childs et al (1972). The increasing absorption in the polycrystalline material as the wavelength decreases below 8 micrometers represents scattering by grain boundaries, which would be expected as the wavelength approaches the grain size. Other, minor features of the two spectra of Fig. 3.7, such as the small absorption peaks, were attributed to trapping in the vicinity of impurity ions.

The vertical scale for the single-crystal absorption spectrum (the upper curve of Fig. 3.7) represents the optical density (OD), i.e., $\log_{10} I_0/I$, where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. The vertical scales for the polycrystalline absorption spectra in this chapter (the lower curve of Fig. 3.7 and also Figs. 3.6, 3.8, 3.9, and 3.10) are also optical density scales, but the zero point of these scales has been shifted an arbitrary amount to permit display of the spectrum.

In their paper on UO₃, Tsuboi et al (1962) reported results on optical absorption in the far infrared region for UO₂. They identified the absorption observed for UO₂ at 24,300 nm with the absorption expected from the fluorite structure, since it was the only one having

Figure 3.7. Infrared Absorption Spectra of ThO_2 as Measured by Bates (1967).

the width and intensity characteristic of absorptions due to lattice vibrations, i.e., stretching and contracting of the metal-oxygen bond. From this observation, they calculated the stretching force constant, K , of the equation

$$\chi = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{Eq. (3.3)}$$

where

χ = frequency of absorption,

c = velocity of light,

μ = reduced mass of vibrating bodies, such that $(1/\mu) = (1/m') + (1/m'')$, m' and m'' being the masses of the oxygen and uranium atoms.

Their calculated value for K was 1.05×10^{15} mol/N·m. Comparing this value with those obtained on other U-O compounds, they found that this force constant varied such that K was proportional to the U-O distance, as would be expected from theory. Since the value from the 24,300 nm absorption of UO₂ agrees with this relation, that particular absorption can be ascribed to lattice vibration. That is, if it is assumed that the one very strong absorption observed corresponds to that expected from lattice vibration, it is possible to calculate a value of the stretching force that is consistent with the values calculated from other U-O compounds. Unfortunately, there are no absorption measurements in this region of the far infrared for ThO₂ to compare with those for UO₂.

Berman (1967) investigated the optical absorption spectra of ThO₂-UO₂ solid solutions, using mixtures of 2 weight percent of the oxide, as a powder, mixed with KBr and compacted into 1 mm thick wafers in an evacuated die. The peaks described for thoria by Childs et al (1972) could not be detected in these dilute mixtures; Berman observed a featureless spectrum for thoria from 650 to 2700 nm. As urania was added, however, the absorption spectrum of this substance appeared, as shown in Fig. 3.8.

Gruen (1954) showed that, as the urania content in ThO₂-UO₂ solid solutions increased, the minimum wavelength at which measurable light could be passed (not necessarily the true absorption edge) increases to 700 nm. In the process, the solid solutions become increasingly opaque at the violet end of the visible spectrum, with the opaque region moving toward the red as the uranium increased. ThO₂-UO₂ solid solutions appear greenish to the eye. Thin sections of monocrystalline UO₂ appear a deep cherry-red to the eye when a strong source of light is viewed through them; the edge of the significant transmission of light in this material is just inside the red edge of the visible spectrum. Single crystals of pure thoria are colorless by transmitted visible light.

The wavelengths of the peaks shift slightly toward larger values as the urania content is increased. This shift may be attributed to the changing dimensions of the $[(Th,U)O_8]^{-12}$ complex as the unit cell size changes, and is shown in Fig. 3.9. As the material is oxidized to hyperstoichiometric compositions, the well-defined peaks of the absorption spectrum are degraded, and can no longer be resolved. The

Figure 3.8. Near-infrared Absorption Spectra of ThO_2 , UO_2 , and Intermediate Compositions.

total optical absorption of the material increases with increasing oxidation, particularly at short wavelengths. As a result, the green or brown color of finely ground stoichiometric solid solutions changes to black, for oxidized material.

Figure 3.9. Wavelength Shift with Composition of Absorption Bands in Near-infrared Spectra of UO_2 - ThO_2 Solid Solutions.

However, although the peaks of the UO_2 absorption spectrum are obscured, another peak, at a wavelength of approximately 1600 nm, appears, and its intensity increases with increasing oxygen content. The intensity varies in a manner that would be expected if it were proportional to the content of U^{+5} ion. In highly oxidized, high-thoria solid solutions, in which the valence of the uranium ions can reach or exceed +5 (see Chap. 4), another peak appears, at 1360 nm, which may be attributable to the U^{+6} ion. Peaks appear very prominently near these positions in the optical absorption spectrum of U_3O_8 . Typical spectra of hyperstoichiometric materials are shown in Fig. 3.10.

Figure 3.10. Changes in the Spectrum of $\text{Th}_{0.6}\text{U}_{0.4}\text{O}_2$ with Oxidation.

Because ThO_2 has a high refractive index (see below, Sect. 3.5.3) there has been some interest in the use of thin-layer coatings (200—400 nm thick) of thoria on optical-component substrates for use as mirrors, beam-splitters, narrow-band filters, polarizers, and the like. Sokolova (1974) investigated the properties of such coatings, which she formed by evaporation and deposition on quartz discs. On decreasing wavelength, absorption began to be significant at 330 nm, increasing to high values at 250 nm. This absorption could be moved toward lower wavelengths (280—220 nm) by heating from 473 to 973 K. On the basis of these observations Sokolova calculated the expected performance of an 11-layer narrow band filter (which was not actually fabricated). Such a filter with ThO_2 layers, fabricated to absorb at a wavelength of 255 nm, would show a sharper and more intense optical absorption than comparable filters using HfO_2 or ZrO_2 layers.

3.5.2 Fluorescence and Thermoluminescence

Luminescence is the general term given to describe the process whereby a crystal absorbs energy by radiation and reemits energy in the form of visible light. The process is called fluorescence if the material emits light simultaneously with its excitation, and phosphorescence if the reemission takes 10^{-7} seconds or longer. There are a number of ways to produce luminescence, and some of these have been studied for ThO_2 .

Harvey et al (1973) reported observing fluorescence in pure thoria, in thoria doped with 0.14 mole percent CaO , and in thoria doped with 0.28 mole percent Y_2O_3 . The materials were excited by being exposed to ultraviolet radiation; a portion of this radiation, on being absorbed, was reradiated at longer wavelength and, as a result, a faint blue color could be observed in the visible range. The fluorescent output could be resolved into bands which, in pure thoria, occurred at 395.4, 434.6, and 464.0 nm. These can be related to energy absorbed at 238.9, 227.1, and 252.7 nm, respectively, corresponding to the γ , α , and δ absorption bands (Table 3.6) of Childs et al (1972). The relative intensities of the fluorescent emission bands varied with the dopants; there were also minor shifts in wavelength (on the order of 3 nm) from the values observed in pure thoria. The result suggests that the same defect centers are present in pure and doped thoria, although in slightly different concentrations. The fluorescence was not greatly affected in wavelength or intensity by heating of the material in reducing or oxidizing environments.

Claudel et al (1975) confirmed these results on oxalate-derived thoria, and found that the intensity of the fluorescence increased when the temperature was lowered to 77 K, but that the relative intensities between the various wavelengths, the general configuration of the

fluorescence emission spectrum, did not change. In thoria derived from the calcining of thorium nitrate, however, a number of discrete peaks appeared above the normal fluorescence profile at 77 K, and the maximum of the normal fluorescence profile was shifted. These effects were attributed to impurities.

If excitation occurs at a low temperature and the temperature of the crystal is subsequently raised, resulting in the emptying of the electron traps and the emission of visible light, the process is called thermoluminescence because it appears as if the luminescence is thermally produced. Temperatures are, however, well below those needed for normal incandescence in the visible range.

Harvey and Hallet (1976) investigated the thermoluminescence of nominally pure thoria single crystals in the temperature range from 77 to 673 K. At least five trapping centers and four recombination centers were found at room temperature and above, and at least eight additional trapping centers were identified between cryogenic and room temperatures. These were ascribed to trivalent lanthanide ions present at concentrations on the order of 5 ppm. The effect observed at 77 K could be enhanced by two orders of magnitude if the sample was first exposed to ultraviolet radiation at room temperature. Deliberate doping with Ca^{+2} , Y^{+3} , and Ta^{+5} led to decreases in the thermoluminescence. Fe^{+2} (in thoria exposed to reducing atmospheres) and Fe^{+3} (in thoria exposed to oxidizing atmospheres) also probably contributed to the thermoluminescent effect.

Rodine and Land (1971), in a similar study on undoped, flux-grown thoria crystals, observed the absorption edge at 213 nm and a peak in thermoluminescence excitation at 210 nm. They associated these with a band gap of 5.75 eV in nominally pure thoria. The ultraviolet cutoff thus coincides with the peak of the thermoluminescent excitation spectra.

Bressat et al (1975) prepared thoria with the following impurities, present on the order of 0.1 mole percent: Zr^{+4} , U^{+6} , Ce^{+4} , Bi^{+3} , Sm^{+3} , Ca^{+2} , Pr^{+3} , and Pb^{+2} . (Only one such impurity was present in any one sample.) They then examined the photoluminescence (luminescence induced by visible light, ultraviolet rays, or X-rays) of these products at room temperature and observed results comparable to those reported above: a small peak at 393 nm and a broad peak centered at 440 nm. For the samarium-doped thoria, however, several additional, very sharp peaks were observed at 565, 610, and 620 nm.

Bressat et al (1975) also examined adsorboluminescence, in which the excitation is caused by the adsorption of gases. In this work, hydrogen or oxygen were admitted to an evacuated chamber at 723 K at 21–26 kPa after a thorough degassing of the doped thoria sample in the chamber. This phenomenon has the characteristic that only the F-centers on the surface of the material take part in the luminescence. In place of the broad peaks at 393 and 440 nm, there was a single very

broad peak with a maximum in the 510—610 nm region. For the samarium-doped material, the sharp peaks continued to appear at 565, 610, and 620 nm. One exception was noted to the above generalization: the praseodymium-doped thoria showed two peaks of moderate sharpness, at 635 and 710 nm, in place of the very broad peak.

Effects on luminescence behavior resulting from changes in the oxygen vacancy concentration in thoria-yttria solid solutions were examined by Nāfe et al (1982). Two compositions were studied $\text{Th}_{0.9}\text{Y}_{0.1}\text{O}_{1.95}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$. Oxygen vacancy concentrations were varied by annealing the materials at 1400 K in oxidizing and reducing atmospheres. Those samples that were annealed in oxygen showed higher intensities than samples annealed in hydrogen. The decrease with time in the intensity of luminescence was also greater for the materials annealed in oxygen. Thermoluminescence also depended on the sample pretreatment. Nāfe et al (1982) attributed these results to the mobility of the electrons which was higher for the samples annealed in oxygen.

3.5.3 Optical Constants

(a) Refractive Index

The refractive index (n) of thoria was measured by Ellis and Lindstrom (1964), who found that it was 2.105 at a wavelength of 589.3 nm, 2.110 at a wavelength of 564.1 nm, and 2.135 at a wavelength of 435.8 nm; an error band of ± 0.005 was given for the refractive index determinations. The results of these measurements show that the refractive index varies only slightly with wavelength. Thoria is optically isotropic, and therefore will show no birefringence (interference colors) when viewed by transmitted light between crossed polarizers; however, Frondel (1958) states that anomalous birefringence is sometimes observed in naturally occurring thoria. Such anomalous birefringence can generally be attributed to strain.

The exceptionally high refractive index of this material results in a critical angle of only 28° . A light ray approaching a surface, from within the material, at an angle greater than this cannot leave the material; it will, instead, be totally reflected from the surface, back into the interior of the sample. To maintain a useful degree of transparency, suitable for the transmission of images in such material, it would be necessary for coarse or single-crystal material to have most optical paths free of internal surfaces on the scale of millimeters. Such specimens have not been made except on a research scale. Typical large-grain polycrystalline thoria is white and translucent; the transmission of light can be detected by the illumination of thin edges.

(b) *Extinction Constant*

The radiation contribution to the thermal conductivity of dielectric solids (see Chap. 6) is given by

$$\lambda_r = \frac{16}{3} \sigma_s n^2 T^3 L_r \quad \text{Eq. (3.4)}$$

where

λ_r = radiation contribution to the thermal conductivity

σ_s = Stefan-Boltzmann constant = $5.6697 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$

n = refractive index of the material

T = temperature, K

L_r = mean free path of the radiant energy, m.

This equation is also written as

$$\lambda_r = \frac{16}{3} \frac{\sigma n^2 T^3}{k} \quad \text{Eq. (3.5)}$$

where k = extinction coefficient, m^{-1} , the reciprocal of the photon mean free path, L_r .

The extinction coefficient, k , is the sum of the absorption coefficient A and the scattering coefficient Σ , which includes reflections at interfaces within the material. The terms *absorption coefficient* and *extinction coefficient* have been used interchangeably in the literature; however, they are equivalent only in the case of single crystals, where $\Sigma = 0$. The extinction coefficient k can be evaluated from the Lambert-Beer law

$$I_s/I_o = \exp(-ks) \quad \text{Eq. (3.6)}$$

where

I_s = intensity of the transmitted light

I_o = intensity of the incident light

s = sample thickness.

The extinction coefficient k and the refractive index n are assumed to be independent of temperature and of the wavelength of the radiant energy λ in Eqs. (3.4) and (3.5); i.e., the equations are valid only for *gray absorbers*. Although n varies little with temperature or wavelength, k can be a function of these variables. Thus to evaluate the extinction coefficient from the measured spectral absorption

spectrum it would appear that values of $k(\lambda)$ are needed for $0 < \lambda < \infty$. For a given temperature, however, k can be evaluated for a range of wavelengths. This integrated or *average* value is referred to in the literature as the *Rosseland absorption coefficient*.

In practice the extinction coefficient can be obtained from the Lambert-Beer expression. Thus, from Eq. (3.6).

$$k = \frac{2.303 \log(I_0/I_s)}{s} \quad \text{Eq. (3.7)}$$

or

$$k = \frac{2.303(OD)}{s} \quad \text{Eq. (3.8)}$$

where the optical density (OD) is defined as $\log(I_0/I_s)$.

The extinction coefficient k is related to the extinction constant κ through the equation

$$\kappa = \frac{k\lambda}{4\pi} \quad \text{Eq. (3.9)}$$

The refractive index n and the extinction constant κ are the optical constants of the real and imaginary parts of the complex index of refraction $N_{\lambda,T} = n - i\kappa$.

There is little information on the evaluation of the extinction coefficient from the absorption spectra for ThO_2 comparable to that for UO_2 reported by Browning (1980). However, Chan and Ma (1981) reported calculations of the extinction constant κ for ThO_2 from the absorption data of Bates (1967) discussed above in Sect. 3.5.1. The authors referred to their tabulated values as extinction coefficients (k) but, in the terminology used here, their values are extinction constants (κ), calculated from Eqs. (3.8) and (3.9). The thickness of the single-crystal specimens in the work of Bates (1967) shown in Fig. 3.7 is given by Chan and Ma (1981) as 0.048 cm. Since this value was not reported by Bates, it is assumed that Chan and Ma (1981) obtained this information through private communication.

The Chan and Ma (1981) tabulated values for the extinction constant (or in their nomenclature, the extinction coefficient k) for single-crystal ThO_2 vary from 0.0035 (at a wavelength of 10 μm) down to zero (where the curve in Fig. 3.7 shows an absorption of zero, in the vicinity of 7 μm), upward again to about 0.0003 (near the ultraviolet cutoff at 213 nm). There is no information on the temperature dependence of the extinction constant.

Probably of more general applicability than the specific values given for the calculated extinction constants are the comparisons between these and comparable values for single-crystal UO_2 tabu-

lated by Chan and Tseng (1979). The values for UO₂ vary from 0.0013 at a wavelength of 10 μ m, downward to 0.0002 at 8 μ m, then upward to 0.43 near the ultraviolet cutoff. As shown in Fig. 3.8, UO₂ passes about an order of magnitude less light than ThO₂ under comparable conditions in the near infrared (1800—2800 nm), and the difference increases as the wavelength moves toward the visible range (below 700 nm). Solid solutions of ThO₂-UO₂ occupy intermediate positions.

3.6 THERMAL RADIATIVE PROPERTIES OF ThO₂ AND ThO₂-UO₂

Emittance, reflectance, absorptance, and transmittance, the thermal radiative properties that describe the transport of energy by radiation, are properties of real (as opposed to ideal) specimens. Emissivity and the other properties ending in *ivity* are the intrinsic properties of the material of which the particular specimen is composed. The intrinsic property is approximated by values obtained from measurements on opaque specimens that have clean, optically smooth surfaces. Thus, the emittance, ϵ , is expressed as the ratio of the radiant energy of a body at a given temperature to that of a black body at the same temperature; emissivity is the emittance of a specimen that has an optically smooth surface and is thick enough to be opaque.

In some investigations, total emittance, integrated over all wavelengths, is determined, usually as a function of temperature. In others, spectra are given of the variation of emittance with wavelength at a specific temperature or temperatures. In typical modern work, equipment comparable to that described by Clark and Moore (1966) is used. A double-beam spectrophotometer alternately samples, compares, and appropriately adjusts two optical trains—one containing the sample, and the other a reference black body; the degree of adjustment needed to nullify the alternating output signal is read as the emittance. In this technique, most of the corrections, such as those due to nonlinear absorption of the instrumental optics, are nullified, since they are the same in both optical trains.

In the case of nonopaque materials such as thorium, however, a significant source of error remains: a finite portion of the energy is transmitted optically. This may account for the differences among the various investigations. It is not possible to establish the extent to which optical losses have affected the various sets of results in the literature. Accordingly, all results are termed emittance in this review, although some authors state that their results are emissivities.

Figure 3.11 presents the results of two determinations (Pirani, 1939, and Pears, 1962) of total emittance of polycrystalline thorium as a function of temperature. The results of Pears (1962) may be characterized by stating that the total emittance is approximately 0.3 at

Figure 3.11. Determinations of Total Emittance of Polycrystalline Thoria.

temperatures below 2000 K; at that temperature, it increases sharply to 0.6—0.7. The emittances reported by Pirani (1939) indicate an increase at low temperatures, but these values represent an increased fraction of a very small amount of total emitted energy.

Figures 3.12 and 3.13, respectively, show determinations of spectral emittance as a function of wavelength for thoria at 1600 K (solid lines), in the visible range, and in the near and midinfrared up to a wavelength of 15 μm . Also shown in Figs. 3.13 and 3.12 with dashed or dotted lines, are, respectively, the determinations at 1400 and 1200 K in the infrared, and a representative selection of available spectra of thoria-ceria solid solutions in the visible (as compiled in Gmelin, 1955). The highly anomalous emittance spectra of $\text{ThO}_2\text{-CeO}_2$ solid solutions in the visible range account for the lemon-yellow color observed when these materials are heated to incandescence. This property was utilized commercially in the Welsbach Gas Mantle (see Chap. 1).

Figure 3.14 shows emittance determinations on ThO_2 by Karow and Bober (1979) from 1500 K to the melting point and beyond, for a midvisible and a midinfrared wavelength. It indicates that the emittance is approximately constant at these wavelengths, from the temperature range of Fig. 3.12, up to the melting point (3640 K). The

Figure 3.12. Spectral Emittance of Thoria and Thoria-Ceria (Visible).

curve shows an inflection at the melting point for both wavelengths; liquid ThO_2 has a higher emittance than solid material in the visible, and a lower emittance in the infrared.

The data in Fig. 3.14 at 1600 K are in reasonable agreement with the 1600 K spectrum of Fig. 3.13 at the 10.6 μm wavelength. For the visible wavelength, however, Fig. 3.14 (top) indicates a far higher emittance than the corresponding point in Fig. 3.12. This discrepancy, as well as the discontinuities between the various investigations in Figs. 3.11 and 3.12, and the difficulty of reconciling the relatively constant curves of the solid in Fig. 3.14 and the sharp increase in Fig. 3.11, indicate that the state of information on the emittance of thoria has some difficulties yet to be resolved.

Figure 3.13. Spectral Emittance of ThO₂ (Infrared).

Kneissl and Richmond (1968) measured the normal optical reflectance of a sphere of sintered, polycrystalline ThO₂ at wavelengths of 0.63 μm , in the visible, and 1.15 μm , in the near-infrared. In the visible, the reflectance was approximately 85 percent from 300 to 1300 K; it declined to approximately 80 percent as the temperature was raised to 1950 K. Values of the near-infrared measurements were typically about 5 percent lower than the corresponding measurements at 0.63 μm .

Figure 3.14. Variation of Emittance with Temperature Above 1500 K for ThO_2 and UO_2 (Karow and Bober 1979). (Courtesy, International Atomic Energy Agency, Vienna)

3.7 MAGNETIC PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

When a substance is placed in a uniform magnetic field, it responds by generating a field of its own. In many magnetic media, including,

as far as is known, thoria and its cubic oxide solid solutions, the strength of this induced field is proportional to the amount of material present and also to the strength of the imposed field. The proportionality constant χ is termed the magnetic susceptibility. If the amount of material is specified as one mole, the molar susceptibility χ_m , the ratio between the applied and the induced field, has dimensions of mol^{-1} . (It is customary to use the multiplier 10^{-6} , i.e., $\times 10^{-6} \text{mol}^{-1}$.) Materials with negative values of χ (and χ_m) are termed diamagnetic; the induced field is opposite in direction from the applied field. When the orientations of the fields are parallel, the material is paramagnetic and χ is positive.

It is theoretically possible to calculate χ_m from Avogadro's Number and the magnetic moments of the individual atoms; these magnetic moments, in turn, are derivable from the electron orbital configuration. In practice, however, for large atoms, physical measurements on macroscopic samples are used. Typically, these involve apparent weight changes of samples placed along the axis of a solenoid when a known current is permitted to flow.

In substances for which there is no significant interaction between the induced dipoles, the cumulative effect of the individual atoms on the magnetic susceptibility is additive. Accordingly, the molar magnetic susceptibility is one of the class of properties described generically as "Property X" in Sect. 4.3.1 of Chap. 4. Given a table of values of χ_m coefficients for various materials, analogous to Table 4.1, it is possible to calculate the molar susceptibility of solid solutions between them; a linear variation with molar composition is assumed. This linear relationship is known as Wiedemann's additivity law in its application to molar magnetic susceptibility.

The molar susceptibility of all substances has a diamagnetic (i.e., negative) component, which arises from the orbitals of electrons around the atoms. Electron spin is largely responsible for a paramagnetic contribution to the susceptibility, provided that there is no spin in the opposite direction that cancels this component. The total measured magnetic susceptibility of a paramagnetic material is therefore the algebraic sum of these two contributions. The paramagnetic component, if it is present, is typically two to three orders of magnitude larger than the diamagnetic component.

The diamagnetic component of the molar magnetic susceptibility is usually independent of temperature. For diamagnetic substances such as pure thoria, which have no significant paramagnetic component, the total measured susceptibility should be essentially independent of temperature. Trzebiatowski and Selwood (1950) obtained values of $-10.6 \times 10^{-6}/\text{mol}$ at 298 K, and $-21.1 \times 10^{-6}/\text{mol}$ at 83 K, for the molar susceptibility of pure thoria, and adopted a mean value of

-15.8×10^{-6} /mol (at all temperatures) for their subsequent work. Goto (1968) used a value of -11×10^{-6} /mol for ThO₂, also for all temperatures.

The U⁺⁴ ion is paramagnetic, and the diamagnetic contribution in urania and urania-thoria solid solutions must therefore be calculated, rather than observed directly. In this calculation, it is assumed (1) that the susceptibilities of the materials present are additive; (2) that the susceptibility of the thoria corresponds to the values given above; and (3) that the temperature dependence of the paramagnetic contribution follows the Curie-Weiss Law, Eq. (3.10) below. Trzebiatowski and Selwood (1950) used values of -12×10^{-6} and -35×10^{-6} /mol for the diamagnetic contributions of O⁻² and U⁺⁴, respectively, or -59×10^{-6} /mol for pure UO₂. Goto (1968) gave values of -12 and -26×10^{-6} /mol, respectively, or -50×10^{-6} /mol for UO₂. Slowinski and Elliott (1952) reported a value of -43×10^{-6} /mol for UO₂. Appropriate consensus values are -15×10^{-6} /mol for ThO₂ and -50×10^{-6} /mol for UO₂.

All the investigators mentioned above are in agreement that the paramagnetic contributions for urania and urania-thoria solid solutions closely follow the Curie-Weiss Law throughout the ranges covered in their studies. Together, these represent temperatures from 66 to 300 K, and compositions from 2 to 100 mole percent UO₂. To a certain extent, this involves a circular argument (because of assumption (3), above); however, the paramagnetic component is sufficiently close to the total measured susceptibility that any large departure from the Curie-Weiss Law could be detected. This law states that

$$\chi_p = C/(T + \phi) \quad \text{Eq. (3.10)}$$

where

- C = Curie Constant
- ϕ = Weiss Temperature
- T = temperature of measurement in K
- χ_p = paramagnetic component, of the molar susceptibility, in reciprocal moles (of U⁺⁴).

Figures 3.15 and 3.16 show the values of C and ϕ , respectively, obtained by Trzebiatowski and Selwood (1950), and by Slowinski and Elliott (1952), from their magnetic susceptibility measurements on ThO₂-UO₂ solid solutions.

For the Curie constant C, these investigators, and also Comly (1968) and Goto (1968), agree that the value approaches unity at infinite dilution of the U⁺⁴ ion. Accordingly, the data were fit by

Figure 3.15. Values of Curie Constant C for U^{+4} Ion, Calculated from Magnetic Susceptibility Measurements on ThO_2 - UO_2 Solid Solutions.

nonlinear regression analysis to a mathematical model that was constrained to pass through 1 at $U = 0$, where U = mole fraction of UO_2 . The determination of C is subject to substantial errors at high U^{+4} dilutions; accordingly, the two data points at $U = 0.02$ and 0.05 , shown on Fig. 3.15, are questionable and are therefore omitted from the regression analysis. The resulting equation, represented on the figure by the dashed line, is:

$$C = 1 + 0.24 U^{0.563} \text{ K/mol} \quad \text{Eq. (3.11)}$$

The data for the Weiss Temperature ϕ , in Fig. 3.16, were fit to a linear equation:

$$\phi = 21.05 + 201.9 U \text{ K} \quad \text{Eq. (3.12)}$$

Figure 3.16. Values of the Weiss Temperature ϕ for U⁴⁺ Ion Calculated from Magnetic Susceptibility Measurements on ThO₂-UO₂ Solid Solutions.

Accordingly, the combined consensus equation, for the molar magnetic susceptibility of the unoxidized ThO₂-UO₂ solid solution, including the correction for the diamagnetic component, is:

$$\chi_m = U \left(\frac{1 + 0.24 U^{0.563}}{T + 21.05 + 201.9 U} - 5 \times 10^{-5} \right) - 1.5 \times 10^{-5}(1 - U)(\text{mol}^{-1}) \quad \text{Eq. (3.13)}$$

where

- χ_m = molar susceptibility, per mole of unoxidized solid solution
- T = temperature, kelvin
- U = mole fraction of UO₂ in (U,Th)O₂.

Equation (3.13) is valid only for unoxidized (stoichiometric) material. The contours in Fig. 3.17 represent molar susceptibilities as calculated by Eq. (3.13); the plotted points represent locations at which Trzebiatowski and Selwood made measurements. (The individual measurements of Slowinski and Elliott (1952) are not available.) The digits shown adjacent to the points represent the percentages by which the measurements differ from the equation.

The individual U^{+4} ion is a magnetic dipole, i.e., it may be considered as a small bar magnet. The magnetic moment μ of this dipole is the torque exerted on it when it is placed in a unit magnetic field, which is defined here as one tesla, T. If such a field occurred uniformly

Figure 3.17. Molar Magnetic Susceptibility of ThO_2-UO_2 . (Contours represent values calculated by means of Eq. (3.13). Points represent locations of measurements by Trzebiatowski and Selwood (1950); accompanying digits are percent above or below calculated value.)

over 1 m^2 within a single, circular loop of wire, and decayed uniformly over 1 second to zero, an electromotive force of 1 volt would be generated between the ends of the wire.

The magnetic moment is related to the Curie Constant C by the equation

$$\mu = \beta \sqrt{C} \quad \text{Eq. (3.14)}$$

where β is a constant corresponding to 2.84 Bohr Magnetons, or $2.63 \times 10^{-23} \text{ J/T}$. As infinite dilution of the U^{+4} ion is approached, $C = 1$ and $\mu = \beta$, which is the value of the magnetic moment appropriate to a field generated by electron spin only.

Magnetic susceptibility measurements on UO_2 by Comly (1968) showed that, at very low temperatures, UO_2 becomes antiferromagnetic, i.e., the U^{+4} dipoles interact with each other so that their directions are either parallel or 180° removed from the direction of the overall field, with the reversed dipoles being in the minority. The temperature at which this transition from paramagnetic to antiferromagnetic behavior takes place is the Néel temperature, T_N .

From measurements of lattice parameter versus temperature (see Fig. 3.18), Marples (1976) observed a sharp decrease of $2.5 \times 10^{-5} \text{ nm}$

Figure 3.18. Lattice Parameter Versus Temperature for ThO_2 and UO_2 (from Marples, 1976). (Courtesy, North-Holland Publishing Company)

in the lattice parameter of UO_2 at 32 K on cooling, and therefore placed the T_N value at this temperature. He identified the transition as first order and contrasted this transition with the λ -type anomaly at 28.7 K in the heat capacity curve for UO_2 found by Jones et al (1952). Marples (1976) also pointed out that the later heat capacity measurements on UO_2 (Huntzicker and Westrum, 1971) showed a very sharp transition at 30.44 K which was characteristic of a first-order change. Thoria does not show such a transition in the lattice parameter-temperature curve, as can be seen from Fig. 3.18.

Comly (1968) measured the magnetic susceptibility of UO_2 , ThO_2 , and $\text{UO}_2\text{-ThO}_2$ solid solutions in the temperature range $1.7 \text{ K} \leq T \leq 55 \text{ K}$. In UO_2 , Comly (1968) found a sharp decrease of about 10 percent in χ at the Curie Point on cooling. The temperature of this point decreases linearly with decreasing U, reaching absolute zero at approximately $U = 0.59$. The magnitude and sharpness of the discontinuity in χ also decreased with decreasing U. Solid solutions with $U < 0.59$ exhibit a paramagnetic state at all temperatures, except for the diamagnetic materials with compositions in the immediate vicinity of pure thoria. However, high-thoria solid solutions ($0.052 \leq U \leq 0.101$), in the temperature range examined by Comly, have susceptibilities that fall below the values that would be predicted by the Curie-Weiss Law, using the coefficients of Eq. (3.14). The decrease from the predicted value is approximately linear, beginning at about 60 K and reaching approximately one-third the predicted value of 1.7 K.

White and Sheard (1974) reported some thermal expansion data at low temperatures (1.5 to 35 K) on ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$ solid solutions which show that magnetic contributions to the thermal expansion persist up to about 80 mole percent ThO_2 . The Néel temperature, T_N , was reduced from 30.40 K in the case of UO_2 to 14 K for $\text{UO}_2\text{-25 mole percent ThO}_2$. A plot of the thermal expansion data is shown in Fig. 3.19.

Goto (1968) determined magnetic susceptibilities of oxidized $\text{ThO}_2\text{-UO}_2$ solid solutions from 77 to 500 K. His results were reevaluated, using the equations of Sect. 4.4.4 to determine the relative contents of U^{+4} , U^{+5} , and U^{+6} in his samples. Equation (3.13) was then used to calculate the paramagnetic contribution of U^{+4} , as well as the total diamagnetic contribution, to the values measured by Goto; these were subtracted from his values, and the residuals examined.

Of the 15 samples for which Goto provides susceptibility measurements, two (designated by him as "2e" and "3e") have compositions lying to the right of (i.e., higher than) the $[\text{U}^{+6}] = 0.01$ contour, as

Figure 3.19. Linear Coefficient of Thermal Expansion for ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$ (from White and Sheard, 1974). (Reproduced by permission of Plenum Publishing Corporation.)

drawn in Fig. 4.8 of Chap. 4. (The mean uranium valence given by Goto is higher than the consensus for the oxidation limit of Table 4.2; it was assumed that the samples were at the consensus oxidation limit.) In the remaining samples, the U^{+6} content was less than 1 percent of the cations present, and its contribution to the magnetic susceptibility was assumed to be negligible. However, the two highly oxidized samples did not show anomalous total magnetic susceptibilities or residual susceptibilities. Accordingly, it seems likely that U^{+6} is diamagnetic; its contribution to the susceptibility is small, negative, and already taken into account in the evaluation of Eq. (3.13).

The entire residual susceptibility was therefore attributed to the U^{+5} ion, and the molar susceptibility of U^{+5} was calculated on this basis. Results are shown in Fig. 3.20. It is clear that U^{+5} is paramagnetic, though less so than U^{+4} , and that the temperature dependence is comparable to that of Eq. (3.10), which represents evaluation of the Curie-Weiss Law. Three of Goto's samples gave results not in accord with the remainder. These were his samples 2d, 4c, and 5b (marked in Fig. 3.20 by encircled digits). The highly oxidized samples, 2e and

Figure 3.20. Molar Magnetic Susceptibility of U⁺⁵ Calculated from Results of Goto (1968).

3e, did not behave in any anomalous manner. When the data represented by the encircled digits were eliminated, the remainder could be fit to the equation:

$$\chi_m^{U^{+5}} = \frac{0.468}{T + 159} \text{ (mol}^{-1} \text{ of U}^{+5}\text{)} . \quad \text{Eq. (3.15)}$$

It was not possible to detect, in Goto's data, significant variations with composition of the Curie Constant (0.468 K/mol) or the Weiss Temperature (159 K) for U⁺⁵.

Dawson and Roberts (1956) also reported data for the magnetic susceptibility of oxidized urania-thoria solid solutions at 300 K. How-

ever, their analyses for the degree of oxidation include some values considerably in excess of the maximum limits found by later workers, and questions could be raised concerning the reliability of U⁺⁵ concentrations calculated from these data. Accordingly, U⁺⁵ magnetic susceptibilities were not calculated from these results.

3.8 SUMMARY

Thoria shows the fluorite-type lattice with the other actinide dioxides, including urania. Insofar as its lattice and structure-determined properties differ from those of the other oxides, these differences must be attributed to the relatively minor quantitative variations in metal-to-oxygen distance, bond strength, and degree of ionic character,—all properties which are closely interrelated.

To the extent that a property is structurally controlled, it should be similar to the other actinide dioxides, particularly UO₂. Among the properties that are largely or entirely structurally controlled are density, unit cell size, and lattice energy. Thoria has values quite similar to UO₂, and predictable when the identity of the cation is taken into account, for these properties.

There now appears to be direct evidence from neutron scattering measurements that Frenkel disorder in the oxygen sublattices of both ThO₂ and UO₂ develops at high temperatures.

Among the other properties largely influenced by atomic and electronic structure are optical absorption, refractive index, fluorescence and luminescence, magnetism, and the nature and concentration of crystal defects. Pure, single-crystal thoria is colorless, with a refractive index above 2 and a nearly featureless absorption spectrum from its ultraviolet absorption edge, at a wavelength of about 213 nm in the ultraviolet, upward to about 14 μm in the midinfrared. As such, it serves as a matrix in which the effects of various materials in solid solution may be studied and identified.

Thoria has served in an essentially analogous way in magnetic studies; the pure material is diamagnetic with a small, known, predictable magnetic susceptibility.

In those studies that have used thoria as a matrix for the examination of lanthanides and actinides in solid solution, the phenomena to be examined arise from the electron orbitals or from the fact that interstitials, or vacancies, or both, in the structure cause anomalous phenomena in the electron orbitals. At the level of the lattice, ThO₂ and UO₂ have very similar properties. This is the basis of the statement made, and also applied, in this chapter and others in this book that data on urania may be used to explain, verify, and occasionally permit estimates to be made for the corresponding values for thoria.

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Chapter 4

PHASE EQUILIBRIA

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4.1 INTRODUCTION

The thorium-thorium dioxide system and the phase relationships between thorium dioxide and other oxides are discussed in this chapter. The fluorite-type dioxides enter very extensively into a wide variety of solid solutions. As a result, the nuclear designer has available an assortment of materials, the compositions of which can be varied over continuous ranges to secure optimum properties. Among the materials that may be incorporated into a single, fluorite-type phase are fertile and fissile materials, ThO_2 , UO_2 , and PuO_2 ; materials with exceptionally high, or exceptionally low, neutron absorption cross sections, such as ZrO_2 , HfO_2 , or Gd_2O_3 ; and materials, such as CaO , which are useful additives because they "stabilize" ZrO_2 , i.e., convert it to a fluorite-type material, and improve the sinterability of the extremely refractory ThO_2 .

Changes in composition, in solid solutions that are part of a continuous compositional series with thorium dioxide, take place by cation substitution. If the substitute cation has a valence other than that of the tetravalent thorium cation, oxygen ions are omitted from the anion lattice, i.e., oxygen vacancies are formed, to maintain electrical neutrality. Lattice parameter and density measurements show that altrivalent cation substitution in thoria is accommodated by oxygen vacancies and not by cation interstitials. There are no significant anions that can substitute for the oxygen anions.

4.2 THE THORIUM-OXYGEN SYSTEM

The thorium-oxygen system was delineated by Benz (1969), who compacted various mixtures of crystal-bar thorium metal and thorium dioxide powder. The resulting pellets were sintered in vacuum at 1873–2273 K,

resintered (after crushing) at 2373 K, and heated in helium at temperatures up to the melting point of pure ThO_2 , which he placed at 3663 K.* The resulting thorium-oxygen phase diagram is shown as Fig. 4.1.

In this diagram, the hypostoichiometric limit of the fluorite-type phase, the curve immediately to the left of the right edge of the figure, represents the series of compositions that are in equilibrium with liquid thorium containing the maximum amount of oxygen that the molten metal can accommodate. They therefore are the fluorite-type phases containing the minimum amount of oxygen (or the maximum amount of anionic vacancies) that can be accommodated at that temperature. If the general formula of hypostoichiometric thoria is written as ThO_{2-x} , then x varies from zero, at the right side of the diagram (ThO_2), to the maximum value represented by this limiting line.

This curve begins to depart significantly from $x = \text{zero}$ at the eutectic temperature which is the lowest temperature at which molten thorium metal (with a small amount of oxygen) can exist. Benz places this temperature at 2008 ± 20 K; at this temperature, the maximum value of x is 0.015. The maximum value of x increases approximately linearly with rising temperature, until a value of 0.13 ± 0.04 is reached at the monotectic temperature of 3013 ± 100 K. As temperature increases above this point, the maximum attainable value of x decreases, reaching zero at 3663 K. At this point, solid and liquid ThO_2 are in equilibrium.

Ackermann and Tetenbaum (1980) reexamined the position of the lower phase boundary of ThO_{2-x} from 2005 to 2500 K and found a somewhat lesser degree of hypostoichiometry than was observed by Benz in this region (see Fig. 4.2). Ackermann and Tetenbaum (1980) used the vapor phase equilibration, or isopiestic technique, in which thoria disks were equilibrated with ThO vapor rather than with molten thorium, as had been the case in the Benz investigation. The equilibrated vapor is produced at each desired temperature by a mixture of thorium liquid contained in a ThO_{2-x} (solid) cup. Since the equilibrated disk is not in contact with the liquid thorium, this vapor phase equilibration technique removed the possibility of capillary penetration of the wafer oxide by the liquid metal which may have resulted in low values for oxygen (higher level of hypostoichiometry) in Benz's results.

As discussed in Chap. 3, thorium dioxide heated at high temperatures (above 2000 K) in nonoxidizing atmospheres becomes hypostoichiometric (ThO_{2-x}) and darkens in color. Unless heating is quite prolonged or at a very high temperature, the value of x in this material is likely to be considerably less than the maximum for the temperature, as shown in Fig. 4.1. If the value of x is sufficiently large, it can be determined by

*In this book, the melting point of thorium dioxide is taken as 3640 K (see Chap. 5).

Figure 4.1. Thorium-Oxygen Binary, according to Benz (1969). (Courtesy, Journal of Nuclear Materials)

measuring the weight gain as the material is reoxidized to stoichiometric thorium (ThO₂). This operation can be accomplished by heating in air at temperatures below those causing the hypostoichiometry. As a result, the material returns to its normal white color. Changes in unit cell size can also be observed and can be correlated with composition. Carniglia et al

Figure 4.2. Lower Phase Boundary (l.p.b.) and Congruently Vaporizing Composition (c.v.c.) as a Function of Temperature for Hypostoichiometric ThO₂, according to Ackermann and Tetenbaum (1980).

(1971) observed such changes; the cell size decreased by about 0.5 percent when ThO₂ was rendered hypostoichiometric to the extent of ThO_{1.997}. There was also a decrease in Young's modulus, from 199 to 182 GN/m², and a considerable increase in mechanical strength.

Carniglia et al (1971), however, did not reach the maximum limit of hypostoichiometry which would be under conditions in which three phases would be present: oxygen-deficient thorium, oxygen-saturated thorium metal, and an overlying atmosphere with a very low partial pressure of oxygen. There are two components in this system: thorium and oxygen. According to the Gibbs Phase Rule, there can therefore be only one degree of freedom. These conditions can exist in equilibrium only along a curve, which is represented by the left edge of the thorium stability field in Figs. 4.1 and 4.2. The oxygen partial pressures in the Carniglia et al (1971) study were not sufficiently low to be in equilibrium with thorium metal. Their hypostoichiometric compositions therefore represent points somewhere in the interior of the fluorite-phase stability field.

Carniglia et al (1971) gave the following equation for the partial pressure of oxygen, P_{O_2} , in equilibrium with thoria having x moles of oxygen deficiency, at temperature T (kelvin):

$$\log x = 1.870 - [(0.340 \times 10^4)/T] - [(\log P_{O_2})/6] \quad \text{Eq. (4.1)}$$

where

P_{O_2} = partial pressure of oxygen, in atmospheres

T = absolute temperature, kelvin

and

x = moles of oxygen deficiency per mole of material.

Carniglia et al stated that Eq. (4.1) is applicable at values of T from 1673 to 2173, and values of $\log P_{O_2}$ from -2 to -6 .

The presence of the factor of 6 in the denominator of Eq. (4.1), i.e., x varies as $P_{O_2}^{-1/6}$, implies that the oxygen vacancies are predominantly doubly charged. Similarly, a predominance of singly charged oxygen vacancies leads to a $P_{O_2}^{-1/4}$ dependency and a predominance of neutral vacancies to a $P_{O_2}^{-1/2}$ dependency.

Ackermann and Tetenbaum (1980) suggested that singly charged oxygen vacancies predominate at temperatures of 2673 to 2928 K. From their measurements, at these temperatures, of oxygen potentials above bivariant ThO_{2-x} compositions, they estimated the oxygen partial pressure dependency to be approximately proportional to $P_{O_2}^{-1/4}$. (See Chaps. 5 and 6 for additional discussion of the hypostoichiometric thoria phase.)

The congruently vaporizing compositions were also reported by Ackermann and Tetenbaum (1980) (see Fig. 4.2). These compositions were determined over the temperature range from 2400 to 2820 K by weight gains on oxidation of thoria residues after partial vacuum vaporization. The thoria residues were reported to be not as dark as those obtained on the measurements of the lower phase boundary, but again, the samples returned to the original white color after oxidation. The vaporization process is discussed in greater detail in Chap. 5.

Hoch and Johnston (1954) suggested that there is another stable oxide of thorium in the condensed state: the solid monoxide, ThO , stable above 2100 K. Subsequent work, however, indicated that solid ThO is metastable. Ackermann and Rauh (1973) obtained the solid monoxide of thorium by thermal decomposition of the residue from the incomplete dissolution of thorium metal in hydrochloric acid. This residue, as a black precipitate,

had been shown by Katzin (1958) to have the empirical formula $\text{ThO} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, and Ackermann and Rauh (1973) confirmed the composition. When the black precipitate was heated in high vacuum at temperatures up to 1173 K, it disproportionated into metallic Th and ThO_2 , which appeared in a diffractogram of the product as strong peaks at characteristic positions for these materials. There were, however, some low-intensity peaks that were identified with a face-centered-cubic compound with the cell size of 0.5302 nm. Ackermann and Rauh identified this material as ThO , and also reported a UO analogue, prepared in the same way, with a cell size of 0.500 nm. These metastable phases constituted only a minor portion of the material, and gradually disappeared with continued heating.

4.3 THE NATURE OF THORIUM DIOXIDE SOLID SOLUTIONS

4.3.1 Vegard's Law Behavior

In the phase equilibrium diagrams of primary interest, the composition of pure ThO_2 represents one edge of a stability region of some significant extent, over which the composition can vary continuously in the direction of the other components. Within this region, the materials consist of one homogeneous cubic phase, in which other cations substitute for thorium ions, and vacancies substitute for oxygen ions.

As far as is known, these substitutions occur randomly in solid solutions composed primarily of thorium dioxide. Ordered solid solutions, if they existed, would be manifested by so-called superlattice peaks: anomalous, weak diffraction peaks that become possible when the ordered atoms effectively enlarge the unit cell size, i.e., the repeat distance, to some multiple of its previous value. Such superlattice peaks have not been observed in solid solutions consisting primarily of thoria.

Since the composition of these solid solutions can be changed by increments as small as one additional atom, it can be expected that the properties, in general, will follow a smooth curve in their variation with composition. Furthermore, since these are cubic solid solutions, certain sorts of variations with composition, such as those that are dependent on crystallographic direction, are prohibited.

As a special case, these smooth curves can be, at least approximately, straight lines. The best known case of such behavior is Vegard's Law, which states that the unit cell size of cubic solid solutions varies linearly with molar composition. Vegard's Law may be considered one of a set of such laws which, in the general case, can be stated as: *In cubic or amorphous solid solutions, property X varies linearly with composition.* Another specifically named law in this class is the Law of Gladstone and Dale (1864), in which *property X* is the refractive index divided by the

density. In this very early work, compositions by weight fraction were used; modern workers use mole fractions. In addition to these, many mechanical properties adhere sufficiently closely to linear behavior for the application of such a law, at least for estimates. Furthermore, for any property, it may be assumed that the variation with composition can be expressed by a polynomial, and therefore, there will be a range of compositions sufficiently dilute that terms higher than the first order will not be significant. This range of essentially linear behavior generally extends at least to 1 mole percent.

There is, however, a class of properties that departs from linearity for compositions in the interior of the phase diagrams. These properties are affected by the higher degree of randomness present in these compositions: entropy (by definition), and also the various thermodynamic properties related to entropy. The free energy is one of these, since it is equal to $\Delta H - T\Delta S$, ΔS being the entropy term. The free energies of the solid solution and the molten liquid solution which lie above it in the phase diagram behave in this manner. At the melting point, the free energies of the two solutions are equal. The departure from linearity with composition is larger in the case of the liquid solution because the entropy term is larger. The problem of determining the liquidus and solidus is that of determining the line along which the difference between the solid and liquid free energies is zero. This problem is discussed in Sect. 4.4; for the present purpose, it is appropriate to point out that the temperatures of the liquidus and solidus are functions of entropy, and therefore are among the properties that can be expected to vary from linearity with composition.

Enthalpy and the enthalpy changes associated with phase transformations, such as melting, also behave nonlinearly with composition across the phase diagram. They form a curve that is convex upward, reaching a maximum at some composition in the interior of the phase diagram, i.e., the value is higher than would be indicated by linear interpolation between the end members.

Given a table of appropriate coefficients, it is possible to obtain a good estimate of the value of any particular linear property X in a solid solution of known composition. The mole fraction of each component is multiplied by a listed coefficient, and the sum of these products represents the value for the solid solution. Values of these coefficients, for use in Vegard's Law calculations in fluorite-type dioxides, are given in Table 4.1. In this case, property X is the unit cell size as determined by X-ray diffraction. The listings in Table 4.1 are those for which adequate measurements are available.

In cases for which complete cubic solid solution series exist, the coefficients are simply the measured values for the pure end members. Where it is not possible to form a complete series, coefficients can be estimated by

TABLE 4.1—VEGARD'S LAW COEFFICIENTS FOR FLUORITE-TYPE OXIDE SOLID SOLUTIONS*

Tetravalent Ions		Trivalent Ions†	
Th	0.55975	Y	0.5394
Pa	0.5505	Sm	0.5539
U	0.54705	Eu	0.5512
Np	0.5434	Gd	0.5425
Pu	0.5396	Oxidized Uranium Ions	
Am	0.5376		
Cm	0.5372	U ⁺⁵	0.5408†
Ce	0.5408	U ⁺⁶	0.553†
Pr	0.5394		
Tb	0.5220		
Hf	0.5115†		
Zr	0.5163†		

*Values are in nanometers and represent measurements reported in the JCPDS File (1982).

†Incomplete solid solutions; extrapolated.

extrapolating from measurements of solid solutions of known compositions. This was necessary for zirconium dioxide and also for the oxides of the trivalent lanthanides. The mole fraction of lanthanide sesquioxide should be calculated on the assumption that the formula is $\text{LnO}_{1.5}$ (Ln = any lanthanide).

Table 4.1 lists separate values for U^{+4} , U^{+5} , and U^{+6} . In unoxidized thoria-urania solid solutions, the cell size can be calculated using the coefficients for Th^{+4} and U^{+4} . Where there is slight to moderate oxidation, the calculation can be performed by assuming that the oxidized uranium consists entirely of a separate species, U^{+5} . However, in dilute solutions of urania in thoria, oxidized to the maximum extent possible, a significant portion of the uranium consists of U^{+6} . The relative concentrations of these ions and the determinations of the associated Vegard's Law coefficients are discussed in Sect. 4.4.4.

Theoretically, a table comparable to Table 4.1 could be prepared for any property X following a linear law. Among the solid solutions in which thoria is the solvent, however, extensive experimental confirmation is available only for Vegard's Law. Some writers, such as Cohen and Berman (1966), Skavdahl and Chikalla (1967), and Subbarao et al (1965), presented data on the change of lattice parameters as the composition was varied in a known manner. Others, such as Keller et al (1972), essentially assumed the validity of a linear law, and used it in the delineation of the stability field of a cubic phase. Their work can be considered as additional confirmation, since they obtained usable and reasonably consistent results.

Zen (1956) demonstrated that Vegard's Law is, at best, an approximation. Beginning with the assumption that there is no volume change associated with the formation of a solid solution, he showed that the relationship between cell edge and composition must be expressed by a polynomial with an infinite number of terms, and that the treatment of Vegard's Law consists of ignoring all terms of orders higher than the first. This can be approximately valid only in those cases in which the coefficients for the odd members are reasonably similar. If there is a volume change on mixing, i.e., if the solution is not ideal, the assumptions embodied in Vegard's Law become even more dubious. Zen points out that the practice of some workers, in applying Vegard's Law to noncubic materials, can be countenanced only on the basis that the entire law must be regarded as empirical.

The approximately linear variation of cell size (or diffraction peak position) with molar composition has been extremely useful for estimating the composition of intimately mixed, inseparable phases, since it is generally possible to distinguish and measure the separate, superimposed diffractograms. In this way, compositions of phases in highly impure mixtures can be obtained, and multiphase fields in phase diagrams can be delineated, since the phases in equilibrium with each other define the edges of the field. In calculating the compositions of these phases from the unit cell measurements, linear equations are generally used, and this is often described as the application of Vegard's Law, even in cases, such as the systems involving zirconia, in which the phases are not cubic. It would perhaps be more appropriate to state that the composition was determined by linear interpolation or extrapolation from measurements on single-phase material of known composition, and that these measurements justify the use of linear approximations.

4.3.2 Extent of Solid Solutions

It should be emphasized that, although it may be possible to calculate theoretical cell dimensions of a solid solution of a particular composition through the use of Table 4.1, there is no guarantee that it will be possible to fabricate this composition as a single phase, or that the phase will be cubic if the effort is successful.

The extent of permitted substitution of another cation for thorium in ThO_2 is determined, first, by the electronic charge of the substitute, and secondly, by its size. If the replacement cation is similar to thorium, in either or both these respects, greater substitution is possible. Aside from this general rule, smaller ions are accommodated to a greater extent than comparably mismatched larger ions. Tables of effective ionic radii in oxides are available; see, for example, Shannon and Prewitt (1969) and Shannon (1976). In these tables, the radius of the substituting ion may be compared to that of thorium, which is given in Shannon (1976) as 0.105 nm for a charge of +4 and a coordination number (CN) of 8.

4.3.3 Binary Phase Diagrams

The actinide elements from thorium to californium are known to form fluorite-type dioxides. Among the rare earths, cerium and praseodymium also do, although Pr_2O_3 is more stable than PrO_2 . Zirconia forms a fluorite-type cubic oxide above 2550 K; the fluorite-type structure becomes stable or metastable at room temperature if small amounts of *stabilizers*, such as CaO , are added.

Not all the possible phase diagrams between thorium dioxide and the other fluorite-type dioxides have been fully investigated. As a general rule, however, mismatches as great as 20 percent in ionic radius can be tolerated before complete solid solutions are no longer possible. The ionic radii for the actinide elements thorium through californium, taken from the tabulations of Shannon and Prewitt (1969) and Shannon (1976), are plotted against atomic number in Fig. 4.3. It is seen that mismatches up to

Figure 4.3. Variation of Tetravalent Ionic Radius for 8-Fold Coordination and Dioxide Lattice Parameter with Atomic Number in the Actinide Series.

11 and 12 percent exist for the ions thorium-berkelium and thorium-californium, respectively. Among the nonactinide elements the Ce^{+4} ion is about 8 percent smaller in radius than Th^{+4} ; Pr^{+4} is about 6 percent smaller; Zr^{+4} , which does not form a fluorite-type phase at room temperature, is about 20 percent smaller. These values, together with all available information on specific fluorite-type dioxide binaries that have been investigated, indicate that solid solutions of thorium dioxide and any other fluorite-type dioxide can be prepared in any proportion and that the stability field of the single-phase solid solution extends to the pure end-member on the opposite side of the binary diagram from thoria. Among the binaries where this has been confirmed is $\text{ThO}_2\text{-UO}_2$ (Cohen and Berman, 1966).

The ionic radii and lattice parameters for the actinide oxides decrease with increasing atomic number (Fig. 4.3). As described in Sect. 3.2.2 of Chap. 3, the two values are functionally linked; the closest approach between the centers of an oxygen ion and a cation is $\sqrt{3}/4$, or 43.3 percent, of the lattice parameter, and the oxygen radius contributes a fixed quantity (0.138 nm) to this approach distance. Differences in lattice parameter must therefore reflect differences in cation radius.

In the case of the $\text{ThO}_2\text{-ZrO}_2$ binary, both cations are tetravalent, but the mismatch in ionic size reaches 20 percent. As a result, the compositional region occupied by the single fluorite-type solid solution phase is somewhat restricted. Pure ZrO_2 does not have the fluorite structure below 2573 K; phases of lower symmetry are stable, and much of the interior of the binary diagram consists of multiphase fields in which these low-symmetry phases are in equilibrium with a fluorite-type solid solution. This is also true in the binary systems between thoria and the lanthanides (except ceria, which forms a complete and continuous solid solution). In these, there is the added complication of differing oxidation states. The phases stable in the pure lanthanide oxides, except for CeO_2 , are not fluorite-type dioxides; once again, multiphase fields exist between these phases and the fluorite-type dioxide solid solution. In the $\text{ThO}_2\text{-CaO}$ binary, the mismatch between the ionic radii is small, but the mismatch in oxidation state is large; the extent of the fluorite-type cubic phase region is therefore quite limited. Finally, there is a group of cations (Ti, B, Si, Nb, Ta, V, Mo) for which the mismatch, either in size or charge or both, is sufficiently large that significant mutual solid solution between their oxides and thoria is not possible. For intermediate compositions in these systems, there would be no advantage in free energy decrease if a random single phase were formed. However, in such mixtures, the probability increases that there may be such an advantage for an ordered single phase, i.e., a stable intermediate compound. Accordingly, as the extent of solid solution in a system decreases, the likelihood of intermediate compounds increases.

4.4 THE THORIA-URANIA BINARY SYSTEM

4.4.1 Variation of Lattice Parameter with Composition

Cohen and Berman (1966) studied the thoria-urania system from room temperature to 1473 K, and reviewed the information available from the work of others at temperatures up to 1873 K. Additional information was published by Sata (1965). All authors agree that a fluorite-type cubic solid solution is stable up to the melting point for thoria, urania, and all intermediate compositions, and that the unit cell size of this solid solution, over almost its entire compositional range, adheres closely to Vegard's Law (see Fig. 4.4). Unit cell sizes of intermediate compositions at room temperature can therefore be calculated by assuming a linear variation

Figure 4.4. Unit Cell Size as a Function of Composition in Unoxidized $\text{ThO}_2\text{-UO}_2$ Solid Solutions.

with molar composition between ThO_2 (0.55975 nm) and UO_2 (0.54705 nm). The effect of elevated temperature can then be calculated by applying the equations for linear thermal expansion given in Chap. 5. Given the cell size and the molecular weight of a solid solution, the theoretical density, at zero porosity, can be calculated from Eq. (3.1) of Chap. 3.

Cohen and Berman (1966) reported two observations, on material between 1 and 2 mole percent ThO_2 , in which the cell size appeared to be lower than would be predicted from Vegard's Law. Similar results had been reported by Christensen (1963). These deviations suggest that the solid solution at these low concentrations of ThO_2 is not random, i.e., there is atomic ordering. However, Sabine et al (1974) restudied this region and could not reproduce the anomalous results. The anomaly, which consists of a decrease of about 0.0002 nm below the Vegard's Law value, could be explained if these high-urania compositions had been oxidized to approximately $(\text{U,Th})\text{O}_{2.015}$; the variation in cell size with oxidation is discussed in Sect. 4.4.4. The references offer no firm assurances that this degree of oxidation did not occur in these cases.

Measurements by Christensen (1963) and by Cohen and Berman (1966) show a slight upward departure, over most of the central part of the binary, from the values predicted by Vegard's Law. They are in better agreement with an assumption that there is no volume change on mixing (Fig. 4.4). The maximum difference between the cell sizes calculated using the two assumptions is 8×10^{-5} nm; Vegard's Law calculations are therefore adequate, within the limits of error of measurement, for most applications.

4.4.2 Calculation of Liquidus and Solidus

In these binary systems, contradictory information being lacking, it may be assumed that the liquidus and solidus assume a lenticular shape, comparable to that found for the thorium-urania binary (Fig. 4.5). One corner of the lenticular shape will be at the melting point of thorium, 3640 K; the other corner will be at the melting point of the other component. Since the melting point of thorium is higher than that of any other known oxide, all other points on the liquidus and solidus, with any other component or components, will be lower than 3640 K; adding anything in solid solution to thorium will lower the melting point.

On the assumption that these complete solid solution binaries are ideal solutions, i.e., that there are no volume or enthalpy changes on mixing when they are formed, it is possible to calculate the curves of the liquidus and solidus, given the melting points (T) in kelvin, and enthalpies of fusion (ΔH_m) of the two end-members. (If the solution is not ideal, a simple, lens-shaped configuration of the solidus and liquidus cannot be assumed.) At a

Figure 4.5. ThO₂-UO₂ Solidus-Liquidus.

given experimental temperature T_e , the ratio between the mole fractions of the first component in the solidus and liquidus, S/L , can be found from an equation of the following type, which is discussed in standard texts such as Swalin (1962):

$$\frac{S}{L} = \exp \left[\frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_e} \right) \right] \quad \text{Eq. (4.2)}$$

where R is the gas constant, corresponding to $8.3143 \text{ J/mol} \cdot \text{K}$. By substituting the melting point and enthalpy of fusion of the opposite end-member, the ratio between the two compositions can be calculated in terms of the mole fraction of the second component. The actual positions of the solidus and liquidus may then be calculated by applying the further constraint that the sum of the mole fractions of the two components must equal 1.

The curves for the $\text{ThO}_2\text{-UO}_2$ binary calculated by this method are shown in Fig. 4.5. A tabulation of the data is also given in Table 5.5 in Chap. 5. It was assumed that the melting points of ThO_2 and UO_2 are 3640 and 3120 K, respectively, and that the enthalpies of fusion are 90.8 and 74.8 kJ/mol (see Chap. 5). In Fig. 4.5, the calculated results are compared to experimental determinations by Latta et al (1970), Benz (1969), Lambertson et al (1953), and Christensen (1963) on intermediate compositions and pure end-members of the urania-thoria binary system. The experimental data do not definitely rule out a departure from ideality, of the nature shown in the insert, in the same compositional region as the anomalous cell sizes reported by Christensen (1963) and by Cohen and Berman (1966).

4.4.3 Thoria-Urania-Oxygen Pseudobinary

As discussed in Sect. 4.2 above, thoria does not depart significantly from its stoichiometric composition of ThO_2 at temperatures below 2000 K. The stability of Th^{+4} , and the lack of stability of other oxidation states (excluding zero), can be explained by the electron configuration of thorium which is discussed in Chap. 3.

Since, at these relatively accessible temperatures, thoria cannot vary from stoichiometry, then the other oxide component must, if a pseudobinary phase diagram with variable oxygen is to be of interest. The other oxide must show significant solid solution with thoria and must vary its oxidation state, either continuously or discontinuously. Among such oxides are urania, plutonia, and the oxides of various high-atomic-number lanthanides.

Cohen and Berman (1966) also studied the thoria-urania-oxygen pseudobinary system. On the basis of X-ray diffraction, photomicrography, and chemical analysis, they reached the conclusions summarized below and presented graphically in Fig. 4.6(a).

At 1473 K and lower temperatures, it is not possible to extend the continuous fluorite-type solid solution to any significant extent to hypostoichiometric compositions. Hyperstoichiometric compositions are, however, possible, to an extent varying from $x = 0.25$, i.e., $\text{UO}_{2.25}$, at the urania end, to $x = 0$ at the thoria end. The line representing the maximum value of x in the cubic phase at each composition is termed the oxidation limit.

The $\text{UO}_2\text{-O}$ side of the ternary conforms to the $\text{UO}_2\text{-oxygen}$ binary as determined by Blackburn (1959) and Schaner (1960). A consensus of their work is presented as Fig. 4.6(b). At temperatures of 1300 K or above, urania can be oxidized as a single, continuous cubic solid solution to $\text{UO}_{2.25}$. At lower temperatures, the excess oxygens become ordered and form the phase U_4O_9 . As the temperature decreases toward room temperature, a

Figure 4.6. Thoria-Urania-Oxygen System: (a) Oxidation in the ThO_2 - UO_2 Binary at 1473 K; (b) the UO_2 - U_3O_8 Binary Phase Diagram.

two-phase region of increasing width is formed, in which the ordered U_4O_9 phase is in equilibrium with the less-oxidized UO_{2+x} phase, in which the oxygens are randomly distributed.

Above $x = 0.25$, urania-rich compositions are in equilibrium with phases in the vicinity of U_3O_8 . This association continues as thorium substitutes for uranium in the cubic material at the oxidation limit; the U_3O_8 phase does not accommodate any significant amount of thorium in solid

solution. At some point, however, dependent on the temperature, there occurs, along the oxidation-limit line, the corner of a three-phase field in which the cubic phase is in equilibrium with U_3O_8 and oxygen gas. At compositions more thorium-rich than this, cubic phases along the oxidation limit are in equilibrium with oxygen gas only. When these materials are prepared by oxidizing stoichiometric solid solutions of the appropriate Th/U ratio, U_3O_8 does not form.

If the general formula of cubic solid solutions in this system is written

$$U_y Th_{1-y} O_{2+x} \quad \text{Eq. (4.3)}$$

the corner of the three-phase field on the oxidation limit at 1473 K occurs at approximately $y = 0.5$, $x = 0.25$. As the temperature is increased to 1873 K, the value of x remains at 0.25, but the value of y increases to approximately 0.65, according to Paul and Keller (1971); U_3O_8 will form at higher values of y , but not at lower. The change with increasing temperature can be envisioned as the movement of the corner of the three-phase field along the oxidation limit, in the urania-rich direction, as the temperature increases. The oxidation limit itself remains approximately stationary.

At temperatures below 1300 K, the two-phase field between the ordered U_4O_9 phase and the disordered UO_{2+x} phase extends some significant distance toward the interior of the ternary diagram as thorium is added. The two-phase field of Fig. 4.6(b) can therefore be envisioned as the portal of a "tunnel" or "cave" into the single-phase cubic region shown in Fig. 4.6(a). This "cave" has not been fully delineated; it is difficult to achieve equilibrium conditions in this compositional region. However, two cubic phases (apparently an ordered and a disordered phase) have been observed by Paul and Keller (1971) in materials having as much as 40 mole percent ThO_2 .

In the temperature stability range of the ordered $(U,Th)_4O_9$ phase, thorium can be accommodated in place of uranium up to $y = 0.5$. Rachev et al (1968) reported a binary oxide compound with the composition U_2O_9 , but Paul and Keller (1971) showed that such a compound could not have a separate stability region of its own, and that the material reported by Rachev et al (1968) was $(Th,U)_4O_9$ with the maximum amount of thorium accommodated.

The oxidation limit is apparently fixed by structural and electronic charge considerations. For any given Th/U ratio, it can be calculated as follows. It may be assumed that, if the six cations nearest the vacancy at the center of a unit cell (those at the ends of the "hatpins" in Fig. 3.1 of Chap. 3) are all uranium ions, a single extra oxygen will be accommodated in the unit cell at the oxidation limit, and the composition of the cell will be U_4O_9 . An extra oxygen will be accommodated, also, in all of the unit cells in which one, two, three, or four of the "hatpin" ions are thorium. No extra

oxygen will, however, be accommodated in those cells in which the six ions are all thorium ions. In the cases in which there are five thorium ions and one uranium ion, the calculated results will match those observed by experiment if it is assumed that 18 percent of such unit cells accommodate additional oxygens.

Calculated and measured locations of the oxidation limit are shown in Table 4.2. The table also lists the mean oxidation state of the uranium present, calculated on the assumption that the excess charge of the hyperstoichiometric oxygen ions is neutralized entirely by the oxidation of th.

TABLE 4.2—OXIDATION LIMIT OF HYPERSTOICHIOMETRIC
 $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$

y	Maximum x		Mean U Valence
	(Calculated)	(Measured)	
0.01	0.0030		4.5965
0.02	0.0064		4.6400
0.03	0.0102		4.6808
0.04	0.0144		4.7189
0.05	0.0189		4.7545
0.06	0.0236		4.7877
0.07	0.0286		4.8185
0.08	0.0339		4.8471
0.09	0.0393		4.8735
0.10	0.0449	0.045	4.8979
0.11	0.0506		4.9202
0.12	0.0564		4.9406
0.13	0.0623		4.9592
0.14	0.0683		4.9760
0.15	0.0743		4.9911
0.16	0.0804		5.0046
0.17	0.0864		5.0046
0.18	0.0924		5.0271
0.19	0.0984		5.0362
0.20	0.1044	0.105	5.0439
0.21	0.1103		5.0504
0.22	0.1161		5.0556
0.23	0.1219		5.0597
0.24	0.1275		5.0627
0.25	0.1331		5.0646
0.26	0.1385		5.0656
0.27	0.1439		5.0656
0.28	0.1491		5.0648
0.29	0.1541		5.0631
0.30	0.1591	0.159	5.0606
0.31	0.1639		5.0574
0.32	0.1686		5.0535
0.33	0.1731		5.0490
0.34	0.1775		5.0438

TABLE 4.2—OXIDATION LIMIT OF HYPERSTOICHIOMETRIC
 $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ (Continued)

y	Maximum x		Mean U Valence
	(Calculated)	(Measured)	
0.35	0.1817		5.0381
0.36	0.1857		5.0319
0.37	0.1897		5.0252
0.38	0.1934		5.0180
0.39	0.1970		5.0104
0.40	0.2005	0.200	5.0025
0.41	0.2038		4.9942
0.42	0.2070		4.9855
0.43	0.2100		4.9766
0.44	0.2128		4.9675
0.45	0.2156		4.9581
0.46	0.2182		4.9485
0.47	0.2206		4.9387
0.48	0.2229		4.9288
0.49	0.2251		4.9187
0.50	0.2271	0.0237	4.9086
0.51	0.2291		4.8983
0.52	0.2309		4.8880
0.53	0.2326		4.8777
0.54	0.2342		4.8673
0.55	0.2356		4.8569
0.56	0.2370		4.8465
0.57	0.2383		4.8361
0.58	0.2395		4.8258
0.59	0.2406		4.8155
0.60	0.2416	0.250	4.8052
0.61	0.2425		4.7950
0.62	0.2433		4.7849
0.63	0.2441		4.7749
0.64	0.2448		4.7650
0.65	0.2454		4.7552
0.66	0.2460		4.7455
0.67	0.2465		4.7359
0.68	0.2470		4.7265
0.69	0.2474		4.7171
0.70	0.2478	0.250	4.7080
0.71	0.2481		4.6989
0.72	0.2484		4.6900
0.73	0.2487		4.6812
0.74	0.2489		4.6726
0.75	0.2491		4.6642
0.76	0.2492		4.6559
0.77	0.2494		4.6477
0.78	0.2495		4.6397
0.79	0.2496		4.6397
0.80	0.2497	0.250	4.6242
0.81	0.2498		4.6167

TABLE 4.2—OXIDATION LIMIT OF HYPERSTOICHIOMETRIC
 $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ (Continued)

y	Maximum x		Mean U Valence
	(Calculated)	(Measured)	
0.82	0.2498		4.6093
0.83	0.2499		4.6021
0.84	0.2499		4.5950
0.85	0.2499		4.5881
0.86	0.2499		4.5813
0.87	0.2500		4.5746
0.88	0.2500		4.5681
0.89	0.2500		4.5618
0.90	0.2500	0.250	4.5555
0.91	0.2500		4.5494
0.92	0.2500		4.5435
0.93	0.2500		4.5376
0.94	0.2500		4.5319
0.95	0.2500		4.5263
0.96	0.2500		4.5208
0.97	0.2500		4.5155
0.98	0.2500		4.5102
0.99	0.2500		4.5051
1.00	0.2500	0.250	4.5000

uranium to U^{+5} and U^{+6} . In the region between $y = 0.16$ and $y = 0.40$, the most oxidized fluorite-type compositions contain uranium with a mean oxidation state greater than +5. The maximum uranium valence for the cubic phase is reached at the approximate composition of $\text{U}_{0.27}\text{Th}_{0.73}\text{O}_{2.1439}$, in which the oxidation state of the uranium is +5.0656. To reach this value, some of the uranium must necessarily be oxidized to U^{+6} . The thermodynamic aspects of the oxidation limits for ThO_2 - UO_2 solid solutions are discussed in Chap. 5.

Boekschoten and Kema (1968) studied powder mixtures of ThO_2 and UO_3 at low temperatures, in the vicinity of 500 K. They reported a phase to which they assigned the formula UThO_5 , and also, below 483 K, another compound which they did not fully characterize. It is likely that these materials are part of the poorly defined assemblage of stable and metastable low-temperature phases with compositions in the general vicinity of UO_3 .

4.4.4 Cell Sizes in Cubic $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$

Cell size measurements on the hyperstoichiometric fluorite phase in the thorium-uranium system have been reported by Sata (1965) and by Cohen

and Berman (1966), and are shown graphically in Fig. 4.7. Both references present data only on compositions with values of y close (± 0.005) to exact tenths (i.e., $y \approx 0.100, 0.200, \dots, 0.900$). Accordingly, it is possible to assign symbols to the measurements, representing the approximate value of y . All determinations were made at room temperature.

The cell size decreases with increasing oxidation. Over most of the compositional range of the cubic phase, the room-temperature cell size can be calculated on the basis of Vegard's Law, assuming that only three cations are present: U^{+4} , U^{+5} , and Th^{+4} . The coefficients assigned to these cations are listed in Table 4.1; the values are 0.54705, 0.5408, and 0.55975 nm, respectively. Calculations made on this basis are represented by the solid lines in Fig. 4.7.

Figure 4.7. Comparison of Measured Lattice Parameters with Fitted Equations for Oxidized Thoria-Urania Solid Solutions.

These appear to be in adequate agreement with the data throughout the single-phase region, except for a few samples at, or close to, the oxidation limit at values of y from 0.2 to 0.4. These have cell sizes slightly but consistently larger than would be predicted from less-oxidized material, using the assumption that only three components are present. They are also shown, in Table 4.2, to have significant concentrations of U^{+6} ions.

The unit cell size of cubic phases in this region can be calculated using an equation of the form

$$a_0 = 0.54705 [U^{+4}] + 0.5408 [U^{+5}] + C [U^{+6}] + 0.55975 [Th^{+4}] \quad \text{Eq. (4.4)}$$

where a_0 is the cell size, in nanometers, at room temperature, $[U^{+4}]$, $[U^{+5}]$, $[U^{+6}]$, and $[Th^{+4}]$ are molar concentrations of these ions, on a scale in which their total equals 1, and C is a coefficient subject to determination from the data by regression analysis, using least-squares techniques.

The relative concentrations $[U^{+4}]$, $[U^{+5}]$, and $[U^{+6}]$, which together have a sum of y , are fixed by a reversible reaction

which reaches equilibrium, at any given temperature, at a point determined by the equilibrium constant K_e at that temperature:

$$\frac{[U^{+4}] [U^{+6}]}{[U^{+5}]^2} = K_e \quad \text{Eq. (4.6)}$$

A further constraint is imposed by the requirement that the excess charge of the O_{2+x} oxygens be neutralized by oxidation of the uranium:

$$0.5 [U^{+5}] + [U^{+6}] = x \quad \text{Eq. (4.7)}$$

These relationships were used with the measurements of Fig. 4.7 to determine the best-fit values of the following coefficients using a nonlinear least-squares computer program:

$$C \text{ of Eq. (4.4)} = 0.553 \text{ nm}$$

$$K_e \text{ of Eq. (4.6)} = 5.78 \times 10^{-3} \text{ (dimensionless).}$$

This value of the equilibrium constant is based on X-ray determinations at room temperature, and it therefore may be assumed to apply at room temperature; it is likely that equilibrium is attained in the reaction of Eq. (4.5), since only electrons need move to achieve it.

Given the values of x and y for a composition, as expressed in Eq. (4.3), and the value of K_e , it is possible to calculate $[U^{+4}]$, $[U^{+5}]$, and $[U^{+6}]$ as follows. Using the symbol u for $[U^{+6}]$, a quadratic equation

$$au^2 + bu + c = 0 \quad \text{Eq. (4.8)}$$

is set up, such that

$$a = 1 - 4K_e$$

$$b = y - 2x + 8xK_e$$

$$c = -4K_e x^2$$

Since negative compositions have no meaning, only the positive root need be taken:

$$u = [U^{+6}] = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{Eq. (4.8a)}$$

$$[U^{+5}] = 2(x - [U^{+6}]) \quad \text{Eq. (4.8b)}$$

$$[U^{+4}] = y - [U^{+5}] - [U^{+6}] \quad \text{Eq. (4.8c)}$$

Figure 4.8 shows a contour plot of the value of $[U^{+6}]$ on this basis in the stability region of the cubic, fluorite-type phase. The dashed lines in the high U^{+6} region of Fig. 4.7 show a recalculation of the cell size of these solid solutions, taking four components into account.

The maximum $[U^{+6}]$ in the cubic phase is found in the composition $U_{0.32}Th_{0.68}O_{2.1686}$, for which $[U^{+6}] = 0.031$, $[U^{+5}] = 0.275$, and $[U^{+4}] = 0.014$. This is not the same composition as that previously given for the highest uranium oxidation state ($U_{0.27}Th_{0.73}O_{2.1439}$); that composition contains less U^{+6} , but also less U^{+4} , such that the mean uranium valence is higher.

Over most of the stability region of the cubic phase (the compositions represented by the solid curves in Fig. 4.7) the content of $[U^{+6}]$ is sufficiently low that it need not be taken into account in cell size calculations; and, as a first approximation, this condition may be assumed to prevail at elevated temperatures. The cell size at elevated temperatures can, accordingly, be estimated by calculating the room temperature value, then applying the equations given in Chap. 5 for linear thermal expansion.

However, in the region where the U^{+6} content is significant, it can be expected to be higher at elevated temperatures. This is due to the fact that Eq. (4.5) will be driven to the left, since that represents the more random condition. The value of K_e , the equilibrium constant, will also increase.

Figure 4.8. Molar Concentration of U^{+6} in Oxidized Cubic Thoria-Urania Solid Solutions, Assuming the Equilibrium Constant $K_e = 5.78 \times 10^{-3}$ (Dimensionless)

4.5 THE THORIA-PLUTONIA-OXYGEN SYSTEM

As in the thoria-urania-oxygen system, the thoria-plutonia-oxygen system exhibits an extensive cubic solid solution with the general formula

Figure 4.9 presents a portion of the Pu-O binary, from $\text{PuO}_{1.45}$ to $\text{PuO}_{2.10}$; it represents a consensus of data presented by Vol'skii and Sterlin (1967), Manes and Manes-Pozzi (1975), and Skavdahl and Chikalla (1967). It is convenient, for purposes of clarity, to represent the more oxidized portions of the single phase of Eq. (4.4) by the symbol F, and the less oxidized portions by F', in Fig. 4.9. Skavdahl and Chikalla (1967) characterize their contribution as a *working diagram*, and caution that it may not represent equilibrium relationships. The binary is, in many ways,

Figure 4.9. Plutonia-Thoria-Oxygen System: (a) Oxidation in the ThO_2 - PuO_2 Binary at High Temperatures; (b) the Pu_2O_3 - PuO_2 Binary Phase Diagram.

similar to the U-O diagram of Fig. 4.6(b), except that it is a mirror image. One of the principal features, in both cases, is an extensive stability field of the cubic, fluorite-type phase, extending from $x = 0$ to a limit that was characterized, in the thoria-urania pseudobinary, as the oxidation limit. The lower edge of this field, in the plutonium-oxygen system, may by analogy be termed the reduction limit. There is also an oxidation limit in the plutonium-oxygen binary; the fluorite phase can apparently be oxidized continuously to $x = +0.09$, the excess oxygen being interstitial. According to Skavdahl and Chikalla (1967), however, stoichiometric PuO_2 does not oxidize readily, and these materials have been very little studied.

At temperatures above 650 K, the fluorite phase extends continuously from $\text{PuO}_{1.71}$ to $\text{PuO}_{2.09}$. As the temperature is decreased, a solvus is encountered, analogous to that in the $\text{UO}_2\text{-U}_4\text{O}_9$ system, and at lower temperatures there exists a two-phase field, in which the disordered PuO_{2-x} solid solution is in equilibrium with the ordered phase Pu_4O_7 . Along the reduction limit, the fluorite phase, containing the maximum allowable concentration of defects, is in equilibrium with a phase of lower symmetry, in much the same way as urania at the oxidation limit is in equilibrium with the orthorhombic (pseudohexagonal) phase associated with U_3O_8 .

The problem, as with the urania system, is to determine the nature of the phase boundaries that must connect the configuration of Fig. 4.9 with that known to occur at $y = 1$, i.e., a single crystalline phase which, at temperatures below 2000 K, occupies essentially a single point representing the composition of pure thoria. The only work available is summarized by Skavdahl and Chikalla (1967), and confirms that a continuous solid solution does indeed exist along the join between stoichiometric PuO_2 and ThO_2 . This is represented by the solid, vertical perpendicular at $x = 0$ in Fig. 4.9(a). However, it is reasonable to assume, by analogy with the thoria-urania pseudobinary, that similar geometric and electronic-charge constraints apply. Accordingly, the dashed lines representing the reduction and oxidation limits in Fig. 4.9(a) have been drawn with a configuration similar to the oxidation limit of Fig. 4.6(a). The work of Manes and Manes-Pozzi (1975) on the plutonia-urania pseudobinary shows that the concept of a reduction limit is valid for that system (Fig. 4.10).

There may, however, be a difference in the configuration of the stability fields associated with U_3O_8 , Fig. 4.6(b), and those associated with Pu_2O_3 , Fig. 4.9(b). U_3O_8 cannot incorporate any significant amount of thorium in place of uranium as a solid solution, although Paul and Keller (1971) observed X-ray diffractogram changes indicating that Np may be accommodated in this fashion. It is not known to what extent Th can substitute for Pu in the phases associated with Pu_2O_3 ; however, there are reasons to believe that it may be substantial. Manes and Manes-Pozzi (1975) show (Fig. 4.10) extensive substitution of uranium for plutonium in body-centered-cubic Pu_2O_3 (the *C* modification). Also, the *C* and *H* modifications have structures analogous to the cubic and hexagonal lanthanide

Figure 4.10. Portion of the Urania-Plutonia-Oxygen System, after Manes and Manes-Pozzi (1975).

sesquioxides, which are labeled *C* and *H* in Figs. 4.13 through 4.21. Examination of those figures shows that the phases can accommodate substantial amounts of thorium in solid solution, to the extent of 10 to 20 mole percent.

Accordingly, the *H* phase, in Fig. 4.9, is shown as being able to incorporate some significant but indefinite amount of thorium. Clearly, the stability field cannot extend across the diagram to the nonexistent Th_2O_3 . Therefore, there must be, somewhere in the interior of the diagram, a three-phase field analogous to that in the thorium-uranium pseudobinary. The three phases in equilibrium would be: (1) the *H* phase; (2) fluorite-phase material at some point on the reduction limit; and (3) either PuO or a metallic Pu-Th alloy. This relationship is tentatively shown by the dotted line in Fig. 4.9.

4.6 OTHER THORIUM DIOXIDE BINARY PHASE DIAGRAMS

4.6.1 The Thoria-Zirconia System

The radius of the tetravalent zirconium ion in 8-coordination is given (Shannon and Prewitt, 1969) as 0.084 nm; that of oxygen is 0.138 nm. The

ratio between these two values, 0.609 is well below the value of 0.732 ($= \sqrt{3}-1$), which is generally accepted as the lower limit of stability of the fluorite-type structure. However, the limit of 0.732 applies to nondirectional, ionic-bonded compounds in which the constituent ions can be treated as simple spheres. The fluorite-type zirconia phase reported below may be the result of some highly directional, covalent character to bonding, and does not necessarily contravene this limit.

Cohen and Schaner (1963) studied the zirconia-uranium binary system by X-ray diffraction and photomicrographic techniques. They concluded that pure zirconia existed, in the temperature region between 2573 K and the melting point of 2823 K, as a phase that was continuous with uranium having a fluorite-type structure, and therefore it had the fluorite-type structure itself. Such a cubic phase must occur on the pure zirconia side of the zirconia-thoria binary as well.

In the thoria-zirconia binary, the problem is to determine the nature of the phase relationships in the interior of a phase diagram which is known to have three stable crystalline phases on its zirconia side, and only one on its thoria side. The problem was studied by Duwez and Loh (1957) and by Mumpton and Roy (1960). In both cases, the work was done with zirconia contaminated with hafnia in the percentage range. Mumpton and Roy (1960) had a small amount of very pure material, but it was used only for a determination of the monoclinic-tetragonal transformation point; the result was in agreement with the accepted value of 1363 K.

Mumpton and Roy (1960) subjected very fine-grained, gelatinous mixed precipitates of thoria and zirconia to hydrothermal conditions, i.e., pressurized water at 673 K and below for periods up to one month. They found that single fluorite-type cubic phases formed; however, these were metastable, and reverted to the end-members (with minor amounts of the opposite component) when heated above 673 K, in a wet or dry condition. Below 523 K, the reaction for the formation of the metastable phase was incomplete after one month.

The solid lines in Fig. 4.11 represent the $\text{ThO}_2\text{-ZrO}_2$ binary phase diagram as delineated by Sakurai and Arashi (1975), using starting materials meeting modern standards (99.9+ percent) of purity. The pure oxides were combined, heated and equilibrated in a solar furnace, quenched, and examined by X-ray diffraction. The diagram has been supplemented by dashed lines, representing the high-temperature phase transformation of zirconia observed by Cohen and Schaner (1963), and also by a curve representing the probable configuration of the liquidus.

The form of the phase diagram is essentially that of a continuous solvus, modified on the zirconia-rich side by the zirconia phase transformations. At temperatures up to 2400 K, solid solutions extend up to 5 mole percent of thoria in zirconia, and 25 mole percent of zirconia in thoria.

Fig. 4.11. The Thoria-Zirconia Binary: Solid Lines Are As Drawn by Sakurai and Arashi (1975); Dashed Lines Are Postulated by Belle and Berman.

At temperatures from 2370 K to the top of the solvus at 2670 K, there is a region occupying much of the interior of the binary in which two cubic phases coexist in equilibrium. Above this region, there is another in which a single, cubic, fluorite-type solid solution exists continuously from pure thoria to pure zirconia.

Cohen and Schaner (1960) also observed the region of two cubic phases in their study of the zirconia-urania boundary. However, due to difficulties in attaining equilibrium, they were unable to use the lattice parameters of these phases to delineate the region, which is shown in their diagram as a shaded portion in which metastable relationships were observed. There is little doubt that the thorium-zirconia binary is in fact very similar, in general configuration, to Fig. 4.11.

4.6.2 Thoria-Lanthanide Oxide Systems

The effective ionic radius of the trivalent erbium ion is 0.100 nm, and that of dysprosium is 0.103 nm. The remainder of the trivalent lanthanide radii are in the range between that of terbium (0.104 nm) and lanthanum (0.118 nm). There is a decrease in size with increasing atomic number; however, all are close enough in size to the tetravalent thorium ion such that the mismatch in size is not a limiting factor in determining the extent of solid solution between the lanthanide oxide and thorium dioxide. The factor that prevents the formation of complete solid solutions between thorium dioxide and the lanthanide oxides (except for CeO_2 and perhaps PrO_2) is the mismatch in electronic charge rather than the mismatch in size.

Ceria and praseodymia are cubic, fluorite-type dioxides. Sesquioxides of the formula Ln_2O_3 (Ln = any lanthanide) also exist for those elements. However, a complete solid solution series exists between thorium dioxide and cerium dioxide; this was established many years ago in association with work on the Welsbach gas mantle, which made commercial use of a ThO_2 -1 mole percent CeO_2 solid solution. It may also be assumed that a complete solid solution exists between thorium dioxide and praseodymium dioxide.

Etsell and Flengas (1970) reviewed the earlier work on the extent of solid solution of lanthanide sesquioxides in thoria as part of a study of these materials as anion-deficient electrolytes (see Chap. 6).

The solid solutions formed between thorium dioxide and the lanthanide sesquioxides were investigated by Keller et al (1972). They heated mixtures of oxides in hydrogen and examined the results by X-ray diffraction. When two-phase mixtures were observed, the limiting composition of the cubic, fluorite-type phase was determined by Vegard's Law. General experience with the lanthanide oxides indicates that the resulting solids closely approximated true binaries, in the sense that there were three oxygen atoms for each two lanthanide atoms, and two oxygens for each thorium.

The experimental results for the solubilities of the various lanthanides in thoria as determined by Keller et al (1972) are shown graphically in Fig. 4.12. The amount of lanthanides accommodated in the thoria structure increases with temperature, as is normally observed, and in general

Figure 4.12. Solubility of Lanthanides in Thoria, according to Data of Keller et al (1972).

decreases with both increase in atomic number and mismatch in ionic size. Figure 4.12 represents the edge of the two-phase fields on the thoria-rich sides of the binary diagrams. The solid solution region can therefore be quite extensive; it can range up to 70 mole percent at higher temperatures, as shown at the high point for neodymium at 2173 K.

Keller et al (1972) did not investigate element 58 (cerium), which enters into complete solid solution as the dioxide, or element 61 (promethium), which is radioactive and does not occur to a significant extent in nature.

Binary systems between thoria and individual lanthanide sesquioxides have also been studied by Diness and Roy (1969) and by Sibieude and Foex (1975). Figures 4.13 through 4.21 represent the work of Sibieude and Foex. They show that the maximum extent of the thoria-rich fluorite

Figure 4.13. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of La₂O₃, according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

phase, labeled C in the drawings, occurs at the eutectic or peritect temperature which, for the lanthanides studied, occurs in the vicinity of 2650 K. The diagrams also show various phases labeled A, B, X, H, and Ψ_n or Ψ_n^1 or Ψ_n^* with various subscripts, which may be characterized as products with the stability fields shown. The maximum compositional extent of the fluorite phase is in the vicinity of 50 mole percent ThO₂, 50 mole percent Ln₂O₃, i.e., Th_{0.33}Ln_{0.67}O_{1.67}. In such solid solutions, there is a vacancy in one out of every six oxygen positions, or more than one, on the average, in every unit cell. Diness and Roy (1969) appropriately characterized these solid solutions as "massively defective".

On the lanthanide-rich side of the diagrams, the extent of solid solution is more restricted. At temperatures below 2000 K, the fluorite phases

Figure 4.14. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Nd_2O_3 , according to Sibieude and Foex (1975). (Courtesy, *Journal of Nuclear Materials*)

with maximum lanthanide content are in equilibrium with lanthanide sesquioxides containing approximately 20 mole percent thorium dioxide. For those lanthanides having C-type sesquioxides (body-centered cubic), this is the phase in equilibrium with the thoria-rich fluorite-type phase. Where the C-type structure is not stable, various intermediate compounds are formed, as shown in the binary diagrams of Sibieude and Foex (1975).

Leitner (1967) presents binary diagrams and data for the thulia-thoria system. Engerer (1967) performed similar studies with tholmia, lutecia, and scandia. The results are in agreement with those described above. No evidence is presented, in the case of the systems with thoria, that these are indeed pseudobinaries, i.e., that they have phases lying outside the true

Figure 4.15. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Sm_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

binary join. The authors investigated, and presented evidence of, variations from stoichiometry in the systems containing uranium, neptunium, and plutonium. The absence of comparable information in the systems containing thorium strongly indicates that the analogous variations from stoichiometry do not occur, or, at least, that they cannot be obtained by comparable methods which, in the case of the other systems, consists of heating stoichiometric material in an oxidizing atmosphere.

4.6.3 The Thoria-Yttria System

Subbarao et al (1965) studied the thoria-yttria binary at temperatures between 1673 and 2473 K. They prepared their materials by precipitating

Figure 4.16. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Gd_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

ixed salts, and calcining and sintering in oxygen. If there had been any tendency at this temperature for oxidation of the thoria-yttria solid solutions, such that the charge on the Y atom were greater than +3, this procedure would be expected to produce such materials. However, it was demonstrated, by means of density determinations, that all samples consisted of mixtures of ThO_2 and Y_2O_3 .

Sibieude and Foex (1975) also studied this system; their results are presented in Fig. 4.21. The configuration of this diagram is very similar to those for the thorium dioxide-lanthanide oxide systems, such as, for example, thoria-erbia, in Fig. 4.19. The single-phase cubic solutions obey Vegard's Law; for the fluorite-type solid solution, the coefficients in Table 4.1 can be used to calculate satisfactory approximations.

Figure 4.17. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Dy_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

Density determinations by Subbarao et al (1965) on the fluorite-type solid solutions showed that the cation lattice was entirely filled with thorium and yttrium atoms. For each two yttrium atoms accommodated, therefore, one oxygen atom was removed from the anion lattice, thereby creating a vacancy.

Figure 4.22 shows the variation in cell size of the cubic phase with composition at room temperature. Figure 4.23 shows the theoretical densities calculated from these data on the basis of cation interstitials and anion vacancies, and demonstrates that the observed densities follow the curve based on the assumption of anion vacancies.

Figure 4.18. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Ho_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

4.6.4 The Thoria-Calcia System

The effective ionic radius of the Ca^{+2} ion, 0.112 nm, compares closely with the value of 0.105 nm for the Th^{+4} ion. However, the mismatch in charge amounts to two electrons per ion. Johnson and Curtis (1954) estimated that the extent of solid solubility of CaO in ThO_2 might be as large as 10 mole percent. This was apparently based on an observation that a sample with that composition appeared to be single-phase. Johnson and Curtis, however, observed no change in cell dimensions.

Jorgensen and Schmidt (1970), in their re-examination of the system, did not confirm these results. They found that ThO_2 -2.0 mole percent CaO ,

Figure 4.19. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Er_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

heated to 2573 K, showed a second-phase precipitate on examination by scanning electron microscopy, and that this composition apparently exceeded the solid solubility limit of CaO in thoria.

An intermediate phase, CaThO_3 , had been reported in the $\text{CaO}-\text{ThO}_2$ binary; however, Möbius et al (1964) and Roeder and Wilson (1975) failed to confirm its existence at temperatures up to 1873 K.

It is known that CaO improves the sinterability of thoria (see Chap. 8). Normally, when one substance is observed to affect the properties of another, it is likely that at least some solid solution has taken place.

Figure 4.20. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Yb₂O₃, according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

However, the alteration may not be the result of solid solution; it may be the result of the action of a separate phase or monolayer on surfaces or grain boundaries. The matter was examined by Jorgensen and Schmidt (1970). They found that the addition of 2 mole percent of CaO did indeed affect the sinterability of thoria; discontinuous grain growth was prevented and sintering was allowed to proceed to theoretical density. These effects were not observed for lesser amounts of CaO. Jorgensen and Schmidt attributed the effect entirely to the second phase, which impedes the migration of grain boundaries in the matrix.

Figure 4.21. Tentative Configuration of the Phase Diagram between Thoria and the Polymorphic Forms of Y_2O_3 , according to Sibieude and Foex (1975). (Courtesy, Journal of Nuclear Materials)

4.7 BINARY COMPOUNDS OF THORIUM DIOXIDE

In systems for which ionic size and charge preclude extensive mutual solid solubility, ordered intermediate compounds can form. In the ThO_2 - SiO_2 binary system, for example, single phases occur only in the immediate vicinity of the ThO_2 composition, the immediate vicinity of the SiO_2 composition, and the immediate vicinity of the midpoint, at which $ThSiO_4$ occurs (Lungu, 1966). The two halves of the binary diagram therefore consist of two-phase fields; in one, nearly pure thoria is in equilibrium

Figure 4.22. Lattice Parameters in the System $\text{ThO}_2\text{-YO}_{1.5}$, after Subbarao et al (1965). (Courtesy, American Ceramic Society)

with thorium silicate, and in the other, thorium silicate is in equilibrium with the form of silica appropriate to the temperature. This binary is shown as Fig. 4.24.

Ordered intermediate phases of other systems include ThTi_2O_6 , ThB_2O_5 , ThW_2O_8 , ThMo_2O_8 , $\text{ThNb}_4\text{O}_{12}$, $\text{ThTa}_4\text{O}_{12}$, and $\text{Th}_3\text{V}_4\text{O}_{16}$. $\text{ThNb}_4\text{O}_{12}$ has been studied by Alario-Franco et al (1982). It is a perovskite-type compound, prepared by mixing 2 moles of Nb_2O_5 to 1 mole of ThO_2 , heating the mixture to melting, and slow cooling. There is no evidence, at temperatures below melting, of any significant extent of solid solution between ThO_2 , Nb_2O_5 , and the intermediate compound. On slow cooling from the melt, the intermediate compound shows three main levels in an order-disorder hierarchy. Similar behavior would be expected in the isostructural compound $\text{ThTa}_4\text{O}_{12}$.

Figure 4.23. Densities of $\text{ThO}_2\text{-YO}_{1.5}$ Solid Solutions, after Subbarao et al (1965). (Courtesy, American Ceramic Society)

4.8 THORIUM DIOXIDE TERNARY SYSTEMS

Roeder and Wilson (1975) examined the $\text{ThO}_2\text{-ZrO}_2\text{-CaO}$ ternary at 1873 K; it is shown as Fig. 4.25. Mark (1959) examined the $\text{MgO-HfO}_2\text{-ThO}_2$ system at 1873 K and its apparent melting surface, which is shown in Fig. 4.26. The subsolidus phase relations at 1873 K are shown in Fig. 4.27. Lungu (1966) published the liquidus surface of a portion of the $\text{SiO}_2\text{-UO}_2\text{-ThO}_2$ ternary; it is shown in Fig. 4.28 and features a two-liquid field.

Hough and Marples (1965) showed the location of a eutectic valley at about 2400 K in the $\text{ThO}_2\text{-PuO}_2\text{-BeO}$ ternary (Fig. 4.29). Reeve and

Figure 4.24. The ThO₂-SiO₂ Binary System. Modified from Lungu (1966). (Courtesy, Journal of Nuclear Materials)

Murray (1959) found a similar configuration for the ThO₂-UO₂-BeO system. In neither case was there any indication of significant solid solubility of BeO in the fluorite-type solid solutions.

Brisi (1959) investigated the ThO₂-UO₂-ZrO₂ system at 1673 and 1273 K in hydrogen. He found that most of the interior of the system is occupied by multiphase fields. However, the continuous solid solution occurring along the ThO₂-UO₂ edge has a stability field extending a few mole percent into the interior of the diagram. At 1673 K, UO₂ can accommodate up to 17 mole percent ZrO₂, and ThO₂ can accommodate only about 1 mole percent ZrO₂. The solubility limit of zirconia in the intermediate compositions falls along an approximately straight line connecting these two points.

The general configuration of these ternaries indicates that reasonably correct estimates of the configurations of comparable systems can be made from known binaries of pairs of components, together with available information on the occurrence of intermediate phases.

The contours of Figs. 4.26 and 4.28 were originally presented in degrees Celsius, but were replotted in degrees kelvin. The replotting was done using optical projections of the originals, and a certain amount of estimation is inherent in the process.

Figure 4.25. Section of the ThO₂-ZrO₂-CaO Ternary System at 1873 K, according to Roeder and Wilson (1975). (Courtesy, American Ceramic Society)

4.9 SUMMARY

Thorium dioxide enters into solid solutions very extensively with other oxides, by accepting their cations as a substitute for thorium in its own crystal structure. When the substituted cation is trivalent or divalent, electrical neutrality is maintained by formation of an equivalent number of vacant oxygen sites. In cases for which a complete series of solid solutions cannot be formed, thorium often can enter, to a significant extent, the structure of the other oxide, substituting for its cations.

Where the solid solutions are incomplete, there exists a two-phase region in which thoria, containing the maximum amount of the other oxide that can be accommodated at the particular temperature studied, is in equilibrium with the appropriate form of the other oxide, containing the maximum amount of thorium.

In certain systems, in which the extent of mutual solid solution is very limited, ordered mixed-oxide compounds can form between the two end-members.

Figure 4.26. Melting Surface of the $\text{MgO-HfO}_2\text{-ThO}_2$ System, according to Mark (1959); Temperatures are in Kelvin. (Courtesy, American Ceramic Society)

While the phase diagrams between thorium and other oxides have been fairly extensively studied, those between uranium and other oxides have been even more extensively studied. They are sufficiently similar that, where information is lacking for thorium, the general configuration can be estimated from the analogous uranium phase diagram.

It is useful to generalize the known or probable phase relationships between thorium and other materials in terms of location in the periodic table.

1. There is complete mutual solid solubility between thorium and the other actinide dioxides, and also between thorium and ceria.
2. Thorium-uranium solid solutions can be oxidized continuously to a definite limit, called the oxidation limit, which can be represented by a curve running from $\text{ThO}_{2.00}$ to $\text{UO}_{2.25}$. In the thorium-plutonium system, similar curves also probably run from $\text{ThO}_{2.00}$ to $\text{PuO}_{1.61}$, and from $\text{ThO}_{2.00}$ to $\text{PuO}_{2.09}$, bounding, between them, the stability field of the fluorite-type phase.

Figure 4.27. Section of the $\text{MgO-HfO}_2\text{-ThO}_2$ Ternary System at 1873 K, according to Mark (1959). (Courtesy, American Ceramic Society)

3. Because of the mismatch in ionic size, thorium and zirconia accommodate each other only to the extent of a few mole percent in solid solution at temperatures below 2000 K. At higher temperatures, complete solid solutions may exist. Similar configurations may be present in the thorium-hafnia system.
4. There are partial solid solutions between thorium and the lanthanide sesquioxides, between thorium and yttria, and also between thorium and scandia. Maximum solubility of these sesquioxides in thorium is found at the eutectic or peritectic temperature, and may extend to 40 mole percent.
5. Among the alkaline earth oxides, there is significant interaction only with CaO , where a special situation exists: although there is a substantial mismatch (+2 for +4) in electronic charge, there is a match in ionic size. Calcia is soluble in thorium to an extent of somewhat less than 2 mole percent.
6. Among the transition elements, thorium forms ordered intermediate mixed oxides with the oxides of boron, silicon, niobium, tantalum, titanium, and vanadium. However, these systems contain no continuous solid solution stability fields of any significant extent below 2000 K.

Figure 4.28. Section of the SiO_2 - UO_2 - ThO_2 Ternary System, according to Lungu (1966); Temperatures are in Kelvin. (Courtesy, American Ceramic Society)

Figure 4.29. Section of the ThO_2 - PuO_2 - BeO Ternary System at Approximately 2400 K, according to Hough and Marples (1965). (Courtesy, Journal of Nuclear Materials)

7. There is no significant interaction with the oxides of the alkali metals, nor with the oxides of iron, cobalt, and nickel.
8. Among the nonmetals, the only one interacting significantly with thorium is oxygen. It is possible, at high temperature, to obtain oxygen-deficient thorium without the introduction of another cation.

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Chapter 5

THERMODYNAMIC AND THERMOCHEMICAL PROPERTIES OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

J. Belle

5.1 INTRODUCTION

This chapter is concerned with the thermodynamic and thermochemical properties of the $\text{ThO}_2\text{-UO}_2$ solid solution system as well as of ThO_2 itself. It thus becomes necessary, in some instances, to include data for UO_2 . Surface properties and chemical reactivity are also discussed.

The thermodynamic properties of ThO_2 have been reviewed and assessed by Godfrey et al (1966), by Peterson and Curtis (1970), and by Rand (1975). The latest assessment of the thermodynamic properties of UO_2 is that by Fink et al (1981). Some of these assessments are incorporated in the discussion in this chapter.

5.2 THERMAL EXPANSION

5.2.1 Introduction

Oxide fuel materials, like other materials, undergo changes in dimensions when heated or cooled. For cubic crystals, such as ThO_2 , UO_2 , and the $\text{ThO}_2\text{-UO}_2$ solid solutions, the expansion or contraction is the same in all directions. As long as phase changes do not occur the dimensional changes are reversible. Dimensional changes are also affected by such processes as sintering, bloating, or irradiation-induced changes (swelling or densification). These topics are excluded from this discussion but are covered in Chaps. 8 and 9. Thermal expansion data at low temperatures (2–283 K) are discussed in connection with magnetic properties in Chap. 3.

If L_0 is the length of a solid body at a reference temperature T_0 (defined here as 298.15 K) and L_T is its length at any temperature T (in kelvin) then the fractional change in length $\Delta L/L_0$ can be approximated by a polynomial as follows:

$$\frac{\Delta L}{L_0} = \frac{L_T - L_0}{L_0} = a + bT + cT^2 + dT^3 + \dots \quad \text{Eq. (5.1)}$$

where $a, b, c, d \dots$ are constants. Equations of this type are empirical formulations of experimental data.

The mean or average linear thermal expansion coefficient is defined as the following:

$$\bar{\alpha}_L = \frac{1}{L_0} \left(\frac{L_T - L_0}{T - T_0} \right) = \frac{\Delta L}{L_0} \left(\frac{1}{T - T_0} \right) \quad \text{Eq. (5.2)}$$

Since thermal expansion increases rapidly and nonlinearly with temperature for many oxides, it is erroneous to apply Eq. (5.2) over too wide a temperature range.

The instantaneous linear thermal expansion coefficient is defined by the expression

$$\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P \quad \text{Eq. (5.3)}$$

or, in terms of fractional change in length,

$$\alpha_L = \frac{\frac{d}{dT} \left(\frac{\Delta L}{L_0} \right)}{1 + \frac{\Delta L}{L_0}} \quad \text{Eq. (5.4)}$$

Methods that have been developed to evaluate the linear thermal expansion of solids at high temperatures all involve continuous or stepwise measurement of the length (or the lattice spacing) as a function of temperature and comparison of the length at various temperatures with some reference temperature. These include, among others, optical interferometry, differential dilatometry and X-ray diffraction. The first two may be characterized as macroscopic or bulk in the sense that they measure the change in dimensions of a visible sample.

Among the mechanisms contributing to the expansion of bulk samples is the accumulation of lattice defects. For example, thermal vacancies are

generated when a material is heated to temperatures close to melting. This accumulation of lattice defects does not affect the cell size as measured by X-ray diffraction, since X-rays measure only the average dilation of the interatomic spacing, whereas the macroscopic length changes measure both this dilation and the dimensional changes resulting from the creation of defects. Indeed, it has been shown theoretically (Eshelby, 1954) and experimentally (Balluffi and Simmons, 1960) that the concentration of thermally generated Schottky defects in a cubic crystal can be determined from the equation,

$$n/N = 3 \left(\frac{\Delta L}{L_0} - \frac{\Delta a}{a_0} \right) \quad \text{Eq. (5.5)}$$

where

n = the number of Schottky defects

N = Avogadro's number

a_0 = the lattice parameter at reference temperature T_0 .

If, however, the thermally generated defects are of the Frenkel type, then thermal expansion should be the same whether measured by X-ray diffraction or by bulk measurements. Ideally, bulk and X-ray diffraction measurements should be made on the same sample.

5.2.2 Thermal Expansion Data for ThO_2

A wide variety of determinations have been made by dilatometry or X-ray diffraction of the linear thermal expansion of ThO_2 at elevated temperatures. Older work was reviewed and assessed by Touloukian et al (1977). Data from 34 different sources obtained by all methods of measurements were tabulated, but only 20 of these sets of data were used in the evaluation. The "recommended" values, i.e., those whose uncertainty was judged to be 5 percent or less, are based on the data for pure ThO_2 , and the data above 2000 K are not included. On the basis of the data used, Touloukian et al (1977) presented a consensus curve represented by

$$\begin{aligned} \% \frac{\Delta L}{L_0} = & -0.179 + 5.097 \times 10^{-4} T \\ & + 3.732 \times 10^{-7} T^2 - 7.594 \times 10^{-11} T^3 \end{aligned} \quad \text{Eq. (5.6)}$$

where L_0 and ΔL represent the length of a sample at, and the length change from, 293 K, and T is in kelvin. Touloukian et al (1977) state that the equation applies from 150 to 2000 K with an accuracy of ± 3 percent.

Earlier, Hoch and Momin (1969) showed that their X-ray diffraction measurements of the thermal expansion of ThO_2 were in excellent agreement with an equation which they derived to fit the dilatometric measurements of Ohnysty and Rose (1964). In addition, their data also agreed well with both the X-ray thermal expansion measurements of Aronson et al (1967) and the bulk expansion measurements of Geller and Yavorsky (1945). From this good agreement of these two types of measurements Hoch and Momin concluded that the type of lattice disorder in ThO_2 was not the Schottky type but could not be defined from these data alone. In the case of UO_2 , which also showed little difference in thermal expansion from X-ray and bulk measurements, Hoch and Momin concluded from other evidence that the lattice disorder was probably of the Frenkel type.

The equation recommended by Hoch and Momin (1969), modified to change the original coefficients in terms of Celsius to kelvin, is the following:

$$\% \frac{\Delta L}{L_0} = -0.2426 + 7.837 \times 10^{-4} T + 9.995 \times 10^{-8} T^2 \quad \text{Eq. (5.7)}$$

Curves developed from the two sets of coefficients in Eqs. (5.6) and (5.7) are shown in Fig. 5.1; the results are almost identical. Figure 5.1 also shows good agreement of these equations with the more recent X-ray measurements of Hirata et al (1977).

Extrapolation to temperatures higher than those covered by measurement should be made with caution. It is suggested that Eq. (5.7) be used for extrapolation in preference to Eq. (5.6) recommended by Touloukian et al (1977) because the latter equation was derived to fit data between 150 and 2000 K, and the former equation agrees with the available experimental data above 2000 K. Recommended values for the linear thermal expansion of ThO_2 including extrapolated values are shown in Table 5.1.

The volumetric thermal expansion coefficients are related to the linear coefficients as follows:

$$\frac{\Delta V}{V_0} = 3 \left(\frac{\Delta L}{L_0} \right) + 3 \left(\frac{\Delta L}{L_0} \right)^2 + \left(\frac{\Delta L}{L_0} \right)^3 \quad \text{Eq. (5.8)}$$

$$\bar{\alpha} = \frac{1}{T - T_0} \left[3 \left(\frac{\Delta L}{L_0} \right) + 3 \left(\frac{\Delta L}{L_0} \right)^2 + \left(\frac{\Delta L}{L_0} \right)^3 \right] \quad \text{Eq. (5.9)}$$

and

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = 3\alpha_L \quad \text{Eq. (5.10)}$$

Figure 5.1. Consensus Equations and Later Data for the Linear Thermal Expansion of Thoria.

where

$\frac{\Delta V}{V_0}$ = the fractional change in volume

$\bar{\alpha}$ = the mean volumetric thermal expansion coefficient

α = the instantaneous volumetric thermal expansion coefficient,
equal to three times the instantaneous linear thermal expansion
coefficient.

TABLE 5.1—RECOMMENDED VALUES FOR LINEAR
THERMAL EXPANSION OF ThO₂*

Temperature (kelvin)	% ($\Delta L/L_0$)	Expansion Coefficient $\times 10^{-6}$	
		Mean	Instantaneous
298.15	0.0	8.43	8.43
400	0.087	8.53	8.63
500	0.174	8.63	8.82
600	0.264	8.73	9.01
700	0.355	8.83	9.20
800	0.448	8.93	9.39
900	0.543	9.03	9.58
1000	0.641	9.13	9.77
1100	0.740	9.23	9.96
1200	0.842	9.33	10.2
1300	0.945	9.43	10.3
1400	1.05	9.53	10.5
1500	1.16	9.63	10.7
1600	1.27	9.73	10.9
1700	1.38	9.83	11.1
1800	1.49	9.93	11.3
1900	1.61	10.0	11.5
2000	1.72	10.1	11.6
2100	1.84	10.2	11.8
2200	1.96	10.3	12.0
2300	2.09	10.4	12.2
2400	2.21	10.5	12.4
2500	2.34	10.6	12.5
2600	2.47	10.7	12.7
2700	2.60	10.8	12.9
2800	2.74	10.9	13.1
2900	2.87	11.0	13.3
3000	3.01	11.1	13.4
3100	3.15	11.2	13.6
3200	3.29	11.3	13.8
3300	3.43	11.4	14.0
3400	3.58	11.5	14.1
3500	3.72	11.6	14.3
3600	3.87	11.7	14.5
3640	3.93	11.8	14.5

*Calculated from Eq. (5.7)

For all practical purposes, the last two terms in Eqs. (5.8) and (5.9) can be dropped without significant error. The volumetric thermal expansion coefficients calculated from the linear thermal expansion coefficients are shown in Table 5.2.

TABLE 5.2—RECOMMENDED VALUES FOR VOLUMETRIC
THERMAL EXPANSION OF ThO₂*

Temperature (kelvin)	% ($\Delta V/V_0$)	Expansion Coefficient $\times 10^{-6}$	
		Mean	Instantaneous
298.15	0.0	25.3	25.3
400	0.261	25.6	25.9
500	0.524	25.9	26.5
600	0.793	26.3	27.0
700	1.07	26.3	27.6
800	1.35	26.9	28.2
900	1.64	27.2	28.8
1000	1.94	27.6	29.3
1100	2.24	27.9	29.9
1200	2.55	28.2	30.5
1300	2.86	28.6	31.0
1400	3.18	28.9	31.6
1500	3.51	29.2	32.1
1600	3.85	29.6	32.7
1700	4.19	29.9	33.2
1800	4.54	30.2	33.8
1900	4.90	30.6	34.4
2000	5.26	30.9	34.9
2100	5.63	31.3	35.5
2200	6.01	31.6	36.0
2300	6.40	32.0	36.5
2400	6.79	32.3	37.1
2500	7.19	32.6	37.6
2600	7.60	33.0	38.2
2700	8.01	33.4	38.7
2800	8.43	33.7	39.2
2900	8.86	34.0	39.8
3000	9.30	34.4	40.3
3100	9.74	34.8	40.8
3200	10.2	35.1	41.3
3300	10.6	35.5	41.9
3400	11.1	35.9	42.4
3500	11.6	36.2	42.9
3600	12.1	36.6	43.4
3640	12.3	36.7	43.6

*Calculated from Eq. (5.7)

5.2.3 Thermal Expansion Data for UO₂

Many expressions have been proposed for the thermal expansion of solid UO₂. Of the 43 sets of data tabulated in the TPRC assessment (Touloukian et al, 1977) only 5 sets were used in the evaluation, and these are for pure

"stoichiometric" UO_2 only. Touloukian et al (1977) do not provide "recommended" values as they do in the case of ThO_2 but suggest "provisional" values because of the many uncertainties in the data as a result of variations in stoichiometry.

However, there is an arbitrary character to the selection of data for use in the TPRC assessment. Data obtained on $\text{UO}_{2.01}$ are used despite the deviation from stoichiometry. Also, some X-ray expansion data (Baldock et al, 1966) are not used, presumably because the UO_2 was reported to be slightly hypostoichiometric ($\text{O}/\text{U} = 1.984$ and 1.991), but other X-ray data (Hoch and Momin, 1969) are incorporated in the consensus despite the fact that they were obtained on hyperstoichiometric oxide ($\text{O}/\text{U} = 2.067$). (Hoch and Momin (1969) claim, however, that the small change in stoichiometry has a negligible effect on the lattice determination of the thermal expansion coefficient.)

These two sets of high temperature X-ray data are important in that they indicate opposite trends. Baldock et al (1966) found their X-ray thermal expansion data to be significantly lower than the bulk expansion data above 1673 K, whereas Hoch and Momin (1969) found their X-ray data to agree with bulk expansion data, particularly with those of Conway et al (1963), over the entire temperature range to about 2500 K.

Baldock et al (1966) suggested that the difference between the bulk and X-ray measurements may be due, as was discussed in Sect. 5.2.1, to the presence of Schottky defects at the higher temperature. Indeed, they proposed a value of 0.91 eV (88 kJ/mol) for the enthalpy of Schottky defect formation from a plot of $\ln(n/N)$ versus $1/T$, where n is the number of Schottky defects, N is Avogadro's number, $n/N = 3 (\Delta L/L_0 - \Delta a/a_0) = e^{S/k} e^{-H/kT}$, S and H being, respectively, the entropy and enthalpy of formation per Schottky defect.

Hoch and Momin (1969), who carried out their studies for the express purpose of checking the findings of Baldock et al (1966), disagreed and suggested the possibility that the thermocouple used by Baldock et al ($\text{W} + \text{W}-26$ percent Re) may have deteriorated during the measurements, thus leading to gross errors in temperature measurement. They proposed that the lattice disorder for UO_2 is Frenkel type (an oxygen atom from a tetrahedral position moving into an empty octahedral site, and not Schottky type, not only because thermal expansions determined by X-ray diffraction and by bulk measurements are equal, but because Frenkel disorder is indicated since the heat capacity of UO_2 shows a rapid increase above 1973 K. (See discussion of heat capacity in Sect. 5.5.)

In a recent assessment of the thermophysical properties of uranium dioxide, Fink et al (1981) present an equation for the fractional change in

length relative to the length at 298.15 K which is based on a fit of the thermal expansion data of Conway et al (1963) and of Christensen (1963a). The equation is

$$\frac{\Delta L}{L_0} = -1.9304 \times 10^{-3} + 5.723 \times 10^{-6} T + 2.487 \times 10^{-9} T^2 + 1.140 \times 10^{-13} T^3, \quad \text{Eq. (5.11)}$$

or in terms of percent,

$$\% \frac{\Delta L}{L_0} = -0.19304 + 5.723 \times 10^{-4} T + 2.487 \times 10^{-7} T^2 + 1.140 \times 10^{-11} T^3 \quad \text{Eq. (5.12)}$$

The linear and volumetric thermal expansion coefficients for UO_2 calculated from Eq. (5.12) are tabulated in Tables 5.3 and 5.4.

5.2.4 Thermal Expansion of $\text{ThO}_2\text{-UO}_2$

The recommended curves of percent linear thermal expansion for both ThO_2 and UO_2 calculated from Eqs. (5.7) and (5.12), respectively, are shown in Fig. 5.2. These curves can be used to estimate expansion values for intermediate compositions in the solid solution system by applying Vegard's law, as discussed in Chap. 4. Figure 5.3 shows a comparison of calculated values with dilatometry measurements on $\text{ThO}_2\text{-10.09}$ and 20.04 mole percent UO_2 (Springer et al, 1967) and with X-ray diffractometry determinations of fractional cell size changes in $\text{ThO}_2\text{-50.5}$ mole percent UO_2 (Kempter and Elliott, 1959). Agreement is satisfactory; variation with composition, in any case, is quite small.

2.5 Volume Expansion on Melting

No data exist for the volume change of ThO_2 on melting, but there is some information on UO_2 which suggests some upper bound value. Christensen (1963a) measured the density of UO_2 between 1553 and 3373 K by high temperature radiography of single crystals sealed in tungsten vessels. The density of the solid at 3073 K was 9.67 g/cc (9.67 Mg/m³); that of the liquid at 3073 K was 8.74 g/cc (8.74 Mg/m³). The volume

TABLE 5.3—RECOMMENDED VALUES FOR LINEAR
THERMAL EXPANSION OF UO_2^*

Temperature (kelvin)	% ($\Delta L/L_0$)	Expansion Coefficient $\times 10^{-6}$	
		Mean	Instantaneous
298.15	0.0	7.24	7.24
400	0.076	7.50	7.76
500	0.157	7.76	8.28
600	0.242	8.03	8.81
700	0.333	8.30	9.34
800	0.430	8.56	9.88
900	0.532	8.84	10.4
1000	0.639	9.11	11.0
1100	0.753	9.39	11.5
1200	0.872	9.66	12.1
1300	0.996	9.95	12.6
1400	1.13	10.2	13.2
1500	1.26	10.5	13.8
1600	1.41	10.8	14.4
1700	1.55	11.1	14.9
1800	1.71	11.4	15.5
1900	1.87	11.7	16.1
2000	2.04	12.0	16.7
2100	2.21	12.3	17.3
2200	2.39	12.6	17.9
2300	2.58	12.9	18.5
2400	2.77	13.2	19.1
2500	2.97	13.5	19.7
2600	3.18	13.8	20.3
2700	3.39	14.1	20.9
2800	3.61	14.4	21.6
2900	3.84	14.7	22.2
3000	4.07	15.1	22.8
3100	4.31	15.4	23.4
3120	4.36	15.5	23.6

*Calculated from Eq. (5.12)

increase on melting was 10.6 percent. Christensen fitted his data to an empirical equation for specific volume as a function of temperature from 0–2800° Celsius,

$$V_T = V_0 (1 + 9 \times 10^{-6} T + 6 \times 10^{-9} T^2 + 3 \times 10^{-12} T^3) \quad \text{Eq. (5.13)}$$

TABLE 5.4—RECOMMENDED VALUES FOR VOLUME EXPANSION OF UO_2^*

Temperature (kelvin)	% ($\Delta V/V_0$)	Expansion Coefficient $\times 10^{-6}$	
		Mean	Instantaneous
298.15	0.0	21.7	21.7
400	0.229	22.5	23.3
500	0.471	23.3	24.9
600	0.729	24.1	26.4
700	1.00	25.0	28.0
800	1.30	25.8	29.6
900	1.60	26.6	31.3
1000	1.93	27.5	32.9
1100	2.28	28.4	34.6
1200	2.64	29.2	36.2
1300	3.02	30.1	37.9
1400	3.42	31.0	39.6
1500	3.84	31.9	41.3
1600	4.28	32.9	43.1
1700	4.74	33.8	44.8
1800	5.22	34.7	46.6
1900	5.72	35.7	48.3
2000	6.24	36.7	50.1
2100	6.78	37.6	51.9
2200	7.35	38.6	53.7
2300	7.94	39.6	55.5
2400	8.55	40.7	57.3
2500	9.18	41.7	59.1
2600	9.84	42.7	61.0
2700	10.5	43.8	62.8
2800	11.2	44.9	64.7
2900	12.0	46.0	66.5
3000	12.7	47.1	68.4
3100	13.5	48.2	70.3
3120	13.7	48.4	70.7

*Calculated from Eq. (5.12)

where

 V_T = the specific volume at temperature T° (Celsius) V_0 = the specific volume at 0° (Celsius).

Figure 5.2. Comparison of Recommended Curves of Percent Linear Thermal Expansion for ThO_2 and UO_2 .

Fink et al (1981) report density equations for both solid and liquid UO_2 which were derived from the expansion data of Christensen (1963a). For solid UO_2 , for $298 \leq T \leq 3120$ K,

$$\rho(\text{Mg/m}^3) = 10.97 (1.0056 - 1.6324 \times 10^{-5} T - 8.3281 \times 10^{-9} T^2 + 2.0176 \times 10^{-13} T^3) \quad \text{Eq. (5.14)}$$

Figure 5.3. Comparison of Measured and Calculated Values of Percent Linear Thermal Expansion of $\text{ThO}_2\text{-UO}_2$ Solid Solutions.

For liquid UO_2 , for $3120 \leq T \leq 3400$ K,

$$\rho(\text{Mg/m}^3) = 10.97 (1.0522 - 8.19 \times 10^{-5} T) . \quad \text{Eq. (5.15)}$$

Densities calculated from these equations indicate a volume increase on melting of 10.5 percent.

It is not recommended that these equations be applied to ThO_2 to estimate the volume change on melting, since ThO_2 and UO_2 differ markedly in their linear and thus volume expansivities. It is seen from Fig. 5.2 that the change with temperature of the percent thermal linear expansion is much greater for UO_2 than for ThO_2 .

5.3 DENSITIES OF ThO_2 - UO_2 SOLID SOLUTIONS

The equations for percent linear expansion permit an evaluation of the fractional change in density of UO_2 or ThO_2 between 298.15 K and a given temperature up to the melting points.

On the assumption that ThO_2 - UO_2 solid solutions are ideal, i.e., there is no volume change accompanying formation of solid solutions (see the discussion of Vegard's Law in Chap. 4), densities of the solid solutions can be calculated by evaluating the molar volumes of the two components at the temperature of interest, then finding the value for the solid solution by linear interpolation. Using the theoretical densities at 298.15 K of 10.00 Mg/m^3 and 10.97 Mg/m^3 , respectively, for ThO_2 and UO_2 , the resulting densities for several compositions are shown plotted in Fig. 5.4.

5.4 CHANGE OF STATE

5.4.1 Melting Temperature

In their compilation of data on thorium ceramics, Peterson and Curtis (1970) cite two values for the melting point of ThO_2 , 3573 ± 100 K from the work of Lambertson et al (1953) on the ThO_2 - UO_2 system and 3663 K from the work of Benz (1969) on the Th- ThO_2 system.

Lambertson et al (1953) reported values for the melting point that ranged from 3558 to 3828 K, but within this range obtained a value of 3623 K by extrapolating melting point data for ThO_2 - UO_2 compositions to pure ThO_2 . However, these workers suggested a lower value, 3575 K, to match the curvature of the temperature-composition diagram at the high ThO_2 side with that at the high UO_2 end. Christensen (1963b) made similar extrapolation from his melting point measurements on ThO_2 - UO_2 and obtained a value of 3543 K, in good agreement with the Lambertson et al lower value.

In his assessment of the thermochemical properties of ThO_2 , Rand (1975) criticized the assumption of symmetrical curvature at both ends of the ThO_2 - UO_2 system. Loss of oxygen could account for the curvature at the UO_2 -rich side, but this condition would not exist to the same extent at the high ThO_2 end. Rand (1975) instead suggested a value for the melting point of 3643 ± 30 K, which is the average of the higher value of Lambertson et al (3623 K) and that reported (Benz, 1969) for the congruent melting temperature (3663 K).

Figure 5.4. Densities of ThO_2 , UO_2 , and Some $\text{ThO}_2\text{-UO}_2$ Solid Solutions as Functions of Temperature.

According to Latta et al (1970), the congruent melting point for UO_2 occurs at the composition $\text{UO}_{2.00}$ and is 3138 ± 15 K. This value is considerably higher than the value of 3073 K reported by Christensen (1963a), but is probably more accurate, as Latta et al point out, because uncertainties with changes in stoichiometry were avoided in the more recent work. In this book we shall use the recommended values for the melting temperatures T_m of 3640 K for ThO_2 (Rand, 1975) and 3120 K (the lower value of the Latta et al, 1970, range) for UO_2 . The limits of error are probably the same for both oxides, i.e., about 30 K.

As discussed in Chap. 4, the $\text{ThO}_2\text{-UO}_2$ phase diagram can be constructed from the melting points and enthalpies of fusion of the end

TABLE 5.5—MELTING TEMPERATURES OF ThO_2 - UO_2 SOLID SOLUTIONS*

Composition (Mole Percent UO_2)	Temperature, kelvin	
	Solidus	Liquidus
0	3640	3640
10	3580	3600
20	3520	3550
30	3460	3510
40	3410	3460
50	3360	3410
60	3310	3360
70	3260	3310
80	3210	3250
90	3160	3190
100	3120	3120

*To nearest 10 K

members. This calculation assumes ideal solution behavior in both liquid and solid states. The melting temperatures so calculated for some intermediate compositions are shown in Table 5.5. An estimated value for the enthalpy of fusion was used for ThO_2 (see Sect. 5.4.2).

Data do not exist on the effect of irradiation on the melting points of ThO_2 and ThO_2 - UO_2 solid solutions, but there are some data on UO_2 . Christensen et al (1964) reported measurements of the melting points of "nearly" stoichiometric UO_2 samples that had been irradiated to various burnup levels from about 0.5 to 23 fission units (see Chap. 9). Measurements were made relative to unirradiated UO_2 , which was assumed to have a melting point of 3073 K. Their data indicated a nearly linear decrease of melting point with irradiation exposure at a rate of about 9 K per fission unit. In earlier work, Christensen (1962) reported an increase in the melting point of about 100 K to a burnup of 0.2 fission units followed by a decrease at higher irradiation levels of about 130 K below the melting point after 23 fission units. It is not known to what extent these observations were influenced by variations in oxygen content. Bates (1970) did not find any influence on the melting point with irradiation at lower temperatures and lower irradiation levels.

5.4.2 Heat of Fusion

There is no direct experimental measurement of the heat of fusion (ΔH_m) for ThO_2 , nor for any ThO_2 - UO_2 solid solution. Ackermann and

Fink (1962) did report an estimated value of 105 kJ/mol for the heat of fusion for ThO_2 from some data on the solubility of ThO_2 in liquid thorium and the assumption of ideal solution behavior. However, this value is considerably higher than the estimate of 90.8 kJ/mol made on the assumption that the molal entropy of fusion is R per atom, i.e., $\Delta H_m/T_m = nR$, where n is the number of atoms in the formula unit.

In the UO_2 case, better agreement is obtained between measurement and the nRT_m estimate. Of the reported experimental determinations, the two that appear most reliable are those by Hein et al (1963) and by Leibowitz et al (1971). In the former work a value of 76.1 kJ/mol was obtained from the observed sharp discontinuity on the enthalpy-temperature plot at the melting temperature of UO_2 . In the latter work a value of 74.0 kJ/mol was obtained from enthalpy measurements of liquid UO_2 to 3500 K. The average of these two determinations, 75.1 kJ/mol, is close to the estimated value of 77.8 kJ/mol. Fink et al (1981) recommend the value of 74.8 ± 1 kJ/mol for the heat of fusion for uranium dioxide from their assessment of the enthalpy data for UO_2 (see Sect. 5.5.1). Thus, the estimated value of 90.8 kJ/mol for the heat of fusion for ThO_2 appears reasonable.

5.4.3 Vapor Pressure

(a) Vapor Pressure of Thoria

Critical reviews (Ackermann and Thorn, 1961; Rand, 1975) of the early work on the determination of the vapor pressure of thoria showed this work to have been in error because of either inaccurate temperature measurement, or reduction of thoria by the effusion cell, or nonequilibrium conditions. The vaporization behavior of thoria appears to be better understood as a result of later measurements (Darnell and McCollum, 1961; Ackermann et al, 1963; Ackermann and Rauh, 1973) that combined mass spectrometric analyses of the vapor species with Knudsen effusion measurements. The data summarized here are from measurements on essentially stoichiometric ThO_2 (Ackermann et al, 1963) and later measurements on the univariant system, $\text{Th}(\mathcal{L}) + \text{ThO}_2(\text{s}) + \text{vapor}$. The major species in the former system is $\text{ThO}_2(\text{g})$; that in the latter is $\text{ThO}(\text{g})$.

Two processes are important in the sublimation or vaporization of thoria; these are represented by the equations $\text{ThO}_2(\text{s}) \rightarrow \text{ThO}_2(\text{g})$ and $\text{ThO}_2(\text{s}) \rightarrow \text{ThO}(\text{g}) + \text{O}$. The solid dioxide evaporates congruently, i.e., the O/Th ratio is the same in the solid phase as in the effusate. In the initial study of the evaporation behavior of the thorium-oxygen system over the temperature range 2000–3000 K (Ackermann et al, 1963), the congruently vaporizing composition above 2800 K was measured as $\text{ThO}_{1.998}$. In later work (Ackermann and Rauh, 1973), the congruently vaporizing composition of the dioxide phase above 2800 K was determined by

approaching it from both the oxygen-rich (ThO_2) composition and from the metal-rich ($\text{ThO}_2 + \text{Th} = \text{ThO}_{1.97}$) composition. In both cases the composition of the residue was found to be $\text{ThO}_{1.994 \pm 0.002}$.

Ackermann and coworkers also showed that $(\text{ThO})_g$ and O in approximately equal amounts are appreciable constituents of the vapor. The partial pressures of $\text{ThO}_2(g)$, $\text{ThO}(g)$ and atomic oxygen (O) over the congruently evaporating dioxide phase are given by the following equations:

$$\log P(\text{ThO}_2)_g, \text{ atm} = 7.96 - 35,070 T^{-1}, 2400-2800 \text{ K} \quad \text{Eq. (5.16)}$$

$$\log P(\text{ThO})_g, \text{ atm} = 8.15 - 36,860 T^{-1}, 2400-2800 \text{ K} \quad \text{Eq. (5.17)}$$

$$\log P(\text{O}), \text{ atm} = 7.56 - 36,860 T^{-1}, 2400-2800 \text{ K} \quad \text{Eq. (5.18)}$$

The total pressure of thorium-bearing species over solid ThO_2 is expressed by

$$\log P_{(e)}, \text{ atm} = 8.26 - 35,520 T^{-1}, 2180-2865 \text{ K} \quad \text{Eq. (5.19)}$$

where $P_{(e)}$, the "effective pressure", was calculated on the assumption that the vapor phase was composed entirely of dioxide molecules. An uncertainty of ± 15 percent was estimated (Ackermann and Rauh, 1973) for each of the pressures. These vapor pressure equations are plotted in Fig. 5.5.

The high-temperature vaporization of hypostoichiometric thoria is discussed in Sect. 5.8.3.

(b) Heat of Sublimation

The terms "heat of sublimation" and "heat of vaporization" are used interchangeably to denote the enthalpy derived from vapor pressure whether or not the temperature range extends above the melting point of the solid. In a strict sense, heat of sublimation refers to the solid-yields-vapor process in the absence of a liquid phase. Where vapor pressure data are available for temperatures beyond the melting point, heat of vaporization is the better term. In the case of UO_2 , for example, both the heat of sublimation (ΔH_s) and the heat of vaporization (ΔH_v) have been determined as well as the heat of fusion (ΔH_m). These quantities are related as follows: $\Delta H_s = \Delta H_v + \Delta H_m$. Ackermann et al (1980) report the average enthalpy of sublimation to be $592.0 \pm 1.2 \text{ kJ/mol}$ from vapor pressure measurements. A value of 599.0 kJ/mol is calculated from the recommended vapor pressure equation for UO_2 (Fink et al, 1981) discussed

Figure 5.5. Plot of Vapor Pressure Equations for ThO_2 .

below. These values are in fair agreement with the value of 596.8 kJ/mol calculated from the recommended (Fink et al, 1981) values for the heats of vaporization (522 kJ/mol) and fusion (74.8 kJ/mol).

The heat of sublimation for the reaction, $\text{ThO}_2(\text{s}) \rightarrow \text{ThO}_2(\text{g})$ from Eq. (5.14) is 671.5 kJ/mol. Since vapor pressure data for temperatures above the melting point do not exist, no experimental value is available for the heat of vaporization. However, a value of 580.7 kJ/mol for ΔH_v can be estimated from the expression, $\Delta H_v = \Delta H_s - \Delta H_m$.

(c) *Sublimation Behavior of ThO₂-UO₂ Solid Solutions*

In a binary system, such as ThO₂-UO₂, the usual mode of sublimation or vaporization is preferential vaporization of the component with the higher volatility. It is inferred from the data on heats of sublimation that the uranium-bearing species will predominate in solid solutions of ThO₂-UO₂. This inference is substantiated from the work of Alexander et al (1967), who determined the partial pressures of UO₂ over two ThO₂-UO₂ compositions, ThO₂-7.80 mole percent UO₂ and ThO₂-19.9 mole percent UO₂, at 2373-2773 K. These transpiration measurements were made in flowing hydrogen or hydrogen-argon mixtures, and consequently the compositions were presumed to be unoxidized. These data are shown in Fig. 5.6 along with vapor pressure data for ThO₂ obtained in the same study. Also plotted in Fig. 5.6 are the vapor pressure equation of Ackermann and Rauh (1973) for ThO₂(g), Eq. (5.16), and the recommended (Fink et al, 1981) vapor pressure equation for solid UO₂, namely,

$$\log P \text{ (MPa)} = 7.774 - 31,284/T \quad \text{Eq. (5.20)}$$

Although the absolute magnitude of the Alexander et al (1967) vapor pressure data may be in doubt, as judged by the disagreement between their data and those of Ackermann and Rauh (1973) for ThO₂, it is clear that the vapor pressures of UO₂ over the solid solutions are significantly higher than the vapor pressure for pure ThO₂. This difference in vapor pressure leads to preferential loss of UO₂ from ThO₂-UO₂ solid solutions at elevated temperatures. The Alexander et al vapor pressure data for the two solid solutions can be represented by the following equations for

ThO₂-7.80 mole percent UO₂:

$$\log P \text{ (atm)} = 7.29 - 32,866/T, 2340-2740 \text{ K} \quad \text{Eq. (5.21)}$$

and for ThO₂-19.9 mole percent UO₂:

$$\log P \text{ (atm)} = 7.79 - 32,430/T, 2400-2760 \text{ K} \quad \text{Eq. (5.22)}$$

The volatilization behavior in an oxidizing atmosphere of ThO₂-UO₂ solid solutions for compositions ranging from 0.063 to 0.5 mole percent UO₂ was examined by Aitken et al (1966) for the temperature range 1473 to 1873 K. Dry air was used as the carrier gas in these transpiration experiments, thus making the solid solutions hyperstoichiometric. The

Figure 5.6. Partial Pressures of Urania over Thoria-Urania Solid Solutions Compared with Total Pressures of Thoria and Urania.

principal vapor species was assumed to be UO_3 , although experimental evidence was not presented. A further discussion of this work is presented Sect. 5.9.

5.4.4 Boiling Point

In the early literature (Mott, 1916) the value for the boiling point of ThO_2 is given as 4673 K. A much lower value, 4573 K, is estimated from the vapor pressure equation, Eq. (5.19), given by Ackermann et al (1963), $\log P_{(e)} = 8.26 - 35,520 T^{-1}$.

5.5 ENTHALPY AND HEAT CAPACITY

5.5.1 Assessment of the Enthalpy and Heat Capacity Data for Uranium Dioxide

There have been many assessments of the enthalpy and heat capacity data for UO_2 , particularly in attempts to explain the anomalous rise in heat capacity at high temperatures. For example, Hobson et al (1974) recommended the equation

$$C_p(\text{UO}_2)_s = 59.827 + 5.329 \times 10^{-2} T - 41.870 \times 10^{-6} T^2 + 12.876 \times 10^{-9} T^3 \text{ J/mol} \cdot \text{K} \quad \text{Eq. (5.23)}$$

which was obtained by differentiating the enthalpy equation derived from a fourth-order polynomial fit "using all the available enthalpy data". This equation does not lead to a smooth fit with the lower temperature values; for example, the value for 298 K calculated from Eq. (5.23) is 72.3 J/mol · K, as contrasted with the values of 64.1 and 63.6 J/mol · K recommended, respectively, by Godfrey et al (1966) and the IAEA Panel (1965).

In the other type of mathematical fit of the data, a quasitheoretical formulation is assumed. For example, Kerrisk and Clifton (1972) fit the extensive UO_2 enthalpy data to a mathematical model that contained separate low temperature and high temperature contributions. Their equation covered the range of data from 298 K to the melting point of UO_2 , 3120 K. The data used were those of Moore and Kelley (1947) from 483 to 1462 K, of Ogard and Leary (1968) from 1338 to 2303 K, of Hein et al (1968) from 1174 to 3107 K, of Leibowitz et al (1969) from 2557 to 3083 K, and of Fredrickson and Chasanov (1970) from 675 to 1434 K. Their equation agreed with the lower temperature measurements because they used the heat capacity value at 298 K recommended by the IAEA Panel (1965) of 63.6 J/mol · K.

The equation recommended by Kerrisk and Clifton (1972) for the molar heat capacity of UO_2 (J/mol · K) is

$$C_p(\text{UO}_2)_s = \frac{K_1 \theta^2 e^{\theta/T}}{T^2 (e^{\theta/T} - 1)^2} + 2K_2 T + \frac{K_3 E_D}{RT^2} \exp(-E_D/RT) \quad \text{Eq. (5.24)}$$

where

$$\begin{aligned}\theta &= \text{Einstein characteristic temperature, is 535 K} \\ K_1 &= 80.10 \text{ J/mol} \cdot \text{K} \\ K_2 &= 3.282 \times 10^{-3} \text{ J/mol} \cdot \text{K}^2 \\ K_3 &= 2.36 \times 10^7 \text{ J/mol} \\ E_D &= 157.71 \text{ kJ/mol}\end{aligned}$$

The best fit value for θ agrees with the value of 542 K recommended by the IAEA Panel (1965) as a result of their analysis of the neutron diffraction measurements of Willis (1963a and b). The first term in Eq. (5.24) is the heat capacity at constant volume, represented by an Einstein function, and dominates at low temperature; the second term is the expansion contribution assumed proportional to T ; and the third term contains a contribution resulting from the formation of Frenkel defects. Thus, E_D was interpreted by Kerrisk and Clifton (1972) as the energy of formation of a single Frenkel-type defect; its value of approximately 157 kJ/mol is close to half the value of 298 kJ/mol estimated earlier by Szwarc (1969) for the formation energy of a Frenkel pair.

Szwarc had proposed that the formation energy of a Frenkel defect pair in the UO_2 lattice was responsible for the excess enthalpy, H_{ex} . He fit the experimental enthalpy data up to the melting point to an equation consisting of two parts: a lattice parabolic portion, $H_L = a + bT + cT^2$, and an additive exponential term, $\Delta H_F \sqrt{2} \exp(\Delta S_F/2R) \exp(-\Delta H_F/2RT)$, where ΔH_F and ΔS_F are, respectively, the enthalpy and entropy for the formation of a Frenkel pair. By fitting the low temperature (below 2100 K) enthalpy data to the parabolic part and the overall data to the total expression, Szwarc derived the value of 298 kJ/mol for ΔH_F , in excellent agreement with the estimate made by Belle et al (1961) from data on oxygen diffusion in uranium dioxide. As Szwarc points out, however, the calculated value for ΔH_F is sensitive to the particular parabolic equation chosen to describe the lattice contribution to the total enthalpy.

A number of authors (MacInnes, 1978; Young, 1979; MacInnes and Chow, 1980; and Harding et al, 1980) have pointed out that the anomalous contribution to the heat capacity of UO_2 has its origin in electronic effects. Thus, MacInnes (1978) criticized the interpretation that the rapid increase in heat capacity is due to the formation of Frenkel defects and suggested instead that the increase in heat capacity is a result of the absorption of energy through electronic excitation. This is more likely, MacInnes suggests, because UO_2 is an ionic semiconductor with a band gap of approximately 2 eV (193 kJ/mol), so that the activation energy of

electronic excitation is considerably less than that of defect formation. MacInnes also points out that the estimate for Frenkel defect formation energy (298 kJ/mol) is much too low; a better value according to theoretical estimates (Catlow, 1977) is about 530 kJ/mol.

Rand et al (1978) adopted the Kerrisk and Clifton (1972) analysis but added another feature, namely, a transition temperature of 2670 K, above which the heat capacity remains constant. The heat capacity and enthalpy data below 2670 K were fit to Eq. (5.24) and its integrated form, and the enthalpy data above 2670 K were fit to an equation representing a constant heat capacity.

This analysis by Rand et al made use of the suggestion by Bredig (1972) that the Hein et al (1968) high temperature UO_2 enthalpy data can be interpreted to show the presence of a "lambda transition" in uranium dioxide at 2670 K (see Fig. 5.7). This "diffuse" or "order-disorder" transition had been suggested by Dworkin and Bredig (1968) as a general characteristic of fluorite and antifluorite crystal lattices, and had been predicted by them for both UO_2 and ThO_2 (see Chap. 3). In Bredig's view the transition is presumably evidence of considerable disorder in the oxygen sublattice, going beyond the anion Frenkel defect formation suggested by Szwarc.

The lambda transition is an example of a "second-order" transition, i.e., the Gibbs free energy and its first derivatives are both continuous but the second derivatives are discontinuous. In contrast, a "first-order" transition is one for which the free energy is continuous, but the first derivatives are discontinuous. Examples of first-order transitions are phase transitions, such as fusion, vaporization, and allotropic transformations. In the second-order transition there is no phase change. By these definitions the Bredig lambda transition would seem to be a second-order transition; however, this classification is not precise since there is a discontinuity in the enthalpy. Although there is no evidence for a phase change at the transition temperatures for ThO_2 and UO_2 , the considerable disorder in the anion lattice may be viewed as a phase change, i.e., a "melting" of the sublattice.

The enthalpy and heat capacity data for solid UO_2 were reexamined Fink et al (1981). They found that the data were best fit by making the third term in Eq. (5.24) electronic in origin and incorporating the transition temperature of 2670 K as proposed by both Bredig (1971) and Rand et al (1978).

The equations recommended by Fink et al (1981) for the heat capacity in J/mol $\cdot$ K for solid UO_2 over the two temperature ranges are as follows: For $298.15 \text{ K} \leq T \leq 2670 \text{ K}$,

$$C_p = \frac{C_1 \theta^2 e^{\theta/T}}{T^2 (e^{\theta/T} - 1)^2} + 2C_2 T + C_3 k e^{-E_a/kT} \left[1 + \frac{(T - T_0) E_a}{kT^2} \right] \quad \text{Eq. (5.25)}$$

Figure 5.7. Excess Heat Capacity for Lambda Transition in Uranium Dioxide (Bredig, 1972).

where

C_p = heat capacity at constant pressure

$C_1 = 78.212 \text{ J/mol} \cdot \text{K}$

$C_2 = 3.8616 \times 10^{-3} \text{ J/mol} \cdot \text{K}^2$

$C_3 = 3.3993 \times 10^8 \text{ J/mol} \cdot \text{eV}$

$\theta = 516.11 \text{ K}$

$E_a = 1.8815 \text{ eV}$

$T_0 = 298.15 \text{ K}$

$k = 8.6144 \times 10^{-5} \text{ eV/K}$ (Boltzmann constant).

For $2670 \text{ K} \leq T \leq 3120 \text{ K}$, $C_p = 167.04$. Note that the value for θ , 516.11 K, derived from the fit of the data differs from the 535 K obtained by Kerrisk and Clifton (1972).

5.5.2 Measurements on ThO_2

(a) Low-Temperature Data

Osborne and Westrum (1953) measured the low-temperature heat capacity at constant pressure (C_p) of ThO_2 from 10 to 305 K and calculated the standard entropy. Their data for ThO_2 did not show the anomalous rise that was observed for uranium dioxide at 28.7 K (Jones et al, 1952) and for neptunium dioxide at 25.3 K (Westrum et al, 1953). Later heat capacity measurements on UO_2 by Huntzicker and Westrum (1971) showed a very sharp transition at 30.44 K which was characteristic of a first order change in contrast to the second order lambda-type anomaly found by Jones et al (1952); (see Chap. 3). Figure 5.8 shows the heat capacities of thorium dioxide, uranium dioxide and neptunium dioxide. The anomalies for UO_2 and NpO_2 are related to the magnetic behavior of these substances (Osborne and Westrum, 1953). The heat capacity of thoria presumably arises entirely from the lattice vibrations, since ThO_2 is diamagnetic (Trzebiatowski and Selwood, 1950; see Chap. 3) and therefore does not provide a magnetic contribution to the heat capacity as do both UO_2 and NpO_2 .

The calculated values of the thermodynamic functions at 50 degree intervals (as well as for 298 K) are given in Table 5.6; the data were taken from Osborne and Westrum (1953) and converted to SI units. The standard entropy at 298 K, $S_{298} = 65.2 \text{ J/mol} \cdot \text{K}$.

(b) High-Temperature Enthalpy Measurements

The available enthalpy data for ThO_2 are extensive, ranging in temperature from 323 to 3400 K. Table 5.7, which is adapted from Fink (1982), provides information on these data. One set of these data were specific heat measurements by Jaeger and Veenstra (1934), reported by them "average values". Fink (1982) lists their data as enthalpy, presumably obtained by integrating the equation reported by Jaeger and Veenstra as a fit of their experimental data.

Godfrey et al (1966) did not include the Jaeger and Veenstra data in their analysis because they judged this older set of data to be of lower accuracy. They fit the rest of the enthalpy measurements that were available to them by the equation (converted to J/mol)

$$H_T^0 - H_{298}^0 = 69.30 T + 4.6696 \times 10^{-3} T^2 + 9.1858 \times 10^5 T^{-1} - 24159 \quad \text{Eq. (5.26)}$$

with an average error of 0.58 percent.

Figure 5.8. Low Temperature Heat Capacities of ThO_2 , UO_2 , and NpO_2 (Osborne and Westrum, 1953).

TABLE 5.6—THERMODYNAMIC FUNCTIONS OF ThO_2 , 10 K–300 K*

Temperature (kelvin)	Heat Capacity (C_p^0 , J/mol · K)	Enthalpy ($H_T^0 - H_0^0$, kJ/mol)	Entropy (S^0 , J/mol · K)	Free Energy Function ($-(G^0 - H_0^0)/T$ (J/mol · K)
10	0.134	0.0003	0.046	0.013
50	10.167	0.1615	4.468	1.238
100	26.133	1.077	16.518	5.753
150	39.94	2.741	29.828	11.556
200	50.08	5.006	42.790	17.757
250	57.07	7.695	54.760	23.98
300	61.88	10.68	65.618	29.85
298.16	61.76	10.56 ± 0.01	65.24 ± 0.08	29.82 ± 0.04

*From Osborne and Westrum (1953)

TABLE 5.7—MEASUREMENTS OF THE ENTHALPY OF ThO_2 *

Experimenter	Temperature Range (kelvin)	Number of Data Points	Deviation from Fit† (%)
Jaeger and Veenstra (1934)†	671-1666	12	1.25
Southard (1941)	905-1594	6	0.46
Southard (1941)	523-1789	16	1.35
Hoch and Johnston (1961)	1458-2758	9	0.87
Victor and Douglas (1961)	323-1174	27	1.21
Springer et al (1967)	374-2261	17	1.76
Fischer et al (1981)	2415-3400	13	0.62

*From Fink (1982)

†Fischer et al (1981)

‡These data were originally specific heat measurements

Differentiation of Eq. (5.26) gives the following heat capacity equation:

$$C_p(\text{ThO}_2)_s = 69.30 + 9.339 \times 10^{-3} T - 9.186 \times 10^5 T^{-2} \text{ J/mol} \cdot \text{K} . \quad \text{Eq. (5.27)}$$

This equation was recommended by Rand (1975), who pointed out that the calculated value of the heat capacity at 298 K, 61.75 J/mol · K, agrees exactly with that determined experimentally at low temperatures by Osborne and Westrum (1953).

The later high-temperature enthalpy measurements of Fischer et al (1981) disclosed a feature unpredicted by the Godfrey et al (1966) fit of the older data: a discontinuity in the slope of the enthalpy-temperature curve at 2950 K. Fischer et al (1981) pointed out that this discontinuity is much more marked than that judged to exist for UO_2 at 2670 K. They also suggested this discontinuity to be the predicted (Dworkin and Bredig, 1968) diffuse transition for ThO_2 .

Fischer et al (1981) compared their measurements with the older data on ThO_2 , most of which was at lower temperatures, and found reasonable agreement in the overlap region. The combined data were fit to a mathematical model similar to that used by Fink et al (1981) for UO_2 with, however, the electronic contribution third term omitted. The 2950 K transition temperature for ThO_2 was determined by a statistical analysis of the data. A plot of the data comparing the data fit with the entire set of

Figure 5.9. Enthalpy of Thoria.

enthalpy measurements on ThO_2 is shown in Fig. 5.9. Note the discontinuity at 2950 K. The following equations were used in the fit: For $298.15 \text{ K} \leq T \leq 2950 \text{ K}$,

$$H_T^0 - H_0^0 = C_1 \theta [(e^{\theta/T} - 1)^{-1} - (e^{\theta/T_0} - 1)^{-1}] + C_2 [T^2 - T_0^2] \quad \text{Eq. (5.28)}$$

where

$$\begin{aligned} T_0 &= 298.15 \text{ K} \\ C_1 &= 68.654 \text{ J/mol} \cdot \text{K} \\ C_2 &= 4.8174 \times 10^{-3} \text{ J/mol} \cdot \text{K}^2 \\ \theta &= 408.14 \text{ K;} \end{aligned}$$

for $2950 \text{ K} \leq T \leq 3400 \text{ K}$,

$$H_T^0 - H_{298.15}^0 = 142.33 T - 192920 \quad \text{Eq. (5.29)}$$

In Eqs. (5.28) and (5.29), enthalpy is in J/mol.

The heat capacity of ThO_2 , from 298.15 K to the transition temperature of 2950 K, can therefore be represented by a two-term equation obtained by differentiation of Eq. (5.28). The heat capacity equation is

$$C_p = \frac{C_1 \theta^2 e^{\theta/T}}{T^2 (e^{\theta/T} - 1)^2} + 2C_2 T \quad \text{Eq. (5.30)}$$

where C_1 , C_2 and θ are as defined above. The heat capacity of ThO_2 from 2950 K to 3400 K (the limit of enthalpy measurements) is constant and equal to $142.3 \text{ J/mol} \cdot \text{K}$.

It thus appears that both UO_2 and ThO_2 show transitions, i.e., discontinuities in the enthalpy-temperature curves, and therefore anomalous increases in heat capacity at the transition temperature. The nature of the transition, represented by the discontinuity, is not clear, however. If the transition represents a true disorder of the oxygen sublattice beyond the formation of anion Frenkel defects, this disordering process should affect transport properties, such as oxygen ion diffusion and ionic conductivity. Unfortunately, such data are not available at these high temperatures (see Chap. 6).

The transition temperatures for urania and thoria are 2670 and 2950 K, equivalent to 0.86 and $0.81 T_m$, respectively. Thus, whatever the process responsible for the change in the two oxides occurs at homologous temperatures. However, there are considerable quantitative differences between urania and thoria. Above the transition temperature, the heat capacities are constant. For urania, this constant value is approximately the heat capacity reached at the transition point; evaluation of the lower-temperature equation at 2670 K gives a result of $166.4 \text{ J/(mol} \cdot \text{K)}$, and the value prevailing above that point is $167.0 \text{ J/(mol} \cdot \text{K)}$. For thorium, however, the equations indicate a very considerable discontinuity; evaluation of the lower-temperature equation at 2950 K gives a value of $96.97 \text{ J/(mol} \cdot \text{K)}$. A sudden increase at this point to $142.3 \text{ J/(mol} \cdot \text{K)}$ represents a 47 percent jump.

The calculated thermodynamic functions ($H_T^0 - H_{298}^0$, C_p^0 , S_T^0 , and $-(G_T^0 - H_{298}^0)/T$) for both ThO_2 and UO_2 are compared in Table 5.8. The transition temperatures for urania and thoria are indicated by the α , β symbols, but this nomenclature does not imply the existence of distinct and separate phases below and above these temperatures.

TABLE 5.8—COMPARISON OF THERMODYNAMIC FUNCTIONS
FOR ThO₂ AND UO₂

Temperature (kelvin)	Heat Capacity C _p ⁰ , J/mol · K		Entropy S ⁰ , J/mol · K		Free Energy Function		Enthalpy H _T ⁰ -H ₂₉₈ ⁰ , kJ/mol	
					- (G _T ⁰ -H ₂₉₈ ⁰)/T J/mol · K			
	ThO ₂	UO ₂	ThO ₂	UO ₂	ThO ₂	UO ₂	ThO ₂	UO ₂
298.15	61.74	63.60	65.2	77.0	65.2	77.0	0	0
300	61.87	63.79	65.6	77.4	65.2	77.0	0.114	0.118
400	66.85	71.30	84.1	96.9	67.7	79.6	6.58	6.91
500	69.78	75.48	99.3	113.2	72.5	84.7	13.41	14.27
600	71.85	78.20	112.3	127.2	78.1	90.6	20.50	21.96
700	73.49	80.17	123.4	139.4	83.8	96.8	27.8	29.88
800	74.89	81.73	133.3	150.3	89.4	102.8	35.19	37.98
900	76.16	83.05	142.2	160.0	94.7	108.6	42.75	46.22
1000	77.34	84.22	150.3	168.8	99.9	114.7	50.42	54.59
1100	78.47	85.29	157.7	176.8	104.8	119.5	58.21	63.06
1200	79.56	86.29	164.6	184.3	109.5	124.6	66.12	71.64
1300	80.61	87.25	171.0	191.2	114.0	129.4	74.13	80.32
1400	81.66	88.2	177.0	197.7	118.3	134.1	82.24	89.09
1500	82.68	89.21	182.7	203.9	122.4	138.5	90.46	97.96
1600	83.70	90.31	188.1	209.6	126.3	142.8	98.78	106.9
1700	84.70	91.64	193.2	215.2	130.1	146.9	107.2	116.0
1800	85.70	93.33	198.0	220.4	133.7	150.8	115.7	125.3
1900	86.70	95.59	202.7	225.5	137.3	154.6	124.3	134.7
2000	87.69	98.68	207.2	230.5	140.6	158.3	133.1	144.4
2100	88.67	102.9	211.5	235.4	143.9	161.9	141.9	154.5
2200	89.65	108.5	215.6	240.3	147.1	165.3	150.8	165.0
2300	90.63	116.0	219.6	245.3	150.1	168.7	159.8	176.3
2400	91.61	125.8	223.5	250.4	153.1	172.0	168.9	188.3
2500	92.59	138.1	227.3	255.8	156.0	175.2	178.1	201.5
2600	93.56	153.6	230.9	261.5	158.8	178.4	187.4	216.1
*2670 (α)	94.25	166.4	233.4	265.8	160.7	180.7	194.0	227.2
*2670 (β)	94.25	167.0	233.4	265.9	160.7	180.7	194.0	227.7
2700	94.54	167.0	234.5	267.8	161.5	181.6	196.8	232.7
2800	95.51	167.0	237.9	273.9	164.2	184.8	206.3	249.4
2900	96.48	167.0	241.3	279.7	166.8	188.0	215.9	266.1
2950 (α)	96.97	167.0	242.9	282.6	168.1	189.6	220.8	274.4
2950 (β)	142.3	167.0	245.0	282.6	168.1	189.6	227.0	274.4
3000	142.3	167.0	247.4	285.4	169.4	191.1	234.1	282.8
3100	142.3	167.0	252.1	290.9	172.0	194.3	248.3	299.4
3120	142.3	167.0	253.0	291.9	172.5	194.9	251.2	302.8
3200	142.3		256.6		174.6		262.5	
3300	142.3		261.0		177.1		276.8	
3400	142.3		265.2		179.6		291.0	

*Transition temperature for UO₂†Transition temperature for ThO₂‡UO₂ Melting temperature

5.5.3 Enthalpies and Heat Capacities of $\text{ThO}_2\text{-UO}_2$ Solid Solutions

The Neumann-Kopp rule has been invoked to estimate heat capacities of solid solutions from values for the end members. For application to the $\text{ThO}_2\text{-UO}_2$ system, the rule would suggest that C_p for $\text{Th}_{1-y}\text{U}_y\text{O}_2 = (1-y)C_p$ for $\text{ThO}_2 + yC_p$ for UO_2 . However, the rule applies to a binary compound formed from the elements and may not apply to a binary solid solution formed from two compounds. Nevertheless, this *Vegard* Law type of approximation (see Chap. 4) appears to be confirmed by experimental data, as described below.

High-temperature enthalpy measurements were recently reported by Fischer et al (1983) for three $\text{ThO}_2\text{-UO}_2$ solid solutions. Discontinuities in the slopes of the enthalpy-temperature curves were also found: at 2900 K for $\text{Th}_{0.7}\text{U}_{0.3}\text{O}_2$, at 2950 K for $\text{Th}_{0.85}\text{U}_{0.15}\text{O}_2$, and at 2850 K for $\text{Th}_{0.92}\text{U}_{0.08}\text{O}_2$ (see Figs. 5.10, 5.11, and 5.12).

In Figs. 5.10 and 5.11 for $\text{Th}_{0.7}\text{U}_{0.3}\text{O}_2$ and $\text{Th}_{0.85}\text{U}_{0.15}\text{O}_2$, respectively, the lines shown are mole averages of the enthalpies of UO_2 and ThO_2 calculated from the integrated form of Eq. (5.25) for UO_2 and Eq. (5.28) for ThO_2 up to the transition temperatures. As is seen, the experimental data are in excellent agreement with the mole average plots. The data follow a linear equation above the transition temperature as shown from the least-squares fit of the experimental data.

The case of the $\text{Th}_{0.92}\text{U}_{0.08}\text{O}_2$ composition is different. The experimental data below the discontinuity at about 2850 K (see Fig. 5.12) fall unexpectedly below the ThO_2 data. Thus, a mole average enthalpy equation is not possible for this composition. However, as in the case of ThO_2 , a nonlinear least-squares fit was applied to the data below the transition at 2850 K and a linear least-squares fit above the transition. The equation applicable below the transition temperature (T_t) was of the same form as that used for ThO_2 by Fischer et al (1981). The data were fit for $298.15 \text{ K} \leq T \leq 2850 \text{ K}$,

$$H_T - H_{298.15} = C_1 \theta (e^{\theta/T} - 1)^{-1} - (e^{\theta/298.15} - 1)^{-1} \\ + C_2 [T^2 - (298.15)^2] \quad \text{Eq. (5.31)}$$

where

$$C_1 = 62.072 \text{ J/mol} \cdot \text{K} \\ C_2 = 6.4546 \times 10^{-3} \text{ J/mol} \cdot \text{K}^2 \\ \theta = 268.87 \text{ K};$$

Figure 5.10. Fit of Enthalpy Data to Equations for $\text{Th}_{0.70}\text{U}_{0.30}\text{O}_2$.

for $2850 \text{ K} \leq T \leq 3300 \text{ K}$,

$$H_T - H_{298.15} = 128.11 T - 155.71 \quad \text{Eq. (5.32)}$$

Figure 5.12 shows the data for this composition, the fit of the two equations, and the indicated transition at 2850 K.

The discontinuities for these solid solution compositions as well as for urania and thoria occur at a nearly constant fraction of the melting points, i.e., the transition temperature (T_r) is about 0.8 T_m (see Table 5.9).

Figure 5.11. Fit of Enthalpy Data to Equation for $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_2$.

Figure 5.12. Data Fit for Enthalpy of $\text{Th}_{0.92}\text{U}_{0.08}\text{O}_2$.

Heat capacities for the $(\text{Th,U})\text{O}_2$ compositions were calculated from mole averages of the heat capacities of ThO_2 and UO_2 , where appropriate, and from differentiation of the equations used to fit the enthalpy data where mole averages did not apply, as in the case of the $(\text{Th}_{0.92}\text{U}_{0.08})\text{O}_2$ composition. These calculated heat capacities and the heat capacities of ThO_2 and UO_2 are shown in Fig. 5.13. The heat capacity of $(\text{Th}_{0.92}\text{U}_{0.08})\text{O}_2$ is not shown below 2300 K because experimental enthalpy data are not available below this temperature. Although the enthalpy data for $(\text{Th}_{0.92}\text{U}_{0.08})\text{O}_2$ fall slightly below that of ThO_2 , the heat capacity for this composition, which was calculated from the fit to the enthalpy data, lies between the heat capacities for $(\text{Th}_{0.85}\text{U}_{0.15})\text{O}_2$ and ThO_2 as expected.

TABLE 5.9—TRANSITION TEMPERATURE (T_r), MELTING TEMPERATURE (T_m) AND T_r/T_m FOR ThO_2 , $\text{ThO}_2\text{-UO}_2$, AND UO_2

Oxide	Melting Point (T_m , kelvin)	Phase Transition (T_r , kelvin)	T_r/T_m
UO_2	3120	2670	0.86
$(\text{Th}_{0.70}\text{U}_{0.30})\text{O}_2$	3460*	2900	0.84
$(\text{Th}_{0.85}\text{U}_{0.15})\text{O}_2$	3550*	2950	0.83
$(\text{Th}_{0.92}\text{U}_{0.08})\text{O}_2$	3590*	2850	0.79
ThO_2	3640	2950	0.81

*Calculated solidus values on the basis of ideal solution behavior (see Chap. 4).

Figure 5.13. Heat Capacities of ThO₂, UO₂, and Intermediate Compositions.

Thus, the assumption that the heat capacities of the thorium-uranium solid solutions vary linearly with molar composition appears to be a reasonable one.

5.5.4 Heat Capacity at Constant Volume

Although heat capacity is generally measured at constant pressure (C_p), calculations are sometimes given in terms of the heat capacity at constant volume (C_v). These two heat capacities are related by the thermodynamic expression

$$C_p - C_v = \frac{\alpha^2 VT}{\beta_T} \quad \text{Eq. (5.33)}$$

where

- α = the instantaneous volume thermal expansion coefficient
- V = the molar volume
- T = the kelvin temperature
- β_T = the isothermal compressibility.

Thus, heat capacity at constant volume can be estimated, if the other quantities in Eq. (5.33) are known. This estimation is made for both ThO_2 and UO_2 as follows.

The adiabatic compressibility (β_s) can be calculated from the relation

$$\beta_s = \frac{3(1 - 2\sigma)}{E_s} \quad \text{Eq. (5.34)}$$

where σ = Poisson's ratio, generally constant with temperature, and E_s = Young's modulus. Since the heat capacities are related to the compressibilities by the expression,

$$\frac{C_p}{C_v} = \frac{\beta_T}{\beta_s}, \quad \text{Eq. (5.35)}$$

β_T can be eliminated from Eqs. (5.33) and (5.35), giving C_v in terms of experimentally determined quantities,

$$C_v = \frac{C_p}{1 + \frac{\alpha^2 VT}{C_p \beta_s}} \quad \text{Eq. (5.36)}$$

The adiabatic Young's modulus of ThO_2 (E_s) was measured as a function of temperature by Wachtman et al (1961) from 77 to 850 K and by Spinner et al (1963b) from 298 to 1578 K, and as a function of porosity by Spinner et al (1963a) for porosities from 3.7 to 39.4 percent. As is discussed in greater detail in Chap. 7, the available data are corrected to 100 percent theoretical density and can be expressed by the relationship

$$E_s (\text{for } \text{ThO}_2) = 249.1$$

$$\times [1.023 - 1.405 \times 10^{-4} T \exp(-181/T)] \quad \text{Eq. (5.37)}$$

for the temperature range 298 to 1300 K and for E_s in GPa. (Above 1300 K the rate of decrease in the modulus is not linear and becomes more rapid, presumably as a result of grain boundary slip.)

Fink et al (1981), in their compilation, cite the following equation, which was taken from Hagrman and Reymann (1979), to be applicable over the temperature range $0 < T < 1600$ K:

$$E_s \text{ (for } \text{UO}_2\text{)} = 226 [1 - 1.131 \times 10^{-4} (T - 273.15)] \\ \times [1 - 2.62 (1 - D)] \quad \text{Eq. (5.38)}$$

where E_s is in GPa and D is the fraction of theoretical density. Olsen (1976) had recommended the identical equation expressed in terms of degrees Celsius.

The value for Poisson's ratio for ThO_2 used in the calculation (0.285) was obtained by Wolfe and Kaufman (1967) from an extrapolation to zero percent porosity of the data of Spinner et al (1963a) for polycrystalline thorium. This value is in excellent agreement with the value of 0.284 calculated by Wolfe and Kaufman from measurements of elastic constants of single crystal ThO_2 reported by Macedo et al (1964). The value for Poisson's ratio for UO_2 recommended in Hagrman and Reymann (1979) is 0.316.

Compressibilities were calculated in the case of ThO_2 for temperatures from 300 to 1300 K using Eqs. (5.37) and (5.34) and in the case of UO_2 for temperatures from 300 to 1600 K using Eqs. (5.38) and (5.34). These data are shown in Table 5.10. Heat capacities at constant volume (C_v) for both ThO_2 and UO_2 calculated using Eq. (5.25) are tabulated along with C_p values in Table 5.11. The difference in the two heat capacities is not negligible, particularly at the higher temperatures; the differences are greater for UO_2 than for ThO_2 .

Although the empirical equation for C_p for ThO_2 (Eq. (5.30)) and the thermodynamic expression for C_p (Eq. (5.33)) have the same form, they are not equivalent. The C_v values calculated from the empirical equation are lower than those calculated from the thermodynamic formula. Similarly, C_2 calculated from $\alpha^2 V / 2\beta_T$, i.e., equating the second term of both equations, is variable and differs from the value of C_2 in the empirical equation.

5.6 HEAT AND FREE ENERGY OF FORMATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

The value recommended by Rand (1975) for the heat of formation of ThO_2 , ΔH_f at 298 K, is -1226.9 ± 1.5 kJ/mol. This value was determined by Huber et al (1952) from measurements of the heat of combustion of thorium. Table 5.12 presents calculated heats and free energies of formation of ThO_2 to 3000 K; the transition temperature for thorium is indicated by the α, β symbols.

TABLE 5.10—CALCULATED COMPRESSIBILITIES FOR ThO₂ AND UO₂

Temperature (kelvin)	Adiabatic Compressibility ($\beta_T \times 10^{-12}, \text{m}^3/\text{J}$)		Isothermal Compressibility ($\beta_S \times 10^{-12}, \text{m}^3/\text{J}$)	
	ThO ₂	UO ₂	ThO ₂	UO ₂
298.15	5.202	4.899	5.283	4.953
400	5.270	4.956	5.376	5.000
500	5.341	5.014	5.474	5.050
600	5.416	5.073	5.578	5.100
700	5.494	5.133	5.687	5.303
800	5.574	5.195	5.801	5.409
900	5.658	5.258	5.920	5.523
1000	5.744	5.323	6.043	5.645
1100	5.833	5.389	6.171	5.777
1200	5.926	5.457	6.304	5.919
1300	6.021	5.527	6.442	6.071
1400		5.599		6.233
1500		5.672		6.407
1600		5.748		6.591

Note: $10^{-6}(\text{MPa})^{-1}$ is equivalent to $10^{-12} \text{m}^3/\text{J}$

These quantities were calculated as follows:

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT \quad \text{Eq. (5.39)}$$

$$\Delta G_T = \Delta H_T - T\Delta S_{298} - T \int_{298}^T \frac{\Delta C_p}{T} dT \quad \text{Eq. (5.40)}$$

where

$$\Delta C_p = C_p(\text{ThO}_2) - \Sigma[C_p(\text{O}_2) + C_p(\text{Th})] \quad \text{Eq. (5.41)}$$

$$\Delta S_{298} = S_{298}(\text{ThO}_2) - \Sigma[S_{298}(\text{O}_2) + S_{298}(\text{Th})] \quad \text{Eq. (5.42)}$$

The values used in the calculation were (1) the recommended ΔH_f value at 298 K; (2) the thermodynamic functions from Table 5.9; and (3) the C_p^0 and S_T^0 values for diatomic oxygen and thorium, respectively, from the compilations of Stull and Sinke (1956) and Rand (1975). The calculated

TABLE 5.11—MOLAR HEAT CAPACITIES OF ThO₂ AND UO₂

Temperature (kelvin)	Heat Capacity at Constant Pressure, C _p (J/mol · K)	Heat Capacity at Constant Volume, C _v (J/mol · K)	C _p -C _v (J/mol · K)
<u>ThO₂</u>			
298.15	61.74	60.79	0.95
400	66.85	65.53	1.32
500	69.78	68.09	1.69
600	71.85	69.76	2.09
700	73.49	70.98	2.51
800	74.89	71.96	2.93
900	76.16	72.79	3.37
1000	77.34	73.51	3.83
1100	78.47	74.17	4.30
1200	79.56	74.78	4.78
1300	80.61	75.35	5.26
<u>UO₂</u>			
298.15	63.60	62.90	0.70
400	71.30	70.23	1.07
500	75.48	73.99	1.49
600	78.20	76.20	2.00
700	80.17	77.57	2.58
800	81.73	78.47	3.24
900	83.05	79.07	3.98
1000	84.22	79.41	4.81
1100	85.29	79.56	5.73
1200	86.29	79.56	6.73
1300	87.25	79.44	7.81
1400	88.21	79.23	8.98
1500	89.21	78.97	10.24
1600	90.31	78.75	11.56

values differ from those tabulated by Rand and used by Ackermann and Tetenbaum (1980) because the calculation incorporates the latest high-temperature enthalpy data for ThO₂.

The derived expression for the free energy of formation for ThO₂ is $\Delta G_f = -1217.6 + 0.1785 T$ kJ/mol. This compares with the expression for UO₂ obtained from the tabulation given in Ackermann et al (1980), $\Delta G_f(\text{UO}_2) = -1081.7 + 0.1707 T$ kJ/mol.

Although the heats of formation of ThO₂ and UO₂ show discontinuities at the respective transition temperatures of 2950 K and 2670 K, the free energies of formation of ThO₂ and UO₂ are continuous through the transitions, suggesting that the transitions are first order.

TABLE 5.12—HEAT AND FREE ENERGY OF FORMATION OF ThO₂

Temperature (kelvin)	Heat of Formation ($-\Delta H_f$, kJ/mol)	Free Energy of Formation ($-\Delta G_f$, kJ/mol)*
298.15	1226.9	1169.3
300	1226.9	1168.9
400	1226.2	1149.7
500	1225.3	1130.7
600	1224.3	1111.9
700	1223.3	1093.2
800	1222.4	1074.7
900	1221.4	1056.3
1000	1220.5	1037.9
1100	1219.6	1019.7
1200	1218.7	1001.6
1300	1217.8	983.6
1400	1216.9	965.6
1500	1216.0	947.6
1600	1215.1	929.8
1700	1214.0	912.0
1800	1212.9	894.3
1900	1211.8	876.6
2000	1210.7	859.0
2100	1210.2	841.4
2200	1209.6	823.8
2300	1209.1	806.3
2400	1208.4	788.8
2500	1207.7	771.3
2600	1206.9	753.9
2700	1206.0	736.5
2800	1205.0	719.1
2900	1204.0	701.8
2950 (α)	1203.5	693.1
2950 (β)	1197.3	693.1
3000	1194.5	684.6

* $\Delta G_f = -1217.6 \pm 1.7 + (0.1785 \pm 0.0009)T$ kJ/mol

On the assumption that the ThO₂-UO₂ solid solution system is ideal, the free energies for compositions Th_{1-y}U_yO₂ can be estimated as follows:

$$\Delta G_f(\text{Solution}) = y(\Delta G_f \text{ for UO}_2) + (1 - y)(\Delta G_f \text{ for ThO}_2) + RT[y \ln y + (1 - y) \ln (1 - y)] \quad \text{Eq. (5.43)}$$

where the third term is the free energy of mixing, ΔG_m .

5.7 MISCELLANEOUS THERMOPHYSICAL PROPERTIES

5.7.1 Debye Temperature

The Debye temperature is a parameter that indicates the frequency distribution of the lattice vibrations of a crystalline solid. It is defined as $\theta_D = h\nu_{\max}/k$, where h and k are the Planck and Boltzmann constants, and $\nu_{\max}$ is the maximum frequency of the elastic vibrations of the solid.

Villis (1963b) reported a value of $\theta_D = 393$ K for ThO₂ from his neutron diffraction measurements, but suggested that a better interpretation of the neutron diffraction data for ThO₂ could be made in the same fashion as had been done by him for UO₂. In the treatment for UO₂ two models were used, one a Debye model representing the vibration of the thorium atoms (acoustic mode) to obtain θ_D , and the other an Einstein model representing the vibration of the lighter oxygen atoms (optical mode) to obtain θ_E , the average Einstein characteristic temperature.

Ali and Nagels (1967) followed the procedure used by Willis and calculated θ_D for ThO₂ and two values of θ_E for ThO₂, one on the assumption that the oxygen atoms vibrate isotropically about their normal lattice positions, and the other on the assumption that the oxygen atoms relax along $\langle 111 \rangle$ directions. The values calculated by Ali and Nagels are $\theta_D = 268$ K, $\theta_E = 451$ K (without relaxation) and 508 K (with relaxation).

The Debye temperature can also be determined from low temperature heat capacity data. The heat capacity at constant volume, C_v , at very low temperatures is given by the T^3 law,

$$C_v = \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D} \right)^3 = 1944 \left(\frac{T}{\theta_D} \right)^3 \text{ J/mol} \cdot \text{K} , \quad \text{Eq. (5.44)}$$

where R is the gas constant.

Thus to obtain θ_D , the straight-line fit to a plot of C_v/T^3 or C_p/T^3 as a function of T^2 is extrapolated to absolute zero. Two such estimates have been reported from the Osborne and Westrum (1953) low-temperature heat capacity data discussed in Sect. 5.5.2(a); these were 782 ± 7 K and 259 K reported, respectively, by Wachtman et al (1961) and by Ali and Nagels (1967). The first value seems to be high as judged from the plot shown in Fig. 5.14 from which a value of 244 ± 3 K is calculated. Although the Ali and Nagels calculation agrees with that obtained from the plot in Fig. 5.14, their "Figure 1b" appears to be in error.

Ali and Nagels (1967) reported another estimate of the Debye temperature from data on the elastic constants of single crystal ThO₂ at 298 K

Figure 5.14. Calculation of Debye Temperature from Plot of C_p/T^3 Versus T^2 .

reported by Macedo et al (1964). The definition of the Debye temperature from the elastic constants was given by Ali and Nagels as

$$\theta_D = \frac{h}{k} \left(\frac{1}{4\pi} \frac{n}{V} \right)^{1/3} c_m \quad \text{Eq. (5.45)}$$

where n is the number of degrees of freedom for lattice vibrations per unit cell, V is the volume per unit cell, and c_m is the mean sound velocity. Ali and Nagel suggest that the calculated value of 290 K is a lower limit because room temperature elastic moduli were used.

A summary of the various estimates that have been made of the Debye and Einstein temperatures is given in Table 5.13. These estimates range from about 244 K to about 780 K for the Debye temperature. The only

TABLE 5.13—ESTIMATES OF DEBYE AND EINSTEIN TEMPERATURES FOR ThO₂

Source of Data	Debye Temp. (θ_D , kelvin)	Einstein Temp. (θ_E , kelvin)	Ref.
Neutron diffraction (Willis, 1963b)	393	—	Willis (1963b)
Neutron diffraction (Willis, 1963b)	268	451 508	Ali and Nagels (1967)
Low-temperature heat capacity (Osborne and Westrum, 1953)	782	—	Wachtman et al (1961)
Low-temperature heat capacity (Osborne and Westrum, 1953)	259	—	Ali and Nagels (1967)
Low-temperature heat capacity (Osborne and Westrum, 1953)	244 ± 3	—	Fig. 5.14
Elastic constants (Macedo et al, 1964)	290	—	Ali and Nagels (1967)

estimates for the Einstein temperature (451 K to 508 K) are considerably higher than the empirical value (408.14 K) used in the fit of the experimental enthalpy data discussed in Sect. 5.5.2.

5.7.2 Grüneisen Parameter

The Grüneisen parameter, γ , which is an average measure of lattice anharmonicity, is related to the volume thermal expansion coefficient, the thermal expansivity α , the volume V , the adiabatic compressibility β_s , and the heat capacity at constant pressure C_p by the expression

$$\gamma = \frac{\alpha V}{\beta_s C_p} \quad \text{Eq. (5.46)}$$

Evaluation of the Grüneisen parameters for both ThO₂ and UO₂ as functions of temperature is shown in Table 5.14. The Grüneisen parameter varies somewhat with temperature for both oxides, but in opposite directions. The average value for both oxides is 1.84, suggesting little difference in anharmonicity in the two lattices. This conclusion is at variance with results of both neutron diffraction measurements (see Chap. 3) and

TABLE 5.14—GRÜNEISEN PARAMETER FOR THORIA AND URANIA

Temperature (kelvin)	Volume Thermal Expansion Coefficient, α ($\text{K}^{-1} \times 10^{-6}$)	Molar Volume V ($\text{m}^3/\text{mol} \times 10^{-6}$)	Adiabatic Compressibility, β_s ($\text{m}^3/\text{J} \times 10^{-12}$)	Molar Heat Capacity, C_p ($\text{J}/\text{mol} \cdot \text{K}$)	Grüneisen Parameter, γ , Dimensionless
<u>ThO₂</u>					
298.15	25.3	26.40	5.202	61.74	2.08
400	25.9	26.47	5.270	66.85	1.95
500	26.5	26.54	5.341	69.78	1.88
600	27.0	26.61	5.416	71.85	1.85
700	27.6	26.69	5.494	73.49	1.83
800	28.2	26.76	5.574	74.89	1.81
900	28.8	26.84	5.658	76.16	1.79
1000	29.3	26.92	5.744	77.34	1.78
1100	29.9	27.00	5.833	78.47	1.76
1200	30.5	27.08	5.926	79.56	1.75
1300	31.0	27.16	6.021	80.61	1.74

TABLE 5.14—GRÜNEISEN PARAMETER FOR THORIA AND URANIA—Continued

Temperature (kelvin)	Volume Thermal Expansion Coefficient, α ($\text{K}^{-1} \times 10^{-6}$)	Molar Volume V ($\text{m}^3/\text{mol} \times 10^{-6}$)	Adiabatic Compressibility, β_s ($\text{m}^3/\text{J} \times 10^{-12}$)	Molar Heat Capacity, C_p ($\text{J/mol} \cdot \text{K}$)	Grüneisen Parameter, γ , Dimensionless
<u>UO_2</u>					
298.15	21.7	24.62	4.900	63.60	1.72
400	23.3	24.67	4.956	71.30	1.63
500	24.9	24.73	5.014	75.48	1.62
600	26.4	24.80	5.073	78.20	1.65
700	28.0	24.86	5.133	80.17	1.69
800	29.6	24.94	5.195	81.73	1.74
900	31.3	25.01	5.258	83.05	1.79
1000	32.9	25.09	5.323	84.22	1.84
1100	34.6	25.18	5.389	85.29	1.89
1200	36.2	25.27	5.457	86.29	1.94
1300	37.9	25.36	5.527	87.25	1.99
1400	39.6	25.46	5.599	88.21	2.04
1500	41.3	25.56	5.672	89.21	2.09
1600	43.1	25.67	5.748	90.31	2.13

elastic constant measurements on single crystals (see Chap. 7) which show a greater degree of anharmonicity for the UO_2 lattice. Momin and Karkhanavala (1978) also calculated Grüneisen parameters for ThO_2 and UO_2 , and reported values of 1.5 ± 0.1 and 1.9 ± 0.1 for ThO_2 and UO_2 , respectively, in agreement with the conclusion that UO_2 is more anharmonic than ThO_2 . However, it should be noted that Momin and Karkhanavala used the Wachtman et al (1961) expression for the adiabatic Young's modulus for ThO_2 uncorrected for porosity. Moreover, they extended the applicability of the Young's modulus equation to 2300 K, beyond its valid range. It would appear, therefore, that the Grüneisen parameter is not a quantitative index with which to judge relative anharmonicities of ThO_2 and UO_2 .

5.8 THERMODYNAMIC PROPERTIES OF HYPOSTOICHIOMETRIC THORIA

The thermodynamic properties of the thorium-oxygen system at high temperatures were investigated in detail by Ackermann and coworkers (see Ackermann et al, 1963; Ackermann and Rauh, 1973; and Ackermann and Tetenbaum, 1980). Those aspects of these studies that were concerned with the thorium-oxygen phase diagram and ThO_2 vapor pressure of nearly stoichiometric ThO_2 were discussed, respectively, in Chap. 4 and in Sect. 5.4.3 above. In this section, the thermodynamic aspects of oxygen-deficient thoria are reviewed.

5.8.1 Oxygen Potential Measurements

As was discussed briefly in Chap. 4, Carniglia et al (1971) reported that the value of x in hypostoichiometric ThO_{2-x} varies as $P_{\text{O}_2}^{-1/6}$, for a limited range of compositions ($0 \leq x \leq 0.003$) and temperatures (1673 to 2173 K). Ackermann and Tetenbaum (1980) extended the ranges of composition and temperature, and evaluated oxygen potentials.

The oxygen potential, or the partial molar free energy of oxygen, is defined as

$$\Delta \bar{G}_{\text{O}_2} = RT \ln P_{\text{O}_2} \quad \text{Eq. (5.47)}$$

and is thus readily calculated from the equilibrium oxygen pressure. $\Delta \bar{G}_{\text{O}_2}$ depends on both the temperature and composition, and thus a nonstoichiometric phase shows bivariant behavior.

Ackermann and Tetenbaum (1980) used the following sources of data in making their thermodynamic calculations for the nonstoichiometric ThO_{2-x} phase: (1) the vapor pressure data for the lower phase boundary composition (Ackermann and Rauh, 1973); (2) the vaporization data for the congruently vaporizing composition (Ackermann et al, 1963); and

(3) the moisture content of the $\text{H}_2\text{O}/\text{H}_2$ carrier gas determined from the transpiration experiments reported in Ackermann and Tetenbaum (1980).

The results of the oxygen potential determinations above the bivariant ThO_{2-x} composition for temperatures of 2400 to 2655 K are shown in Fig. 5.15; data for the UO_{2-x} phase (Tetenbaum and Hunt, 1968) are also shown. Note the sharp decrease in oxygen potential for a small change in stoichiometry for the ThO_{2-x} phase. This small extent of nonstoichiometry

— a wide range of oxygen potential at these high temperatures contrasts with the behavior of the UO_{2-x} phase, which has a larger degree of nonstoichiometry for a smaller range of oxygen potential. This difference illustrates the much higher stability of the ThO_{2-x} phase.

Figure 5.16 is a plot of the oxygen potential ($\Delta\bar{G}_{\text{O}_2}$) versus $\log x$ for the various temperatures investigated and for compositions ranging from the congruently vaporizing composition to the lower phase boundary composition. On the assumption of a linear fit of the data, Ackermann and Tetenbaum (1980) estimate the oxygen partial pressure dependency of x in ThO_2 to be approximately proportional to $P_{\text{O}_2}^{-1/4}$ over the temperature range from 2400 to 2655 K. This result contrasts with that obtained by Carniglia et al (1971). The latter set of data implies that the oxygen vacancies are doubly charged, whereas the pressure dependency found by Ackermann and Tetenbaum (1980) suggests that the oxygen vacancies in hypostoichiometric ThO_{2-x} are singly charged.

5.8.2 Free Energy of Formation of ThO_{2-x}

Ackermann and Tetenbaum (1980) also estimated the partial molar enthalpies and partial molar entropies of solution of oxygen in ThO_{2-x} for selected compositions; these estimates are shown in Table 5.15. Using these values and the known standard free energy of formation for stoichiometric ThO_2^* (see Table 5.12) Ackermann and Tetenbaum calculated the standard free energies of formation of hypostoichiometric thoria compositions as a function of composition for the various isotherms investigated. A plot of their results is shown in Fig. 5.17. In Table 5.16 are

the calculated equations for the standard free energies of formation of hypostoichiometric compositions.

Figure 5.17 shows that the standard free energy of formation of hypostoichiometric thoria becomes less negative, i.e., the oxide becomes less stable, with increasing deficiency of oxygen, and the stability of the hypostoichiometric phase decreases with increasing temperature for a fixed composition. It is also seen that, for a fixed O/M ratio and temperature, the free energy of thoria is more negative than that of urania, and therefore the ThO_{2-x} phase is more stable than the UO_{2-x} phase.

The values given in Table 5.12 are slightly different from those used by Ackermann and Tetenbaum, as pointed out in Sect. 5.6.

Figure 5.15. Oxygen Potentials Above ThO_{2-x} Phase (After Ackermann and Tetenbaum, 1980).

5.8.3 High-Temperature Vaporization of ThO_{2-x}

Ackermann and Tetenbaum (1980) also reported the results of the transpiration measurements of the total pressure of thorium-bearing species above the hypostoichiometric ThO_{2-x} phase in the temperature range

Figure 5.16. Oxygen Potential as a Function of Stoichiometric Defect in ThO_{2-x} (After Ackermann and Tetenbaum, 1980).

from 2400 to 2655 K; these data are shown in Fig. 5.18. Also shown are the earlier vapor pressure data of Ackermann et al (1963) obtained from effusion measurements on nearly stoichiometric ThO_2 ; the vapor pressure data of Ackermann and Rauh (1973) for the lower phase boundary composition; and the total pressure of uranium-bearing species above UO_{2-x} at 2600 K from the data of Tetenbaum and Hunt (1970).

The data in Fig. 5.18 show that the total pressure of thorium-bearing species increases considerably when stoichiometric thorium is reduced toward the lower phase boundary. Ackermann and Tetenbaum (1980) attribute this increase in pressure to the increasing contribution of the ThO gaseous species as the degree of hypostoichiometry increases.

TABLE 5.15—PARTIAL MOLAR ENTHALPIES AND ENTROPIES
OF SOLUTION OF OXYGEN IN ThO_{2-x} *

O/Th	$-\Delta \bar{H}_{\text{O}_2}$	$-\Delta \bar{S}_{\text{O}_2}$
	kJ/mol	J/mol · K
1.955	1592 ± 18	317 ± 7
1.960	1598 ± 17	323 ± 7
1.965	1605 ± 15	331 ± 6
1.970	1615 ± 14	341 ± 5
1.975	1623 ± 14	350 ± 6
1.980	1638 ± 15	364 ± 6
1.985	1653 ± 15	379 ± 6
1.990	1676 ± 16	403 ± 6
1.995	1718 ± 25	444 ± 10
1.998	1764 ± 39	494 ± 15

*Ackermann and Tetenbaum (1980)

Ackermann and Tetenbaum (1980) suggest that the difference in the curves for UO_{2-x} and ThO_{2-x} is related to the more complex vaporization process for UO_{2-x} which involves gaseous UO and UO_3 as well as UO_2 . As a result, the congruently vaporizing composition for UO_{2-x} is considerably different from the stoichiometric composition, whereas this is not true for ThO_{2-x} . As a result uranium-bearing species will predominate in the sublimation of solid solutions of $\text{ThO}_2\text{-UO}_2$, a conclusion reached from vaporization data discussed in Sect. 5.4.3 above.

TABLE 5.16—EQUATIONS FOR THE STANDARD FREE
ENERGIES OF FORMATION OF ThO_{2-x} *

O/Th	$\Delta G_f^0 = -A + BT, \text{ kJ/mol}$	
	A	B
2.000	1218	0.1785
1.995	1214	0.1773
1.990	1209	0.1760
1.985	1205	0.1752
1.980	1202	0.1739
1.975	1197	0.1731
1.970	1186	0.1698
1.965	1182	0.1689
1.960	1178	0.1681
1.955	1174	0.1672

*After Ackermann and Tetenbaum (1980). Recalculated using new value of ΔG_f^0 for stoichiometric thorium ($-1217.6 + 0.01785 T$)

Figure 5.17. Free Energies of Formation of Hypostoichiometric ThO_{2-x} Compared With UO_{2-x} (After Ackermann and Tetenbaum, 1980).

5.9 THERMODYNAMICS OF THE $\text{ThO}_2\text{-UO}_2\text{-O}$ SYSTEM

By analogy with ThO_{2-x} and UO_{2-x} , thorium-uranium solid solutions can be expected to become hypostoichiometric ($\text{Th}_{1-y}\text{U}_y\text{O}_{2-x}$) at sufficiently high temperatures and at sufficiently low oxygen pressures; unfortunately, there is no information for this region of the $\text{ThO}_2\text{-UO}_2\text{-O}$ phase diagram. In contrast, the hyperstoichiometric region has been studied extensively. A discussion of the oxidation limits from the phase diagram

Figure 5.18. Total Pressure of Thorium-Bearing Species Above the ThO_{2-x} Phase (Ackermann and Tetenbaum, 1980).

viewpoint (Cohen and Berman, 1966) was presented in Chap. 4. In this section, the thermodynamic aspects of this pseudobinary system are examined.

5.9.1 Oxygen Potentials and Activity Coefficients

Thermodynamic information for single-phase $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ has been obtained in separate studies using a variety of techniques and covering various ranges of temperatures and compositions. In the earlier work of Anderson et al (1954) and of Roberts et al (1958) measurements were made of the oxygen pressures (P_{O_2}) in equilibrium with various ThO_2 - UO_2 solid solutions at various temperatures. It was found that, at a fixed

temperature, higher oxygen pressures were necessary to oxidize the uranium to the same oxidation state. Aronson and Clayton (1960) determined oxygen potentials ($\Delta\bar{G}_{\text{O}_2} = RT \ln P_{\text{O}_2}$) from electromotive force measurements for $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ at 1250 K; high UO_2 concentrations ($0.29 \leq y \leq 0.90$) and high levels of nonstoichiometry ($0.02 \leq x \leq 0.16$) were investigated. Much later, Tanaka et al (1972) reported similar measurements at the same temperature for lower UO_2 contents ($0.048 \leq y \leq 0.295$) and lower levels of nonstoichiometry ($x < 0.029$).

The most recent oxygen potential measurements for $\text{ThO}_2\text{-UO}_2$ are those of Ugajin (1982) and Ugajin et al (1983). In the former work, Ugajin studied compositions of 5, 10, and 20 mole percent UO_2 having oxygen-to-metal (O/M) ratios ranging from 2.0004 to 2.0243; measurements were made at three temperatures (1273, 1373, and 1473 K). In this work the degree of nonstoichiometry, x , in the $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ solid solutions was determined from measured weight changes using a thermobalance under controlled atmosphere conditions set by a combination of CO and CO_2 gases. The oxygen potentials corresponding to the degree of nonstoichiometry were measured with an oxygen sensor made of a solid electrolyte tube of ZrO_2 -8 mole percent Y_2O_3 .

Tanaka et al (1972) compared their oxygen potential measurements with those of Aronson and Clayton (1960) and with similar data on UO_2 and concluded that nonstoichiometry of $\text{ThO}_2\text{-UO}_2$ solid solutions is similar to that of UO_{2+x} . In a review paper Woodley and Adamson (1980) made a similar comparison, which also included data on oxidized urania-plutonia solid solutions; they concluded that the oxygen potentials of thorium-uranium solid solutions are approximately independent of the uranium content and are determined primarily by the uranium valence. Ugajin (1982), on the other hand, concluded from his measurements that the oxygen potentials of $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ are not independent of the uranium content but decrease negatively with decreasing uranium content at a constant valence of uranium. These data are shown in Figs. 5.19 and 5.20 along with the thorium-uranium data of Aronson and Clayton (1960) and Tanaka et al (1972) and the calculated curves from the consensus of UO_{2+x} data given by Perron (1968). Some of the free energy equations reported by Perron in his statistical assessment are listed in Table 5.17.

Figure 5.19 is a comparison of the Ugajin (1982) data of 1273 K with the data of Tanaka et al (1972) and Aronson and Clayton (1960), both at 1250 K, and the calculated UO_{2+x} curve for 1250 K from the Perron consensus. Only the earlier data of Tanaka et al (1972) and Aronson and Clayton (1960) appear to agree with the UO_{2+x} data at the lower uranium valences. The deviations from the UO_{2+x} curve are more apparent for the 1473 K data comparison shown in Fig. 5.20. These results suggest that, unlike the stoichiometric $\text{ThO}_2\text{-UO}_2$ solid solution, the hyperstoichiometric thorium-uranium solutions are not ideal. If they were ideal, the oxygen potentials of the mixed oxide and of urania would be equal for a fixed uranium valence and would, therefore, fall on the same curve.

Figure 5.19. Oxygen Potentials as a Function of Uranium Valence for UO_{2+x} and $Th_{1-y}U_yO_{2+x}$ at 1250–1273 K.

TABLE 5.17—OXYGEN POTENTIALS FOR STOICHIOMETRIC AND HYPERSTOICHIOMETRIC URANIA FOR TEMPERATURE RANGE 873–1873 K*

Oxide Composition	$\Delta\bar{G}_{O_2}$ (kJ/mol)
$UO_{2.0000}$	$-502.5 + 0.1168 T$
$UO_{2.0100}$	$-262.9 + 0.0150 T$
$UO_{2.0250}$	$-260.4 + 0.0267 T$
$UO_{2.0500}$	$-281.4 + 0.0536 T$
$UO_{2.1000}$	$-316.7 + 0.0966 T$
$UO_{2.2000}$	$-309.3 + 0.1265 T$

*From Perron (1968)

Figure 5.20. Oxygen Potentials as a Function of Uranium Valence for UO_{2+x} and $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ at 1473 K.

Ugajin et al (1983) obtained a more complete set of oxygen potential data for the $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2+x}$ solid solution, from which they derived values for the partial molar entropy and for the partial molar enthalpy of solution of oxygen in this composition. Figure 5.21 shows the oxygen potential data at temperatures of 1273, 1373, and 1473 K. Table 5.18 lists the thermodynamic data. The partial molar entropy $\Delta\bar{S}_{\text{O}_2}$ and the partial molar enthalpy $\Delta\bar{H}_{\text{O}_2}$ of solution in the oxide were calculated from the thermodynamic equations:

$$\Delta\bar{S}_{\text{O}_2} = \partial(\Delta\bar{G}_{\text{O}_2})/\partial T \quad \text{Eq. (5.48)}$$

and

$$\Delta\bar{H}_{\text{O}_2} = \Delta\bar{G}_{\text{O}_2} + T\Delta\bar{S}_{\text{O}_2} \quad \text{Eq. (5.49)}$$

TABLE 5.18—PARTIAL MOLAR ENTROPIES AND ENTHALPIES OF SOLUTION OF OXYGEN IN $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2+x}$ *

O/M	Uranium Valence	$-\Delta\bar{S}_{\text{O}_2}$ (J/mol · K)	$-\Delta\bar{H}_{\text{O}_2}$ (kJ/mol)
2.000	4.00	126	557
2.002	4.02	115	416
2.003	4.03	111	381
2.005	4.05	105	346
2.007	4.07	107	336
2.010	4.10	109	328
2.015	4.15	115	323
2.020	4.20	119	318
2.022	4.22	121	318

*Ugajin et al (1983)

Ugajin (1982) treated the hyperstoichiometric $\text{Th}_{1-y}\text{U}_y\text{O}_{2+xy}$ as a pseudobinary solution made up of $(1-y)\text{ThO}_2$ and $y(\text{UO}_{2+x})$ and calculated activity coefficients for UO_{2+x} ; these are shown in Table 5.19. It is seen that the activity coefficients are greater than unity and increase with an increase in the value of x , i.e., the hyperstoichiometric $\text{Th}_{1-y}\text{U}_y\text{O}_{2+xy}$ solid solutions deviate increasingly from ideality as the extent of oxidation increases. Figure 5.20 also shows that the deviation from ideality in ThO_2 - UO_2 solid solutions increases with increase in thorium content. Note from Fig. 5.20 the good agreement of the Ugajin (1983) measurements on UO_2 with the Perron (1968) consensus.

Woodley (1981) made similar activity coefficient calculations from his measurements of oxygen potentials of urania-plutonia and thoria-plutonia solid solutions. The calculated activity coefficients for PuO_{2-x} dissolved in UO_2 or ThO_2 showed that these solid solutions are nearly ideal when

TABLE 5.19—CALCULATED ACTIVITY COEFFICIENTS FOR UO_{2+x} IN $\text{Th}_{0.80}\text{U}_{0.20}\text{O}_{2+0.2x}$ AT 1473 K*

x	2+0.2x	Uranium Valence	Activity Coefficient γ
0.1	2.020	4.20	1.125
0.075	2.015	4.15	1.087
0.050	2.010	4.10	1.049
0.025	2.005	4.05	1.014
0.015	2.003	4.03	1.004
0.010	2.002	4.02	1.000

*From Ugajin (1982)

Figure 5.21. Oxygen Potential as a Function of Uranium Valence for $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2+x}$ at 1273, 1373, and 1473 K (After Ugajin et al. 1983).

stoichiometric but become increasingly nonideal as the plutonium valence decreases. Moreover, thoria-plutonia solid solutions are less ideal than urania-plutonia solutions. The calculated activity coefficients for PuO_{2-x} dissolved in ThO_2 are shown in Table 5.20.

For both nonstoichiometric $\text{ThO}_2\text{-UO}_2$ and $\text{ThO}_2\text{-PuO}_2$ solid solutions, it appears from the work of Ugajin (1982) and Woodley (1981) that the

TABLE 5.20—ACTIVITY COEFFICIENTS FOR PuO_{2-x} DISSOLVED IN ThO_2^*

Pu Valence	$\gamma_{\text{PuO}_{2-x}} (\text{Th}_{0.75}\text{Pu}_{0.25}\text{O}_{2-x})$		
	1000°C	1100°C	1200°C
3.92	1.006	1.006	1.004
3.84	1.055	1.057	1.041
3.76	1.145	1.138	1.102
3.68	1.258	1.242	1.182
3.60	1.410	1.368	1.275

*From Woodley (1981)

deviations from ideality are positive, i.e., the activity coefficients are greater than one. This is seen from the free energy change for the reaction

which may be written as follows:

$$\Delta G_m = RT [(1-y) \ln (1-y) + y \ln a_{\text{UO}_{2+x}}] \quad \text{Eq. (5.50)}$$

$$\Delta G_m = RT [(1-y) \ln (1-y) + y \ln y + y \ln \gamma_{\text{UO}_{2+x}}]$$

where $a_{\text{UO}_{2+x}}$ and $\gamma_{\text{UO}_{2+x}}$ are, respectively, the activity and the activity coefficient of UO_{2+x} , and ΔG_m is the free energy of mixing (see Eq. 5.43). For an ideal solution, the activity coefficient is equal to one and the expression reduces to

$$\Delta G_m = RT [X_A \ln X_A + X_B \ln X_B] \quad \text{Eq. (5.51)}$$

where X_A and X_B are mole fractions of components *A* and *B*, respectively.

If the activity coefficient is less than unity, however, the deviation from ideality is negative. Such a deviation for oxidized thoria-uranium was found by Aitken et al (1966) from their determination of the thermodynamic activity of uranium dioxide in $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$. These workers used the transpiration method to measure the partial pressures of UO_3 over thoria-uranium solid solutions, in a carrier gas of dry air, and calculated UO_2 activities. They examined solid solutions with values of *y* between 0.06 and 0.50, and values of *x* corresponding to the oxidation limit for each value of *y*, at a temperature of 1573 K. The oxygen partial pressure corresponded to that in dry air at 1 atmosphere; P_{O_2} was therefore 0.2 atmosphere. The

values obtained were corrected to $x = 0$, and showed that, for stoichiometric solid solutions, the activity of UO₂ is essentially equal to the concentration y , and the solutions are therefore ideal. For example, at $y = 0.25$, $x = 0$, the activity a_{UO_2} given for 1573 K and 0.2 atmospheres of oxygen is 0.24, i.e., approximately y , and the activity coefficient is essentially unity. The oxidation limit at this composition is $x = 0.13$; for material at the oxidation limit, the value of a_{UO_2} has decreased to 0.061, or 25 percent of its stoichiometric value. The percentage decreases with increasing values of x ; at compositions for which the oxidation limit permits cubic materials with $x = 0.25$, the activity is 18 percent of its stoichiometric value.

Aitken et al (1966) concluded that nonideal behavior can be attributed to the excess oxygen and suggested that the negative departure is a result, principally, of the localized interaction of the oxygen interstitials with the uranium ions. A plot of their calculated free energies of formation for both the stoichiometric and hyperstoichiometric solid solutions at 1573 K is shown in Fig. 5.22.

These results of Aitken et al (1966) are, obviously, opposite to those obtained by Ugajin (1982) from oxygen potential measurements. Aitken et al suggest that the hyperstoichiometric solid solution departs negatively from ideal behavior, whereas Ugajin concludes that the departure is positive. However, both agree that the stoichiometric solid solution is ideal.

A different view of the stoichiometric solid solution is that by Bamberger and Baes (1970), who obtained activity coefficient data for UO₂ and ThO₂ from the exchange of U⁴⁺ and Th⁴⁺ ions between a molten salt (LiF-BeF₂-ThF₄-UF₄) and ThO₂-UO₂ solid solutions. The exchange reaction, which can be written as $\text{U}^{4+}(f) + \text{Th}^{4+}(o) \rightleftharpoons \text{U}^{4+}(o) + \text{Th}^{4+}(f)$, where f refers to molten fluoride and o to the solid oxide solution, was carried out at 853–1053 K.

Bamberger and Baes (1970) suggest that the solid solution oxide phase behaves as a regular solution with activity coefficients related to mole fractions as follows:

$$\log \gamma_{\text{UO}_2} = \frac{A}{T} (X_{\text{ThO}_2})^2 \quad \text{Eq. (5.52)}$$

and

$$\log \gamma_{\text{ThO}_2} = \frac{A}{T} (X_{\text{UO}_2})^2 \quad \text{Eq. (5.53)}$$

where γ = activity coefficient, A is a constant = 275 K, and X = mole fraction; T is in K.

Figure 5.22. Free Energy of Formation of $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ (Aitken et al, 1966).
(Reprinted with permission of American Chemical Society)

They suggest that the enthalpy of mixing is not zero, as is the case for an ideal solution, but that $\Delta H_m = 5265 \text{ J/mol} (X_{\text{UO}_2})(X_{\text{ThO}_2})$. For a 50 mole percent solid solution, $\Delta H_m = 1316 \text{ J/mol}$.

Although it is more likely that the stoichiometric solid solution is ideal rather than regular because of the good agreement with Vegard's law (see Chap. 4), the type of deviation from ideality for the hyperstoichiometric solution is not definite. However, because the Ugajin (1982) data are more direct, more extensive and appear to be more precise, it is judged that $\text{ThO}_2\text{-UO}_{2+x}$ deviates positively from ideal behavior.

5.9.2 Oxygen Potentials and Gibbs Free Energies of Formation

The oxygen potentials of $\text{ThO}_2\text{-UO}_2$ and UO_2 fuels have an important nuclear application: the oxygen potential ($\Delta\bar{G} = RT \ln P_{\text{O}_2}$) defines whether a given fission product will become oxidized. If the Gibbs free energy of formation of the fission product oxide (ΔG_f°) is more negative than the oxygen potential of the fuel, the fission product element will tend to form a stable oxide. If, on the other hand, the free energy of formation of the fission product oxide is less negative than the oxygen potential of the fuel, the fission product will exist in elemental form. As is seen from Figs. 5.19 through 5.21, however, there is a region in the immediate vicinity of stoichiometry where there is a large change in oxygen potential for a very small change of oxygen content. Uncertainty therefore arises concerning the stable form of the fission product when the free energy of formation of its oxide falls within this range.

A convenient way to present such information is the Ellingham plot, a graphical representation of the standard free energies of formation of oxides from the elements, in which ΔG_f° is plotted against temperature. This is shown in Fig. 5.23 for some common fission product elements and their oxides. The data on free energies of formation were taken from the tabulation by Blackburn and Johnson (1982). The quantities are expressed in terms of one mole of oxygen gas. This permits a comparison of the relative reducing or oxidizing tendencies of the various solid phases. From such a plot one can obtain the partial pressure of oxygen in equilibrium with the oxide and metal.

For nearly stoichiometric UO_2 and, by inference from the data in Figs. 5.19 and 5.20, for nearly stoichiometric $\text{ThO}_2\text{-UO}_2$, the oxygen potential of the fuel is in the vicinity of about -280 to about -500 kJ/mol. (Note that these oxygen potential values are considerably less negative than the free energies of formation of ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$.) Thus, those fission products such as barium, zirconium, and yttrium, the oxides of which have high negative free energies of formation (-1000 to -1100 kJ/mol O_2) will become oxides, whereas those such as palladium and ruthenium, the oxides of which have low negative free energies of formation (around -200 kJ/mol O_2) will remain in the uncombined state. Molybdenum is a borderline case. These considerations are discussed further in Chap. 9.

5.9.3 Oxygen Potentials and Vapor Pressures

Ugajin et al (1983) used their experimental oxygen potential data to estimate the sublimation behavior of the $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2+x}$ solid solution. In these calculations they assumed (1) that the vapor phase consists of the

Figure 5.23. Free Energy of Formation of Several Oxides per Mole of Oxygen as a Function of Temperature.

following gaseous species: ThO_2 , ThO , UO_2 , UO , UO_3 , and O_2 ; (2) that the stoichiometric (or nearly stoichiometric) solid solution is ideal; and (3) that positive deviations from ideality occur for oxygen-to-uranium ratios greater than 2.01.

Figures 5.24 and 5.25 are plots at 2000 and 2300 K, respectively, of their calculated vapor pressures for $\text{UO}_3(\text{g})$, $\text{UO}_2(\text{g})$, $\text{ThO}_2(\text{g})$, and O_2 as a function of uranium valence. These calculations reveal the surprising result that the principal metal-bearing species over the stoichiometric solid solution ($\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2.000}$) is $\text{UO}_3(\text{g})$ rather than $\text{UO}_2(\text{g})$. With increasing nonstoichiometry the partial pressures of $\text{UO}_2(\text{g})$ and $\text{ThO}_2(\text{g})$ are essentially constant, whereas the partial pressure of UO_3 increases rapidly.

Figure 5.24. Calculated Vapor Pressures of Main Gaseous Species over $\text{Th}_{0.8}\text{U}_{0.2}\text{O}_{2+x}$ at 2000 K (After Ugajin et al, 1983).

Also shown in Figs. 5.24 and 5.25 are values extrapolated from the vapor pressure equations of Ackermann et al (1963) and of Alexander et al (1967), namely, Eqs. (5.16) and (5.22), respectively. Note the good agreement of the Ugajin et al (1983) calculations for the stoichiometric solid solution with the Ackermann and Rauh (1973) extrapolated values for $\text{ThO}_2(\text{g})$.

Figure 5.25. Calculated Vapor Pressures of Main Gaseous Species over $Th_{0.8}U_{0.2}O_{2+x}$ at 2300 K (After Ugajin et al. 1983).

In comparing their results with extrapolated values from the Alexander et al (1967) transpiration measurements, Ugajin et al (1983) suggest that the vapor species in the Alexander et al experiments was $UO_3(g)$ rather than $UO_2(g)$. This assumption is not warranted because the transpiration measurements were made in hydrogen and hydrogen-argon atmospheres. Therefore, it is more likely that low-oxygen potentials were obtained and that the ThO_2 - UO_2 solid solution was stoichiometric.

5.10 CHEMICAL REACTIVITY

5.10.1 Thermal Stability in Air

As was discussed in Chap. 3, thoria is exceedingly stable to high temperatures and does not oxidize to a higher oxide. It can, however, adsorb water vapor and CO_2 on exposure to air; this property is discussed in ct. 5.11, below. The $\text{ThO}_2\text{-UO}_2$ solid solution, on the other hand, can be oxidized in air to limits which depend on the UO_2 content in the solid solution. These limits are discussed in Sect. 5.9, above, and in Chap. 4.

Furuya (1970) made a thermogravimetric study of the low temperature oxidation behavior of $\text{ThO}_2\text{-UO}_2$ powders. Solid solutions of $\text{Th}_y\text{U}_{1-y}\text{O}_2$ were oxidized in air under conditions of linearly increasing temperature from room temperature to 873 K. For UO_2 -rich compositions ($y = 0$ to 0.20), oxidation occurred in two distinct stages, as was the case for UO_2 reported by Aronson et al (1957). In the first stage, oxidation proceeded to an O/M ratio of 2.33 with the material remaining cubic in contrast to the tetragonal U_3O_7 formed on oxidation of pure UO_2 . The O/M ratios attained after the second stage of oxidation ranged from 2.65 in the case of pure UO_2 to 2.40 for the 20 mole percent ThO_2 solid solution. A mixture of orthorhombic and cubic phases was observed in these oxidized solid solutions.

For the intermediate compositions ($y = 0.25$ to 0.40) the two oxidation stages merged into essentially one stage; there was an initial plateau at an oxidation level of $\text{O/M} = 2.32$ to 2.34 followed almost immediately by another plateau at an oxidation level equivalent to an O/M of 2.35 to 2.37. And, finally, for the ThO_2 -rich compositions ($y = 0.50$ to 0.80) there was a single oxidation stage resulting in O/M values that ranged from 2.24 in the case of the 50 mole percent ThO_2 solid solution to 2.10 in the case of the 80 mole percent ThO_2 solid solution.

One kinetic study performed at 523 K (isothermal annealing) in air on $\text{Th}_{0.1}\text{U}_{0.9}\text{O}_2$ showed kinetic behavior very similar to that observed by Aronson et al (1957) for pure UO_2 .

5.10.2 Stability in High-Temperature Water

The corrosion behavior of ThO_2 and various $\text{ThO}_2\text{-UO}_2$ compositions up to 50 weight percent UO_2 was studied in high temperature (633 K), alkaline (pH 10) flowing water, both degassed and oxygenated (5 and 100 ppm) as part of a study of the behavior in such media of various oxide nuclear fuels including UO_2 (Markowitz and Clayton, 1970). The results of the exposure tests confirmed earlier work (Belle, 1961) in showing that sintered compacts of UO_2 are extremely resistant to corrosive or erosive

attack in high-temperature water in the absence of oxygen, but corrode rapidly in the flowing, oxygenated high pH water system. The ThO_2 samples displayed good corrosion resistance even in oxygenated high-temperature water; this result is not surprising since thorium forms no higher oxide than ThO_2 . In the case of the ThO_2 - UO_2 solid solutions, no corrosion attack was noted for any of the oxide compositions in either the nonoxygenated water or in the water containing 5 ppm O_2 .

Exposure of ThO_2 - UO_2 solid solution of two compositions (ThO_2 20 weight percent UO_2 and ThO_2 -50 weight percent UO_2) to water oxygenated to 100 ± 10 ppm, the highest level tested, showed high weight gains. However, all the specimens retained their mechanical integrity throughout the test period of 140 days, forming a surface-oxidized phase. This oxidized phase was found, by X-ray diffraction analysis, to be cubic, probably of the M_4O_9 type. This result suggests that an M_4O_9 type of single phase region exists in the low temperature ternary phase diagram for ThO_2 - UO_2 - O_2 .

5.10.3 Compatibility Behavior

Tabulations of miscellaneous chemical interactions of thorium with various liquids and with metals have been made by Peterson and Curtis (1970) and are not repeated here. Grossman and Kaznoff (1966) reported that thorium did not react with cesium vapor after a 300-hour test at 533 Pa at temperatures up to 1873 K. It has also been reported (Reed, 1954) that thorium shows essentially no corrosion with liquid sodium containing 10 ppm oxygen at temperatures of 1073 to 1773 K. Comparable data for ThO_2 - UO_2 do not exist.

5.10.4 Dissolution Reactions

ThO_2 and ThO_2 - UO_2 solid solutions can be dissolved in nitric acid to which a small amount of hydrofluoric acid is added. The hydrofluoric acid acts as a catalyst and not simply as a solvent (Bond, 1958; Shying et al, 1970). Rate data for the dissolution reaction are affected by many variables, e.g., sample size and particle size of the solute, reaction temperature, concentrations of the nitric and hydrofluoric acids, and concentrations of other ions in solution (Bond, 1958; Shying et al, 1970, 1972; Takeuchi et al, 1971; Tallant et al, 1983). See Chap. 10 for chemical details concerning reprocessing of ThO_2 and ThO_2 - UO_2 .

5.11 SURFACE PROPERTIES

5.11.1 Surface Energy

Theoretical estimates and experimental measurements of the surface energies of ThO_2 and UO_2 show considerable variation. Kolar (1963)

measured the rise in temperature on wetting a high-surface area UO_2 powder and arrived at a figure of 0.49 J/m^2 for the heat of immersion in water of UO_2 . This quantity represented the difference in energy between a UO_2 -air interface and a UO_2 -water interface. Similarly, heats of immersion in water of ThO_2 were measured by Holmes and Secoy (1965), by Holmes et al (1966), and by Fuller et al (1968) but, as discussed in Sect. 5.11.2, the data revealed complex behavior, suggesting that surface energies estimated from such measurements are in gross error.

Livey and Murray (1956) reported a value of 0.642 J/m^2 for the surface energy of UO_2 from measurements of contact angles of wetting of liquid metals. They also estimated a value of 0.530 J/m^2 for the surface energy of ThO_2 from an assumed straight-line relationship between surface energy and the reciprocal of molar volume for "similar compounds", e.g., alkali halides.

Benson et al (1963) made theoretical calculations of the surface energies of both thorium dioxide and uranium dioxide. Their first approach, using an ionic model, was very sensitive to the values assumed for compressibilities and led to values of 0.81 and 0.15 J/m^2 for ThO_2 and UO_2 , respectively; the value for UO_2 was judged to be too low. They also estimated the surface energies for the two oxides using the Born-Haber cycle and obtained values of 1.15 J/m^2 for ThO_2 and 1.03 J/m^2 for UO_2 . Implicit in these calculations is the assumption of negligible covalency in the bonding of UO_2 and ThO_2 , the same assumption made in the calculation of cohesive energies discussed in Chap. 3. Benson et al questioned the suitability of the Livey and Murray (1956) approximation and recommended the values calculated from the Born-Haber cycle approach.

Tasker (1979) presented theoretical calculations of the surface energies of the (111) and (110) surfaces of UO_2 using a fully ionic model. The calculated minimum surface energy for the (111) surface, 1.069 J/m^2 , agrees with the Benson et al (1963) estimate of 1.030 J/m^2 .

Results from high-temperature multiphase equilibration or wetting techniques on uranium dioxide showed the strong effect of stoichiometry (Modkin and Nicholas, 1973, 1977, and 1978; Nikolopoulos et al, 1977).

These techniques have not been used on ThO_2 .

In a series of papers Matzke and coworkers (Matzke, 1980; Matzke et al, 1980; Inoue and Matzke, 1980; Inoue and Matzke, 1981; and Matzke, 1983) reported *fracture* surface energies for a number of nuclear fuel materials including ThO_2 . The experimental technique that was used is the Hertzian indentation method, in which a flat surface of the brittle solid is indented elastically by a sphere under increasing load. The fracture surface energy is determined from the observed crack behavior. As pointed out by Matzke et al (1980), this technique results in a surface energy that is not necessarily identical with the surface energy as determined by a wetting technique at high temperatures.

For ThO_2 , Matzke (1980) reported a room-temperature fracture surface energy, γ , of $2.5 \pm 0.2 \text{ J/m}^2$. In the case of UO_2 , Matzke et al (1980) obtained a room-temperature value of $1.8 \pm 0.3 \text{ J/m}^2$; they also found that the fracture surface energy increased with the degree of hyperstoichiometry for UO_{2+x} . In subsequent measurements of the fracture surface energy of ThO_2 from room temperature to 673 K, Inoue and Matzke (1981) found that γ decreased strongly with temperature to about 623–673 K, where it leveled off at a value of approximately 1.4 J/m^2 .

Unable to make direct comparison with other experimental measurements on ThO_2 at higher temperatures because such data do not exist, Inoue and Matzke (1981) compare their results with those obtained on UO_2 . They suggest that the surface energies of ThO_2 and UO_2 are in approximately the same ratio as the heats of sublimation or the elastic moduli. Using this correlation they state that the γ value for ThO_2 at about 673 K agrees favorably with much of the high-temperature data for UO_2 . They also estimate a temperature dependency for γ of ThO_2 by assuming that the value for γ of $\text{ThO}_2(\text{s})$ at its melting point is also greater than that of $\text{UO}_2(\text{s})$ at its melting point by the same ratio.

If the recommended values for Young's moduli (see Chap. 7) and for the heats of sublimation (see Sect. 5.4.3(b)) are used, the ratio $\gamma \text{ ThO}_2 / \gamma \text{ UO}_2$ becomes 1.1 (Inoue and Matzke (1981) suggested 1.2) resulting in a temperature dependence of $-2.5 \times 10^{-4} \text{ J/m}^2 \cdot \text{K}$, as compared with the value of -3.5×10^{-4} for UO_2 reported by Nikolopoulos et al (1977).

5.11.2 Adsorption of Gases and Liquids by Thorium Dioxide

(a) Adsorption of Water Vapor

The nature of the surface adsorption of liquid water and of water vapor by thoria was studied extensively by Fuller et al (1966, 1969), by Holmes et al (1968), and by Gammage et al (1970). A variety of techniques, including calorimetric, gravimetric, and infrared absorption measurements, were used. Results of these experimental observations showed that adsorption of water vapor on thoria is tenacious and that the binding of water to the oxide surface is complex.

In the first in a series of reports, Holmes and Secoy (1965) measured the heats of immersion in water at 298 K of a number of ThO_2 powders whose specific surface areas varied considerably. This variation in surface area was accomplished by calcining at different temperatures the same lot of thorium oxalate powder prepared by precipitation from a nitrate solution with oxalic acid. All calcined powders were pretreated before the calorimetric measurements by vacuum outgassing for 24 hours at temperatures ranging from 373 to 773 K.

Two important observations were made from data on heat of immersion in water of the powders as a function of outgassing temperature. First,

there was a general increase in the heat of immersion with increase of the outgassing temperature given to the powders; values ranged from about 0.450 to 0.575 J/m² for a degassing temperature of 373 K to values of 0.550 to 1.100 J/m² for a degassing temperature of 773 K. Second, the various powder samples had remarkably different energetics with respect to the solid-water interface. One powder, for example, showed not only a low heat of immersion but one that was less dependent on the outgassing temperature. Holmes and Secoy (1965) explained the variation in the measured heats of immersion as a result of the progressive removal of strongly bound chemisorbed water vapor from the powder as the outgassing temperature was increased; on subsequent exposure of the powder to liquid water during the immersion process this chemisorbed water is replaced, accompanied by a large net heat of adsorption as large as 92 kJ/mol.

The complexity of the water vapor adsorption process on thoria was clarified in a number of subsequent papers. A "bare" thoria powder surface adsorbs water in an amount equivalent to three chemisorbed layers. The first water layer is "dissociatively" chemisorbed to form two surface hydroxyl groups per surface thorium ion. Subsequent adsorption is controlled by the slow hydration of each of these surface hydroxyl groups to form the second and third layers. Thus, the total quantity of water involved is the weight equivalent of three chemisorbed monolayers.

It was also shown that, in vacuum, a temperature as high as 1273 K was required to obtain a "dry" weight of thoria; heating in vacuum to 773 K left the oxide surface in a partially hydrated state. Presumably, various degrees of partial hydration are possible, depending on the degassing temperature to which the powder is subjected.

An infrared spectroscopic analytical technique was used by Fuller et al (1968) to elucidate the structure of the adsorbed water layer on thoria surfaces. The results were found to be in accord with the structure proposed on the basis of gravimetric and calorimetric data, i.e., there is considerable hydrogen bonding with one water molecule strongly associated with each of two surface hydroxyl groups in the adsorbed layer.

Dayton (1976) reported some results on the extent of water vapor adsorption by ThO_2 powders that are in agreement with the observations discussed above. This work showed that the water vapor contents of the "as-fabricated" powders were equivalent to about 0.5 to 1.3 monomolecular layers of adsorption; after the powders were exposed to the ambient air for about one month, water adsorption was equivalent to 1.4 to 2.3 monolayers.

In a similar manner, measurements were made of the amount of moisture pickup by degassed, high-density ThO_2 pellets as a function of relative humidity and exposure time. The data showed that the moisture adsorbed by the pellets increased with increasing humidity and increasing

time of exposure to a level approximately equivalent to 1 to 3 monolayers; the uncertainty arises from the uncertainty in the specific surface area of the pellet.

Thorium dioxide is apparently not unique in its interaction with adsorbed water. The work of Webster et al (1965) and of Anderson et al (1965) showed that a clean surface of magnesium oxide is first covered by a layer of hydroxyl ions. Water is then physically adsorbed onto the hydroxylated surface and slowly converts to a more strongly bound species in an amount corresponding to about a monolayer.

(b) Adsorption of CO₂ Gas on ThO₂ Powders

Adsorbed CO₂ gas can influence the adsorptive characteristics of the thorium surface. For example, for some thorium powders that apparently adsorbed less water vapor, it was found that these powders evolved CO₂ when heated above 873 K. It was thought at first that the surface CO₂ originated from residual carbon from the original oxalate decomposition. It was subsequently reported (Gammage et al, 1970, as a private communication from C. S. Shroud and C. H. Secoy) that, according to infrared analysis, thorium dioxide rapidly chemisorbs CO₂ from the atmosphere at room temperature, and this CO₂ can be removed by evacuation only if the temperature is raised to 1173 K. However, Clayton (1976) found that adsorbed CO₂ equivalent to about 0.5 of a monolayer is completely released at a much lower temperature, 773 K.

5.12 SUMMARY

The thermodynamic data for ThO₂ are reasonably consistent and complete. Those thermodynamic quantities, such as heat of fusion and heat of vaporization that have not been measured directly, can be estimated through suitable empirical correlations. On the other hand, a property, such as the volume change on melting, should be determined by experimental measurement.

The discontinuity in the slope of the enthalpy-temperature curve for ThO₂ at about 2950 K is apparently real and results in a large increase in heat capacity, much greater than the gradual increase with temperature that occurs for UO₂. However, the nature of this so-called phase transition (for ThO₂, UO₂, and ThO₂-UO₂ solid solutions) is still uncertain.

Experimental evaluation of the free energies of formation shows that the ThO_{2-x} phase is more stable than the UO_{2-x} phase.

Although thermodynamic data for the solid solutions have been developed for low UO₂ contents only (up to about 30 mole percent UO₂) the stoichiometric or very nearly stoichiometric solid solution is essentially an ideal one and can be treated as such. Where experimental data exist for a particular property, such as thermal expansion or heat capacity, agreement is satisfactory between the measured quantity and the estimate based on the linear variation of the property with molar composition.

The hyperstoichiometric solid solution is not ideal but can be treated as having positive deviations from ideal behavior. These deviations appear to be greater for those hyperstoichiometric solutions that contain higher thorium contents.

Preferential loss of UO_2 from $\text{ThO}_2\text{-UO}_2$ solid solutions at high temperatures occurs because the partial pressure of UO_2 over $\text{ThO}_2\text{-UO}_2$ is higher than the vapor pressure for pure ThO_2 . However, there is some uncertainty concerning the partial pressures of the various gaseous species over hyperstoichiometric $\text{ThO}_2\text{-UO}_2$ solid solutions.

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Chapter 6

TRANSPORT PROPERTIES OF ThO₂ AND ThO₂-UO₂

J. Belle

6.1 INTRODUCTION

Diffusion, electrical conductivity, and thermal conductivity of ThO₂, in common, are largely determined by crystalline imperfections. Diffusion results from atomic defects; electrical conductivity results from both atomic and electronic defects; and thermal conductivity can also be affected by electrons as well as by phonons and photons.

Summaries of the diffusion and electrical conductivity data are followed by a review of the thermal conductivity of ThO₂ and ThO₂-UO₂ solid solutions.

6.2 DIFFUSION PROCESSES IN ThO₂ AND ThO₂-UO₂

6.2.1 Introduction

Diffusion in polycrystalline materials proceeds through individual grains or through so-called short-circuit or high-diffusivity paths. Diffusion through single crystals has only one path unless a substructure is present in the material. Grain boundaries, dislocations, and surfaces are examples of high-diffusivity paths. Before proceeding with a discussion of the ThO₂ diffusion data, a few definitions are given to clarify terms and symbols (see Belle and Berman, 1978; Matzke, 1981).

Fick's first law,

$$J = -D \left(\frac{\partial c}{\partial x} \right),$$

defines the diffusion coefficient D as the constant that relates the flux of matter J to the concentration gradient $(\partial c / \partial x)$ causing the flow. The terms *tracer diffusion coefficient* and *self-diffusion coefficient* refer to

a diffusion process in the absence of a chemical concentration gradient. Thus, if an element i is present in only very dilute concentration in a solid of homogeneous composition and if there are no external driving forces, the concentration of i tends toward an equilibrium distribution as a result of the force of its own concentration gradient ($\partial c_i / \partial x$). Then D is the diffusion coefficient of the tracer element i , often symbolized by D^* or D^T . If the tracer and the medium through which the tracer diffuses are the same element, for example ^{228}Th or ^{232}Th , D is the *self-diffusion coefficient*, D^S .

The terms *lattice*, *bulk*, and *volume* diffusion coefficient have been used interchangeably to describe diffusion within the crystal lattice. In this book, we shall use the term volume diffusion, symbolized by D_v . The term *boundary diffusion coefficient* (D_b) refers to diffusion along an interface, a grain boundary, or dislocations. Diffusion along a surface is symbolized by the coefficient D_s .

The terms *chemical diffusion* and *interdiffusion* refer to diffusion in a chemical potential gradient. In the interdiffusion of ThO_2 and UO_2 , for example, the cations diffuse in a fixed oxygen lattice. Thus, in a simplified way the chemical or interdiffusion coefficient $\tilde{D}$ represents counterdiffusion of thorium and uranium ions, which are related to the individual self-diffusion coefficients by the Darken equation (Darken, 1948),

$$\tilde{D} = X_2 D_1^S + X_1 D_2^S \left(1 + \frac{d \ln \gamma_1}{d \ln X_1} \right) \quad \text{Eq. (6.1)}$$

where

X_1 and X_2 = mole fractions of the diffusion species (Th and U, for example)

D_1^S and D_2^S = respective self-diffusion coefficients

γ_1 = activity coefficient of component 1.

For an ideal, dilute solution the term $(d \ln \gamma_1) / (d \ln X_1)$ becomes zero, and the interdiffusion coefficient is the weighted average of the self-diffusion coefficients.

Intrinsic diffusion refers to a process in which only thermally produced point defects are involved in the diffusion process, whereas *extrinsic diffusion* refers to diffusion resulting from defects introduced through impurities and not through thermal activation. *Defect diffusion* refers to the diffusivity of a particular point defect, such as a vacancy, an interstitial, or an impurity. *Apparent diffusion* is a term used to include contributions from several diffusion paths combined into one diffusion coefficient.

Note that all of these diffusion processes are isothermal, i.e., migration proceeds in the absence of a temperature gradient. *Thermal diffusion* refers to diffusion processes in which temperature gradients affect the migration of the solute within the solid.

To measure the diffusion coefficient, Fick's first law requires a fixed concentration gradient, a condition difficult to establish experimentally in a solid. It is more convenient to measure the change in concentration with time; this is given by Fick's second law,

$$\left(\frac{\partial c}{\partial t}\right) = D \left(\frac{\partial^2 c}{\partial x^2}\right),$$

where D is independent of concentration.

In general, there are two experimental approaches to determine diffusion coefficients: (1) the direct method, which measures the mass flow through a solid by determining the change in the concentration of the diffusing species as a function of time, temperature, and diffusion distance into the solid; and (2) the indirect method in which the diffusion coefficient is determined by measuring some diffusion-controlled phenomenon.

Thorium diffusion in ThO₂ has been measured by depositing a radioactive tracer isotope on the surface of the bulk specimen, annealing the specimen at a constant temperature, and determining the concentration of the tracer by sectioning, by alpha-ray spectrometry, or by decrease in surface activity. Oxygen diffusion in ThO₂ has been measured by the gas-solid isotope exchange technique.

Oxygen self-diffusion coefficients in UO_{2+x} have also been obtained using the nuclear reactions ¹⁸O(p,n)¹⁸F and ¹⁷O(d,n)¹⁸F followed by autoradiography (Murch et al, 1975). For detailed descriptions of the various experimental techniques that have been used, the reader is referred to the listings in the references.

6.2.2 Volume Diffusion

6.2.2.1 Oxygen Self-Diffusion in ThO₂

Unlike the uranium dioxide situation for which oxygen diffusion data are voluminous, there are only three sets of measurements of oxygen self-diffusion in ThO₂. These data are shown in Table 6.1 along with data for UO₂ and PuO₂. In the first of the ThO₂ sets of data, Morgan and Yust (1961) measured the diffusion of oxygen in fine-grain, 10 μm-diameter thoria spheres using the method of heterogeneous isotopic exchange. In this method, as used for oxygen, diffusion is measured indirectly by the exchange of the ¹⁸O isotope in either the gas or solid phase with normal oxygen of the other phase.

TABLE 6.1—OXYGEN SELF-DIFFUSION IN ACTINIDE OXIDES

Oxide	Temp. Range (K)	D_0 (m^2/s)	Activation Energy		Reference
			(kJ/mol)	(eV/atom)	
ThO ₂	873—1673	1×10^{-12}	61.5	0.64	Morgan and Yust (1961)
ThO ₂	1173—1773	4.4×10^{-4}	275	2.9	Edwards et al (1963)
ThO ₂	1118—1484	1.00×10^{-10}	73.6	0.76	Ando et al (1976)
ThO ₂	1484—1919	5.73×10^{-6}	209	2.2	Ando et al (1976)
ThO ₂ *	1372—1917	5.67×10^{-7}	219	2.3	Ando et al (1984)
UO ₂	1053—1523	2.6×10^{-5}	248	2.6	Marin and Contamin (1969)
PuO ₂	1000—1273	1.19×10^{-7}	177	1.8	Deaton and Wiedenheft (1973)
PuO ₂ †	1000—1273	1.30×10^{-6}	202	2.1	Ando and Oishi (1983)

*Polycrystalline

†Data of Deaton and Wiedenheft (1973), recalculated by Ando and Oishi (1983).

The change in ¹⁸O concentration in the gas phase is measured by analyzing samples with a mass spectrometer. This ¹⁸O isotopic exchange technique was first used on a nuclear fuel material (UO₂) with CO₂ as the carrier gas for ¹⁸O (Auskern and Belle, 1958). Morgan and Yust (1961) used the same approach and carried out measurements over the temperature range 873 to 1673 K. The reported results were expressed by the Arrhenius-type equation,

$$D = 1 \times 10^{-8} \exp[-14.7(\text{kcal/mol})/RT] \text{cm}^2/\text{s}.$$

Morgan and Yust qualified their results by stating that the absolute magnitude of the measured diffusion coefficients is uncertain because of uncertainties associated with the evaluation of the equivalent spherical diameter of the ThO₂ particles used. Another qualification can be made to their data: the very low activation energy (14.7 kcal/mol or 61.5 kJ/mol) suggests a considerable grain-boundary contribution to the observed diffusion.

Edwards et al (1963) used the same ¹⁸O isotopic exchange method but with coarser ThO₂ particles prepared by passing sintered ThO₂ particles through a plasma torch. Their results in the temperature range between 1173 and 1773 K were represented by the equation

$$D = 4.4 \exp[-65.8(\text{kcal/mol})/RT] \text{cm}^2/\text{s}.$$

They interpreted the diffusion process to be intrinsic diffusion.

In the third set of measurements on oxygen self-diffusion in ThO₂, Ando et al (1976) used single-crystal ThO₂ prepared by an arc fusion process and, as the carrier gas, an oxygen atmosphere of about 0.27 atm (27 kPa) enriched in the ¹⁸O isotope to about 5 percent. Particles of 100–200 μm diameter obtained by crushing the single crystal were used for the diffusion experiments. The amount of tracer in the solid specimen was determined by measuring the decrease in the mass ratio 34/32 of the gas phase by mass spectrometry. Experiments were carried out over the temperature range 1118 to 1919 K.

Ando et al (1976) expressed their results in the form of two equations:

$$D = 5.73 \times 10^{-2} \exp[-49.9(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

for the higher temperature portion of the temperature range and

$$D = 1.00 \times 10^{-6} \exp[-17.6(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

for the lower temperature portion. The data show (Fig. 6.1) a *knee* in the Arrhenius plot at about 1484 K. Ando et al (1976) reported the break to occur "in the neighborhood of 1100°C", but this is obviously

Figure 6.1. Self-Diffusion Coefficients of Oxygen Ion in ThO_2 as a Function of Temperature.

an error; in a later report, Ando and Oishi (1983) corrected the break temperature to approximately 1200°C . This type of change in the $\log D$ versus $1/T$ plot suggests a mixture of extrinsic diffusion (lower temperature portion) and intrinsic diffusion (higher temperature portion). Ando and Oishi (1981, 1983) interpreted the activation energy for the high temperature regime (209 kJ/mol) as involving both formation and migration energies of an oxygen Frenkel defect pair. On the assumption that the activation energy for the dislocation-enhanced low-temperature extrinsic regime (74 kJ/mol) represents the migration energy for the assumed vacancy migration in ThO_2 , Ando and Oishi (1983) calculated a value of 270 kJ/mol for the formation energy of an oxygen Frenkel pair, i.e.,

$$(209 \text{ kJ/mol} - 74 \text{ kJ/mol}) \times 2 = 270 \text{ kJ/mol} .$$

Ando and Oishi (1979) also explored the effect of atmosphere by determining the self-diffusion coefficient of oxygen in ThO₂ in an ¹⁸O-enriched CO₂ atmosphere in which the oxygen partial pressure was 3×10^{-4} atm (30.4 Pa). A single measurement at 1623 K was in close agreement with the high-temperature equation, suggesting that oxygen diffusion in ThO₂ is not sensitive to oxygen partial pressure.

The results of these sets of measurements are shown in the Arrhenius plot in Fig. 6.1. The Morgan and Yust (1961) line differs considerably from the other sets and probably does not represent volume diffusion. The Edwards et al (1963) data differ from the Ando et al (1976) data in not showing the change in activation energy. This discrepancy between the Ando et al and Edwards et al sets of data is hard to explain on the extrinsic-intrinsic argument, since the single crystal ThO₂ in the work of Ando et al was apparently pure but showed extrinsic diffusion, whereas the extrinsic region was not observed with the samples of Edwards et al which presumably were impure. Ando et al (1976) suggested that a high density of dislocations in the single crystal material, and not impurities, may have been responsible for the observed extrinsic diffusion.

The effect of grain boundaries on oxygen ion diffusion in ThO₂ was reported by Ando et al (1984). Diffusion anneals were carried out in an ¹⁸O-enriched oxygen atmosphere of about 0.24 atm (24 kPa) on high-density (99 percent of theoretical) polycrystalline microspheres 530 μm in diameter. The spheres were fabricated by the sol-gel process and were sintered in air at 1573 K for 3 hours. A further sintering at 1983 K for 24 hours was made to increase the grain size of the particles. This treatment resulted in nonuniform grain growth; the grains in the surface layer had a diameter of about 20 μm, and those in the adjacent interior had a diameter of about 5 μm.

The diffusion data were represented by the expression

$$D = 5.67 \times 10^{-3} \exp[-219(\text{kJ/mol})/RT] \text{cm}^2/\text{s}$$

the temperature range 1372–1917 K. Similar results were obtained with polycrystalline disk specimens. As can be seen from Fig. 6.1, the oxygen self-diffusion coefficients for polycrystalline ThO₂ are about an order of magnitude less than those reported previously by Ando et al (1976) for single-crystal material.

Ando et al (1984) suggested that the lowering effect in the case of the polycrystalline spheres is due to some nondiffusive phase discontinuously distributed along grain boundaries which increases the diffusion path. This hindering second phase could be crystalline precipitates or segregated micropores.

The high temperature regions of the sets of data of Ando et al (1976), Ando et al (1984), and Edwards et al (1963) differ in

magnitude also from similar data for oxygen diffusion in UO_2 and PuO_2 . This is shown in Fig. 6.2, in which a normalized temperature scale is used (T_m is the melting point in K). This type of diffusion coefficient-temperature plot was suggested by Matzke (1976a; 1981) to show the similar behavior for various fluorite materials. However, on an expanded scale restricted to the actinide oxides, differences become more obvious. It is seen that oxygen ion diffusion is greater in ThO_2 than in the other two actinide oxides. The data for oxygen self-diffusion in UO_2 represented by the line shown in Fig. 6.2 are those of Marin and Contamin (1969) and were considered by Matzke (1976a) to be the most representative for stoichiometric UO_2 . The PuO_2 data line shown in Fig. 6.2 is that reported by the original investigators (Deaton and Wiedenheft, 1973) and is not the recalculated version of the data cited by Ando and Oishi (1983).

Figure 6.2. Oxygen Diffusion Data in ThO_2 , UO_2 , and PuO_2 .

(b) *Thorium and Uranium Diffusion in ThO_2*

For oxides having the fluorite structure, metal diffusion is much slower than oxygen diffusion. This has been confirmed for ThO_2 as a result of a number of attempts to determine cation volume diffusion coefficients in ThO_2 and $\text{ThO}_2\text{-UO}_2$; a summary of this work is given in Table 6.2.

Poteat and Morgan (1968) studied the diffusion of ^{230}Th in ThO_2 over the temperature range 1573 to 2573 K. Diffusion coefficients were determined on single crystals and sintered powder specimens for a range of grain sizes from extremely large to a few microns. An organic chelate of ^{230}Th was placed on the specimen surface and dried; the specimen was then annealed in air below 2073 K and in argon at the higher temperatures. Penetration of the isotope was determined by sectioning the specimen, by measuring the degradation in the alpha-particle energy spectra, or by both techniques. The experimental data for single crystals were fit to the equation

$$D = 2.0 \times 10^{-7} \exp[-74.0(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

and those for sintered powder specimens were fit to the equation

$$D = 2.6 \times 10^{-7} \exp[-69.0(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

Two distinctive features were observed: First, diffusion was increased by decreasing grain size. Second, the results indicated an increase in the diffusion coefficient as the measurement zone moved deeper into the specimens. Thus, a substantial part of the observed diffusion must have been due to some short circuit diffusion path. For this reason the data of Poteat and Morgan (1968) should be considered as apparent rather than as volume diffusion coefficients.

Hawkins and Alcock (1968) carried out diffusion studies on ThO_2 pellets of large grain size (100 μm). The pellets were prepared by sintering in vacuum for 5 hours at 2173 K, followed by a 4-hour anneal in vacuum at 2273 K. Presumably the pellets were of high density, but no values were given. The pellets were polished and coated with $^{230}\text{ThO}_2$ by vacuum evaporation or by evaporation of a solution containing the same isotope. Diffusion anneals were performed in vacuum, in air, and in CO/CO_2 mixtures. Alpha-ray spectrometry was used to determine the concentration of the diffusing tracer as a function of the distance below the surface.

Diffusion in ThO_2 was found to be independent of oxygen pressure in the temperature range investigated (1873 to 2373 K). Hawkins and Alcock (1968) believed that their results for ThO_2 , unlike their results for UO_2 , constituted essentially volume diffusion. They reasoned that the grain boundary contribution could be only a very small part of

TABLE 6.2—CATION VOLUME DIFFUSION IN ThO₂ AND ThO₂-UO₂

Cation Isotope	Temp. Range (K)	D ₀ (m ² /s)	Activation Energy		Reference
			(kJ/mol)	(eV/atom)	
²³⁰ Th	1573—2573	2.0×10^{-11}	309.6	3.21	Poteat and Morgan (1968)
²³⁰ Th	1873—2373	1.25×10^{-11}	246.0	2.55	Hawkins and Alcock (1968)
²²⁸ Th	2123—2323	3.5×10^{-5}	625.5	6.48	King (1971)
²³³ U and ²²⁸ Th	1913—2473	5×10^{-5}	627.6	6.50	Matzke (1976b)
²³⁷ U	2073—2273	1.10×10^{-8}	319.6	3.31	Furuya (1968)
²³⁷ U [in (Th _{0.5} U _{0.5})O ₂]	2073—2573	7.59×10^{-8}	359.4	3.72	Furuya (1968)
²³³ Pa	2073—2273	2.91×10^{-9}	315.5	3.27	Furuya and Yajima (1968)
²³³ Pa [in (Th _{0.5} U _{0.5})O ₂]	2073—2273	1.88×10^{-7}	384.1	3.98	Furuya and Yajima (1968)
²³³ U (in UO ₂)	1893—2283	6.8×10^{-9}	411.3	4.26	Reimann and Lundy (1969)
²³⁰ Th [in (Th _{0.5} U _{0.5})O _{2+x}]	1673	--	--	--	Lee and Alcock (1970)
²³⁰ Th [in (Th _{0.25} U _{0.75})O _{2+x}]	1673	--	--	--	Lee and Alcock (1970)
²³³ U [in (Th _{0.5} U _{0.5})O _{2+x}]	1673	--	--	--	Lee and Alcock (1970)
²³³ U [in (Th _{0.25} U _{0.75})O _{2+x}]	1673	--	--	--	Lee and Alcock (1970)

the total diffusion because the grain sizes of the ThO₂ specimens were very large relative to those of the uranium dioxide specimens. The diffusion equation for volume diffusion of ²³⁰Th in ThO₂ was given as

$$D_v = 1.25 \times 10^{-7} \exp[-58.8(\text{kcal/mol})/RT] \text{cm}^2/\text{s}.$$

However, these data can also be interpreted as apparent diffusion coefficients because the possible grain boundary contribution was not separated from the measured diffusion.

King (1971) questioned whether the data of Hawkins and Alcock (1968) represent volume diffusion in the light of his own experiments on thorium diffusion (²²⁸Th) in single crystal ThO₂. King had developed a precision sectioning technique (King, 1970) which allowed the determination of diffusion distances as small as 0.04 μm, and he applied this method to determine diffusion profiles in single crystal ThO₂ using the α-spectrum degradation technique. For his data, which covered the temperature range 2123 to 2323 K, King was able to separate short circuit-enhanced diffusion, presumably arising from dislocations, from apparent volume diffusion. That is, at small penetration distances (x) within the single crystal, a plot of log C (concentration of tracer isotope) versus x² was linear, suggesting volume diffusion; whereas, at large penetration distances log C was approximately linear with distance, suggesting some short-circuit path, e.g., subgrain boundaries or dislocations, for diffusion. The respective equations from Arrhenius plots were given as

$$D_v = 0.35 \exp[-149.5(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

for volume diffusion and

$$D_d \delta = 8 \times 10^{-14} \exp[-37.3(\text{kcal/mol})/RT] \text{cm}^3/\text{s}$$

· dislocation diffusion, where

D_d = dislocation diffusion coefficient

δ = subgrain boundary width.

The values of the apparent volume diffusion coefficients were obtained from the slopes of the log C versus x² plots near the surface.

It thus appears that even in single-crystal material short-circuit diffusion can be an important factor in thorium diffusion in ThO₂, at least at the temperatures investigated. Moreover, King (1971) suggested (as did Reimann and Lundy, 1969) that much of the UO₂ diffusion data reported as volume diffusion may not be volume diffusion because of the short circuit effects.

Matzke reached a similar conclusion from his review (Matzke, 1976a) of the literature and from his own measurements (Matzke, 1976b). In his review, Matzke showed that most of the existing data on supposedly cation volume diffusion in UO_2 and ThO_2 are misleading in that the reported diffusion coefficients are too high and the activation energies too low. He recommended that these data be rejected for one or more of the following reasons: (1) Out-of-date techniques were used; (2) specimens were of poor quality; or (3) the data represented artifacts (contributions from surface diffusion or evaporation-condensation processes) or some other short-circuit diffusion path and were not truly representative of volume diffusion.

Matzke (1976b) studied the diffusion of ^{233}U and ^{228}Th in both polycrystalline (high-density sintered bodies of about 25 μm grain size) and single-crystal ThO_2 at temperatures between 1673 and 2473 K. He found in this temperature range that grain boundary diffusion is the dominant process in polycrystalline ThO_2 . This was true for all diffusion experiments at temperatures up to about 2273 K. In this work, the ^{233}U and ^{228}Th tracer isotopes were placed on the ThO_2 specimens by different techniques: $^{233}\text{UO}_2$ in the form of a thin layer was coated on the ThO_2 surface by flash evaporation from a tungsten ribbon; ^{228}Th atoms were bombarded into the specimens using a ^{232}U recoil source. Penetration profiles of the tracer were measured by high resolution α -spectroscopy. Use of longer-time diffusion anneals and a more careful analysis of the depth and time-dependence of the tracer penetrations presumably avoided the problems associated with the earlier work.

Matzke represented the temperature dependence of the diffusion of ^{233}U in single-crystal ThO_2 by the equation

$$D_v = 0.5 \exp[-150(\text{kcal/mol})/RT] \text{cm}^2/\text{s} ,$$

applicable for the temperature range 1913–2473 K. He also reported two values for the diffusion of ^{228}Th in single crystal ThO_2 (at approximately 2000 and 2425 K) that were in good agreement with the equation for the ^{233}U data, suggesting that the difference in mobility between thorium and uranium ions in ThO_2 is small. The graphical representation of this equation is shown in Fig. 6.3 along with the other data for thorium diffusion in UO_2 (Poteat and Morgan, 1968; Hawkins and Alcock, 1968; King, 1971).

It is seen that the King and Matzke data are in excellent agreement despite some differences in experimental procedures, such as the annealing atmosphere: King used an argon atmosphere and Matzke's work was done in high vacuum. The Matzke and King data are also in fair agreement with the uranium diffusion data of Reimann and Lundy (1969); this is shown (Fig. 6.4) in the normalized Arrhenius plot, where $\log D$ is plotted versus T_m/T rather than $1/T$.

Figure 6.3. Cation Diffusion Coefficients in ThO₂, UO₂, and ThO₂-UO₂ as a Function of Temperature.

Furuya (1968) claimed that he had separated volume diffusion from grain boundary diffusion for the diffusion of uranium in ThO₂ and in an equimolar solid solution of ThO₂-UO₂. The diffusion data for ThO₂ are discussed below, and the data for the solid solution are presented in Sect. 6.2.1(c). Furuya used ²³⁷U as the tracer isotope incorporated in UO₂, which was evaporated onto the ground surfaces of high density pellets (>98 percent of theoretical density) having an average grain size over 60 μm. Gamma-ray spectrometry was used to determine the amount of ²³⁷U penetration. Typical penetration curves showed that the logarithm of the ²³⁷U concentration varied linearly with distance in the deeper region of penetration, characteristic of grain-boundary diffusion. Near the surface, however, volume

Figure 6.4. Cation Diffusion in ThO₂ and UO₂.

diffusion was indicated from a linear plot of the log concentration versus the square of diffusion depth. These results were similar both ThO₂ and ThO₂-UO₂. Furuya (1968) reported the following equations:

$$D_v(\text{U in ThO}_2) = 1.10 \times 10^{-4} \exp[-76.4(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

at 2073 to 2273 K and

$$D_b(2a)(\text{U in ThO}_2) = 2.35 \times 10^{-9} \exp[-47.9(\text{kcal/mol})/RT] \text{cm}^3/\text{s}$$

at 2073 to 2273 K, where D_b and $2a$ are the grain-boundary diffusion coefficient and the grain boundary width, respectively. A plot of the volume diffusion coefficients is shown in Fig. 6.3.

The data of Furuya (1968) suffers from the same deficiencies as do the Hawkins and Alcock (1968) measurements, according to King (1971) in that diffusion profiles near the surface were not determined precisely; the techniques used did not permit such precision.

(c) *Thorium and Uranium Diffusion in Stoichiometric and Hyperstoichiometric $\text{ThO}_2\text{-UO}_{2+x}$*

Furuya (1968) reported both volume and grain boundary diffusion coefficients for the diffusion of ^{237}U in $\text{Th}_{0.5}\text{U}_{0.5}\text{O}_2$; these data were obtained in the same manner as those for ThO_2 . The equations presented are the following:

$$D_v(\text{U in ThO}_2\text{-UO}_2) = 7.59 \times 10^{-4} \exp[-85.9(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

at 2073 to 2573 K and

$$D_b(2a)(\text{U in ThO}_2\text{-UO}_2) = 1.04 \times 10^{-7} \exp[-64.2(\text{kcal/mol})/RT] \text{cm}^3/\text{s}$$

at 2073 to 2573 K. These data are also suspect, according to the criticism given by King (1971) and by Matzke (1976b).

The effect of hyperstoichiometry on measured cation diffusion in $\text{ThO}_2\text{-UO}_2$ solid solutions was examined by Lee and Alcock (1970). These workers measured the diffusion coefficients of ^{230}Th and ^{233}U in hyperstoichiometric $\text{Th}_{0.5}\text{U}_{0.5}\text{O}_{2+x}$ and $\text{Th}_{0.25}\text{U}_{0.75}\text{O}_{2+x}$ at 1673 K using α -ray spectrometry. The degree of nonstoichiometry, which varied from $x = \text{approximately } 0.01$ to $x = 0.22$, was established by carrying out the diffusion anneals in controlled atmospheres of CO/CO_2 gas mixtures. According to Lee and Alcock (1970) the diffusion of both the thorium and uranium tracer isotopes in the hyperstoichiometric solid solution, $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$, can be described by the expression

$$\log D = \frac{2}{5} \left(\log \frac{x}{y-x} \right) + C(T) \quad \text{Eq. (6.2)}$$

where

$C(T)$ = constant for a given temperature

x = deviation from stoichiometry

y = mole fraction of uranium.

Although there is considerable scatter in the experimental data shown in Fig. 6.5, fair agreement with Eq. (6.2) is evident.

As is seen from the data, the measured diffusion coefficients increase considerably with increase in the degree of hyperstoichiometry

Figure 6.5. Diffusion Coefficients of Thorium and Uranium as Functions of Composition and Stoichiometry at 1673 K for $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$. (After Lee and Alcock, 1970.)

and decrease slightly with increase in the mole fraction of uranium. Lee and Alcock (1970) attribute the observed increase in D with increase in x to a vacancy mechanism for cation diffusion. The increase in interstitial oxygen ion (O_i) concentration in hyperstoichiometric $\text{Th}_{1-y}\text{U}_y\text{O}_{2+x}$ leads to an increased concentration of cation vacancies and, therefore, to increased cation diffusion coefficients. Lee and Alcock suggest that the interstitial oxygen ions are associated with two U^{+5} ions in a defect complex ($\text{U}^{+5}\text{-O}_i\text{-U}^{+5}$).

The case for hyperstoichiometric UO_{2+x} is different; the measured diffusion coefficients increase anomalously at large values of x , i.e.,

$$(0.1 < x < 0.25) .$$

These results cannot be explained by a simple vacancy mechanism. Lee and Alcock (1970) suggest rather that the enhanced cation diffusion in UO_{2+x} arises from dislocations formed as a result of the incorporation of microdomains of U_4O_9 into the oxide structure.

For near-stoichiometric compositions ($x \approx 0.003$) Eq. (6.2) predicts a diffusion coefficient for thorium or uranium in the $\text{Th}_{0.5}\text{U}_{0.5}\text{O}_{2+x}$ composition of approximately $2.6 \times 10^{-15} \text{ cm}^2/\text{s}$, which is within an

order of magnitude of the data of Furuya (1968) extrapolated in temperature to 1673 K. At these relatively low temperatures ($<0.6 T_m$), however, it is unlikely that volume diffusion can be measured.

(d) *Diffusion of Other Actinides in ThO₂ and ThO₂-UO₂*

Measurements were made of the diffusion of protactinium in ThO₂ and ThO₂-UO₂ in the temperature range 2073 to 2273 K by Furuya and Yajima (1968) in a manner similar to those made for uranium diffusion by Furuya (1968). The reported diffusion equations are as follows: For volume diffusion,

$$D_v(\text{Pa in ThO}_2) = 2.91 \times 10^{-5} \exp[-75.4(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

and

$$D_v(\text{Pa in ThO}_2\text{-UO}_2) = 1.88 \times 10^{-3} \exp[-91.8(\text{kcal/mol})/RT] \text{cm}^2/\text{s}$$

For grain boundary diffusion,

$$D_b(2a)(\text{Pa in ThO}_2) = 6.66 \times 10^{-11} \exp[-30.6(\text{kcal/mol})/RT] \text{cm}^3/\text{s}$$

and

$$D_b(2a)(\text{Pa in ThO}_2\text{-UO}_2) = 5.64 \times 10^{-8} \exp[-59.7(\text{kcal/mol})/RT] \text{cm}^3/\text{s}$$

The volume diffusion data for Pa in ThO₂ and in ThO₂-UO₂ are also shown in Fig. 6.3.

6.2.3 Short Circuit Diffusion

(a) *Grain-Boundary Diffusion*

Grain-boundary diffusion coefficients are obtained indirectly. They are deduced from diffusion profiles and the assumption that both the effective grain-boundary width and the volume-diffusion coefficients are known. The effective grain-boundary width is generally assumed to be about 0.5 nm. Thus, as Matzke (1976b) pointed out, if the volume-diffusion coefficient (D_v) values used to calculate grain-boundary diffusion coefficient (D_b) values are rejected, the derived D_b values must also be rejected.

The reported information on grain-boundary diffusion in ThO₂ is summarized in Table 6.3, where it is seen that there is little agreement among the sets of data. The data of King (1971), Furuya (1968), and Furuya and Yajima (1968) were given in Sect. 6.2.1. The

TABLE 6.3—GRAIN-BOUNDARY DIFFUSION COEFFICIENTS IN ThO₂ AND ThO₂-UO₂

Diffusing Species	Matrix	D ₀ (m ² /s)	Activation Energy (J/mol · K)	Temp. Range (K)	Reference
Th	ThO ₂	6.3×10^{-5}	393	973—1173	Bannister (1975)
²²⁸ Th	ThO ₂	8.0×10^{-18}	156	2119—2318	King (1971)*
²³⁷ U	ThO ₂	2.35×10^{-13}	200	2073—2273	Furuya (1968)
²³⁷ U	ThO ₂ -UO ₂	1.0×10^{-11}	269	2073—2573	Furuya (1968)
²³³ Pa	ThO ₂	6.66×10^{-15}	128	2073—2273	Furuya and Yajima (1968)
²³³ Pa	ThO ₂ -UO ₂	5.64×10^{-12}	250	2073—2273	Furuya and Yajima (1968)

*Dislocation diffusion coefficient.

low-temperature data of Bannister (1975) were not derived from volume diffusion measurements but were calculated from kinetic data on the sintering of thoria gel.

Matzke (1976b) also estimated some grain-boundary diffusion coefficients for thorium in ThO₂ from his diffusion measurements on polycrystalline ThO₂ below 2273 K. These values were of the order of 10⁻⁷ to 10⁻⁶ cm²/s at 2273 K and 10⁻¹⁰ to 10⁻⁹ cm²/s at 1673 to 773 K.

(b) *Surface Diffusion*

Surface diffusion coefficients can be measured either by mass transfer methods (grain-boundary grooving or scratch decay) or by tracer techniques. Berman (1969) measured surface diffusion coefficients for ThO₂, UO₂, and their solid solutions at temperatures between 1873 and 2773 K in hydrogen, using the thermal grooving method developed by Mullins (1957). In this method, a polycrystalline sample with a polished surface is treated at the temperature of interest for a measured time. After treatment, the surface is examined by interface microscopy and is found to have assumed an angle, in the vicinity of grain boundaries, that represents the resultant of surface tension and grain boundary tension. The grain boundary therefore intersects the surface at the bottom of a shallow groove. The material displaced in the formation of this groove is relocated as ridges on both sides of the grain boundary, parallel to it. If the distance moved by this material is proportional to the fourth power of time, the movement can be ascribed primarily to surface diffusion. Volume diffusion through the body of the sample, and diffusion through the gaseous phase, would be expected to result in a displacement proportional to the cube of time.

In calculating the diffusion coefficient, a value of the surface tension of the material is needed. A value of 1.0 J/m² has been generally assumed for UO₂ on the basis of measurements on other refractory oxides. The work of Inoue and Matzke (1981) indicates that this is an appropriate value for ThO₂ in the temperature range of the measurements, and it appears to be an appropriate consensus value for ThO₂-UO₂ and UO₂ as well.

It could not be established unequivocally from the thoria and thoria-urania data of Berman (1969) that a fourth-power dependence on time prevailed. Nevertheless, on the assumption that the displacement is controlled principally by surface diffusion, the following expressions for the surface diffusion coefficient were calculated and reported by Berman (1969):

For UO₂,

$$D_s = 5.74 \times 10^3 \exp[-507,900/(RT)]$$

For ThO_2 ,

$$D_s = 5.21 \times 10^5 \exp[-593,700/(RT)]$$

For $\text{ThO}_2\text{-UO}_2$,

$$D_s = 8.9 \times 10^{-6} \exp[-217,500/(RT)]$$

where

D_s = surface diffusion coefficient, m^2/s

T = temperature, K

and

$$R = 8.3143 \text{ J/mol}\cdot\text{K}.$$

The expression given for the solid solutions is a fit of all the solid solution data, since the variation in D_s due to composition was found to be less than the scatter of the data. Although the activation energies for ThO_2 and UO_2 are comparable, that for the combined solid solutions is drastically different. No explanation was given for this difference.

There are no other reported surface diffusion data for thoria or thoria-urania solid solutions. The data for UO_2 are extensive but agreement among the various sets is poor. Maiya (1971) used the scratch decay technique in his experiments on UO_2 . He reached the conclusion that vapor transport predominates above about 1950 K in the grain boundary grooving method with UO_2 , and that consequently the method cannot be used for determinations of surface diffusion in this temperature range in pure urania. Thoria and the solid solutions have lower vapor pressures, and the temperature at which the thermal grooving method becomes ineffective for measuring surface diffusion would therefore be somewhat higher.

Maiya (1971) reexamined the earlier grain boundary grooving and scratch decay experiments on UO_2 , applied a vapor transport correction, and suggested the following expression for the surface diffusion coefficient for UO_2 :

$$D_s = 3.4 \times 10^5 \exp[-108(\text{kcal/mol}/RT)]\text{cm}^2/\text{s}.$$

In a subsequent assessment, Matzke (1976a) reported the preexponential factor as $5 \times 10^5 \text{ cm}^2/\text{s}$.

In an attempt to overcome the limitations of the mass-transport techniques for UO_2 , Marlowe and Kaznoff (1968) developed a tracer technique in which the sample was heated with a needle-like source of enriched UO_2 (in ^{235}U) in contact with a polished surface of natural UO_2 . The extent of surface diffusion was then determined by measuring the distribution of alpha activity outward from the point of contact. Transfer of the material through the vapor phase was minimized by sweeping the furnace atmosphere with hydrogen. Also, in this experiment, the use of a sharp needle minimized the cross section of material through which volume diffusion could take place. In a control experiment, the needle was not in contact with the surface, and it was demonstrated that no significant amount of material was transferred under these conditions. The values obtained by Marlowe and Kaznoff appeared, in their calculations, to be reasonably consistent with the results of other investigators who attempted to measure the surface diffusion coefficient by mass transfer methods.

In a critical review of tracer surface diffusion experiments on UO_2 , Olander (1981) concurred that the Marlowe and Kaznoff (1968) results reflected primarily the effects of surface diffusion. However, Olander examined in more detail the problem of calculating the surface diffusion coefficient from the tracer data. He noted, for example, that the control experiment may have demonstrated that there was no significant evaporative transfer, but it did not rule out evaporative loss from all surfaces, which may have removed some of the tracer already deposited. However, Olander established, on the basis of his own observations, that an upper limit to this loss was $1\text{ }\mu\text{m}$ from the surface for an exposure of 20 minutes at 2188 K to flowing hydrogen, —conditions corresponding to the single experiment for which Marlowe and Kaznoff give their observed tracer profile. Olander characterized this factor as “not important”; however, he retained it in his reconsideration of the 2188 K results together with other factors such as the range of alpha particles in the material, effects of cone angle and contact resistance of the source needle, and the depletion of the needle as the experiment progresses. Olander arrived at a value for the surface diffusion coefficient some 3000 times greater than that calculated by Marlowe and Kaznoff and about 4 orders of magnitude larger than that obtained by extrapolation of surface diffusion coefficients obtained from mass transfer methods at lower temperatures.

Zhou and Olander (1984) used the tracer technique to determine surface diffusion coefficients on polycrystalline UO_2 . The spreading of ^{234}U tracer on the surface of a duplex specimen made of enriched and depleted (in ^{235}U) wafers was measured, and a masking technique was used to eliminate gas phase transport. Surface diffusion coefficients were determined from the data through use of a model which included corrections for simultaneous bulk diffusion and an interface resistance between the two wafers. Surface diffusion coefficients thus

corrected ranged from about 0.1 to 2 cm²/s for temperatures from 2033 K to 2373 K. The migrating species was assumed to be the UO₂ molecule. The results can be represented by the equation

$$D_s = 50 \exp[-301(\text{kJ/mol})/RT] \text{m}^2/\text{s}$$

with a 1 to 2 order of magnitude uncertainty range. Comparison of this expression with the equations given by Maiya (1971) and Matz (1976a) shows that, although the preexponential values are similar, the activation energy for the Zhou and Olander data is considerably lower; consequently, the diffusion coefficients are greater and surface diffusion is faster.

6.3 ELECTRICAL CONDUCTIVITY

6.3.1 Introduction

Many studies have been made of the electrical and electrochemical properties of ThO₂ and ThO₂-base solid solutions, prompted by the considerable interest in these materials as high-temperature solid electrolytes. Among the extensive reviews of this work, the reader is referred, in particular, to Lasker and Rapp (1966), Rapp (1968), Etsell and Flengas (1970), Etsell (1972), Kilner and Steele (1981), Tuller (1981). However, significant findings and conclusions are summarized in this section on electrical conductivity.

6.3.2 Defect Equilibria and Electrical Conductivity

The electrical conductivity of a solid is the sum of the partial conductivities of each type of charge carrier,

$$\Sigma_{\text{total}} = \Sigma_i \sigma_i \quad \text{Eq. (6.3)}$$

where

σ_i = partial conductivities in the solid.

These charge carriers can be electronic, e.g., excess electrons in the conduction band (n-type conductivity) or positive holes in the valence band (p-type conductivity), or ionic, e.g., anion or cation interstitials and vacancies. The partial conductivities are given by the equation

$$\sigma_i = C_i Z_i e \mu_i \quad \text{Eq. (6.4)}$$

where

C_i = number of carriers of type i per m^3

Z_i = number of electronic charges, e

e = elementary charge, 1.602×10^{-19} C

μ_i = mobility of the carrier in the solid, $\text{m}^2/\text{s}\cdot\text{V}$.

In those oxides that are predominantly ionic compounds, both electronic and ionic defects are present and both can contribute to the electrical conductivity. For such mixed ionic and electronic conductors, a *transport number* is defined as the fraction of the total electrical conductivity carried by each charge carrier, i.e.,

$$t_i = \sigma_i / \sigma_{\text{total}}$$

Thus, for oxides, the ionic transport number can be expressed as

$$t_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \sigma_{\text{electron}}} \quad \text{Eq. (6.5a)}$$

and, in the case for specific ions,

$$t_{\text{anion}} = \frac{\sigma_{\text{anion}}}{\sigma_{\text{anion}} + \sigma_{\text{cation}} + \sigma_{\text{electron}}} \quad \text{Eq. (6.5b)}$$

Positive hole (p-type) conduction in oxides results from the incorporation of excess oxygen into the lattice, whereas n-type conductivity results from the loss of oxygen from the lattice. The former type is favored by a high oxygen partial pressure in the ambient atmosphere and the latter by a low oxygen partial pressure. Ionic conductivity, because it implies a high lattice defect condition, is almost always independent of oxygen partial pressure.

As discussed in Chap. 3, the predominant ionic defects in thorium are probably the anti-Frenkel type, i.e., oxygen interstitials and oxygen vacancies. Oxygen vacancies can also be introduced by doping ThO_2 with an oxide such as Y_2O_3 . The trivalent yttrium substitutes for the tetravalent thorium, and some oxygen lattice sites become vacant to maintain electrical neutrality.

The relationships between the oxygen partial pressure in the ambient atmosphere and the types of conduction processes in an oxide such as ThO_2 are summarized below. The general treatment is that given by Lasker and Rapp (1966), who developed a dilute solution model for pure and doped thorium using mass action equilibria. The Kröger-Vink notation (Kröger and Vink, 1956) is used.

Positive hole conduction can occur at high oxygen partial pressure (P_{O_2}) in pure (undoped) thoria as a result of an equilibrium between oxygen in the ambient atmosphere, interstitial oxygen ions (O_i'') in the lattice, and positive holes (h')

On the assumption that there is an infinitely dilute solution of defects such that thermodynamic activities may be replaced by concentrations, application of the mass action law leads to

$$K_1 = [O_i'']p^2(P_{O_2})^{-1/2} \quad \text{Eq. (6.7)}$$

where

p = concentration of positive holes.

To maintain electrical neutrality,

$$p = 2[O_i''] \quad ,$$

and from Eq. (6.7),

$$p \propto (P_{O_2})^{1/6} \quad .$$

On the assumption that the positive hole mobility ($\mu_{\oplus}$) is independent of the hole concentration, the p-type electrical conductivity ($\sigma_{\oplus}$) is also proportional to $(P_{O_2})^{1/6}$.

At much lower oxygen partial pressures, ThO_2 should become oxygen-deficient through formation of oxygen vacancies compensated by excess electrons. The equilibrium at high temperatures and low pressures can be represented by the equation,

where

O_O = oxygen in an oxygen lattice site

$V_O^{\bullet\bullet}$ = doubly ionized oxygen vacancy

e = excess electron.

Then, on the same assumption of an infinitely dilute solution of defects,

$$K_2 = [V_O^{\bullet\bullet}]n^2(P_{O_2})^{1/2} \quad \text{Eq. (6.9)}$$

where

n = concentration of excess electrons.

Since

$$n = 2[V_O^{\bullet}]$$

to preserve electrical neutrality,

$$n \propto (P_{O_2})^{-1/6}$$

Again, if the electron mobility $\mu_{\ominus}$ is independent of the concentration of excess electrons, the n -type electrical conductivity $\sigma_{\ominus}$ is also proportional to $(P_{O_2})^{-1/6}$.

The same Kröger-Vink formalism can be used to express the degree of hypostoichiometry x in ThO_{2-x} in terms of the oxygen partial pressure. If the oxygen vacancies are assumed to be doubly ionized, as in Eq. (6.8), x is proportional to $(P_{O_2})^{-1/6}$. As pointed out in Chap. 4, Carniglia et al (1971) obtained oxygen partial pressures in agreement with this relationship for temperatures around 1673 to 2173 K, but Ackermann and Tetenbaum (1980) found good agreement of their data with a $-1/4$ dependency at much higher temperatures (2673 to 2928 K).

As described in more detail in Sect. 6.3.3, experimental results show that, at high oxygen partial pressures, p -type conductivity appears to follow a $1/4$ power dependence on P_{O_2} rather than the $1/6$ power dependence predicted for $\sigma_{\oplus}$ from Eq. (6.7) on the assumption that $p = 2[O_i^{\bullet}]$. At intermediate oxygen partial pressures electrical conductivity is observed to be essentially independent of the oxygen partial pressure.

The P_{O_2} -independent conductivity region was confirmed to be ionic from transport number measurements made by Lasker and Rapp (1966). These authors showed that the observations of predominant ionic conduction at intermediate oxygen pressures and of p -type conduction proportional to $(P_{O_2})^{1/4}$ are consistent and can be rationalized as follows. Either of two assumptions can explain the P_{O_2} -independent region for nominally pure ThO_2 . In one view, the oxide is actually pure and the ionic conductivity is due to a very high concentration of interstitial oxygen ions and oxygen vacancies. In the alternate hypothesis, it is assumed that the nominally pure ThO_2 contains aliovalent impurity ions, and the ionic defects that compensate for these impurity ions result in predominant ionic conductivity. Although the second explanation may appear to be more realistic than the first, either one requires the concentrations of oxygen interstitials and oxygen vacancies to be independent of the oxygen partial

pressure. Then, if $[O_i'']$ is constant in Eq. (6.7), $p \propto (P_{O_2})^{1/4}$ and the p-type conductivity ($\sigma_{\oplus}$) is also proportional to $(P_{O_2})^{1/4}$. Similarly from Eq. (6.9), if $[V_O^-]$ is constant, n and $\sigma_{\ominus}$ become proportional to $(P_{O_2})^{-1/4}$.

These results are represented schematically in the Brouwer diagram (see Kilner and Steele, 1981) shown in Fig. 6.6(a). In this type of diagram the logarithm of the defect concentration is plotted as a function of the oxygen partial pressure. The logarithm of the electrical conductivity is shown schematically in Fig. 6.6(b). Three ranges are apparent: (1) At high P_{O_2} , the conductivity is due to positive holes and varies as $(P_{O_2})^{1/4}$; (2) at intermediate P_{O_2} , the conductivity is ionic, is due to intrinsic or extrinsic (induced by doping) oxygen vacancies, and is independent of the oxygen partial pressure; at low P_{O_2} , the conductivity is due to electrons and varies as $(P_{O_2})^{-1/4}$. Thus, the overall conductivity can be represented by the equation

$$\sigma_{\text{total}} = \sigma_{\text{ionic}} + \sigma_p(P_{O_2})^{1/4} + \sigma_n(P_{O_2})^{-1/4} \quad \text{Eq. (6.10)}$$

The oxygen partial pressures at which $\sigma_{\text{ionic}} = \sigma_p$ and $\sigma_{\text{ionic}} = \sigma_n$ are symbolized by $P_{\oplus}$ and $P_{\ominus}$, respectively. The ionic and p-type conductivities show weaker temperature dependence than the n-type conductivity. As a result, $P_{\oplus}$ and the p-n transition shift to higher oxygen partial pressures with increasing temperature.

Etsell (1972) reported the following approximate relations for $P_{\oplus}$ and $P_{\ominus}$ for both ThO_2 and $\text{ThO}_2\text{-Y}_2\text{O}_3$ solutions (10–20 mole percent $\text{YO}_{1.5}$):

For ThO_2 ,

$$\log P_{\oplus} = -4.5$$

and

$$\log P_{\ominus} = -\frac{60.5 \times 10^3}{T} + 23.3 \quad \text{Eq. (6.11)}$$

For $\text{ThO}_2\text{-Y}_2\text{O}_3$,

$$\log P_{\oplus} = 1.8$$

and

$$\log P_{\ominus} = -\frac{57.9 \times 10^3}{T} + 12.4, \quad \text{Eq. (6.12)}$$

where $P_{\oplus}$ and $P_{\ominus}$ are in atmospheres. Etsell derived these relationships by assuming certain values for the activation energies for p-type and n-type conduction processes.

Figure 6.6. Variation with Oxygen Partial Pressure of (a) Defect Concentration and (b) Electrical Conductivity. (Kilner and Steele, 1981. Reprinted by permission of Academic Press, Inc.)

6.3.3 Electrical Conduction in Pure and Doped ThO₂

Many authors (Subbarao et al, 1965; Steele and Alcock, 1965; Lasker and Rapp, 1966; Bauerle, 1966; Bransky and Tallan, 1970; Choudhury and Patterson, 1974; Maiti and Subbarao, 1976b; Fujimoto and Tuller, 1979, among others) have confirmed that, at high temperatures, ThO₂ and ThO₂-base solid solutions show mixed ionic and electronic conductivity. They have not agreed, however, the precise nature of the oxygen partial pressure dependence, on the presence or absence of an n-type region at very low oxygen partial pressures, or whether the pressure dependence is the same for "pure" ThO₂ as it for ThO₂-base solid solutions.

Early studies of the electrical properties of pure and doped thoria were reviewed by Bates and Schemmel (1972). Rudolph (1959) reported Seebeck measurements that indicated pure ThO₂ to be a p-type conductor in pure oxygen, and electrical conductivity measurements that showed a P_{O₂}-dependence for pure ThO₂ ranging from 1/5.5 to 1/6 at high oxygen partial pressures.

In studies of yttria-doped thoria, Subbarao et al (1965) and Wimmer et al (1967) showed that yttrium substitution for thorium is compensated by oxygen vacancies (see Fig. 4.23 of Chap. 4). Electrical conductivity was found to increase with increased yttria content up to about 5 mole percent YO_{1.5}. Ionic transport measurements showed that the electrical conductivity was only partially ionic. Transport numbers increased with both temperature and yttrium content; t_{ion} was 0.05 for undoped ThO₂ at 1273 K and 0.69 for the 5 mole percent YO_{1.5} addition at 1673 K.

Steele and Alcock (1965) explored the electrical properties of thoria doped with either yttria, calcia, or lanthana and found the type of dopant to have an appreciable effect on the nature and extent of electric conductivity. Five compositions of yttria-doped ThO₂ (1, 4, 10, 15, and 25 mole percent YO_{1.5}) were studied at 1273 K. All compositions showed p-type conductivity at high oxygen pressures and a maximum in conductivity at 15 mole percent YO_{1.5}. Some of these data shown in the plot of conductivity as a function of oxygen partial pressure in Fig. 6.7. Thoria samples doped with 10 and 15 mole percent LaO_{1.5} were found to have higher conductivity than the yttria-doped samples having the same amount of dopant. Three compositions of calcia-doped thoria (2, 5, and 25 mole percent) were found to have a lower total but a higher electronic conductivity than either the La or Y-doped materials.

Lasker and Rapp (1966) carried out the first systematic study of the effects of temperature, oxygen partial pressure, and composition on the conductivity of ThO₂ and ThO₂-Y₂O₃ solid solutions. They developed a dilute solution model (outlined in Sect. 6.3.2) to explain their observations, some of which are shown in Figs. 6.8, 6.9, and 6.10.

The total conductivity (AC) for nominally pure thoria is shown in Fig. 6.8, plotted as a function of oxygen partial pressure ($1\text{--}10^{-27}$ atm) at various temperatures (1073—1373 K). The total conductivity in the high oxygen pressure range (10^{-6} atmosphere to 1 atmosphere) follows a $1/4$ power dependence on P_{O_2} , suggesting p-type conductivity. Lasker and Rapp showed data of Rudolph (1959) and of Steele and Alcock (1965) on their plot.

At intermediate oxygen partial pressures (10^{-10} to 10^{-20} atmosphere) the conductivity is seen to be essentially independent of the oxygen partial pressure. Lasker and Rapp showed that this plateau in conductivity represents the P_{O_2} -independent ionic contribution from results of oxygen ion transport number (t_{O}) measurements at 1273 K as a function of oxygen partial pressure. As shown in Fig. 6.9, the oxygen ion transport number reaches unity at pressures of about 10^{-6} atmosphere and less, depending on the amount of added yttria.

In contrast to that of the oxygen ion, the contribution of the thorium ion to the ionic conductivity of ThO_2 is negligibly small. In a study that combined electrolysis and dilatometry, Duclot and Hammou (1978) measured the thorium ion transport number (t_{Th}) in the temperature range 1273 to 1773 K at oxygen partial pressures ranging from 1 to 10^{-12} atmosphere; they obtained values of the order of 10^{-7} . Thus, in the case of ThO_2 , the ionic and oxygen transport numbers are effectively the same.

Results of AC conductivity measurements for the $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solutions are shown in Fig. 6.10. For all compositions studied (up to 15 mole percent $\text{YO}_{1.5}$) the total conductivities increased, and the range of the ionic region extended to higher oxygen partial pressures with increase in the yttria concentration. These results suggest that the ionic contribution to the electrical conductivity increases with increasing amounts of the aliovalent dopant. This effect is seen more clearly in Fig. 6.11, which is a plot of the ionic conductivity as a function of the mole percent of anion vacancies introduced through additions of either Y_2O_3 or CaO . The other data for the Y_2O_3 dopant are from Steele and Alcock (1965), Bauerle (1966), and Hammou (1975); the data for the CaO additions are from Steele and Alcock (1965) and Maiti and Subbarao (1976b).

On the assumption of the ideal solution model, the ionic conductivity should be proportional to the concentration of anion vacancies, and to the dopant content. It is seen, however, that the ionic conductivity is not a linear function of the amount of additive for concentrations exceeding the equivalent of one percent of anion vacancies. This is confirmed for various temperatures from the work of Hammou (1975) shown in Fig. 6.12. In this work, compositions from $\text{ThO}_2\text{-0.05}$ to 21.45 mole percent $\text{YO}_{1.5}$ were studied at oxygen partial pressures from one to 10^{-20} atmosphere over the temperature range 1318—1661 K. Hammou found that the ionic conductivity varied

Figure 6.7. Electrical Conductivity as a Function of Oxygen Partial Pressure for ThO_2 and $\text{ThO}_2\text{-YO}_{1.5}$ Compositions at 1273 K. (After Steele and Alcock, 1965. Reprinted with permission from Metallurgical Transactions, a publication of the Metallurgical Society of AIME.)

Figure 6.8. Total Conductivity (AC) for ThO_2 as a Function of Temperature and Oxygen Partial Pressure. (After Lasker and Rapp, 1966.)

Figure 6.9. Ionic Transport Number as a Function of Oxygen Partial Pressure at 1273 K for ThO_2 and $\text{ThO}_2\text{-YO}_{1.5}$ Compositions. (After Lasker and Rapp, 1966.)

Figure 6.10. Conductivity (AC) as a Function of Oxygen Partial Pressure at 1273 K for ThO_2 and $\text{ThO}_2\text{-YO}_{1.5}$ Compositions. (After Lasker and Rapp, 1966.)

Figure 6.11. Ionic Conductivity of $ThO_2-Y_2O_3$ and ThO_2-CaO as a Function of Mole Percent Anion Vacancies at 1273 K; Data of Hammou (1975) are at 1318 K.

linearly only for low dopant concentration, e.g., for amounts from 0.05 to 1.0 mole percent $YO_{1.5}$. The ionic conductivity curves showed maxima at approximately 15 mole percent $YO_{1.5}$.

Bauerle (1966) measured the electrical conductivity of nominally pure ThO_2 and $ThO_2-Y_2O_3$ solid solutions at 1273 K and at oxygen partial pressures ranging from 1 to about 10^{-15} atmosphere. The data for total conductivity were described by the expression

$$\sigma = \sigma_1 + \sigma_2(P_{O_2})^{1/4}.$$

Figure 6.12. Ionic Conductivity as a Function of Composition for $\text{ThO}_2\text{-Y}_2\text{O}_3$ at Various Temperatures. (After Hammou, 1975. Reprinted by permission of Société de Chimie Physique.)

The term σ_1 was interpreted as the ionic contribution, i.e., the oxygen ion vacancy conductivity fixed by the cation composition. The term $\sigma_2(\text{P}_{\text{O}_2})^{1/4}$ was interpreted as the positive hole conductivity resulting from the incorporation of excess oxygen into the lattice vacancies.

Figure 6.13 is a plot of the ionic conductivity portion of the conductivity data. Bauerle (1966) pointed out that the nominally pure ThO_2 data (the data marked $\text{ThO}_2(\text{I})$, $\text{ThO}_2(\text{II})$, and $\text{ThO}_2(\text{III})$ on the plot for three samples) fall on the line extrapolated from the high dopant concentration down to the range of 200–400 ppm impurities, a quantity similar to that determined by spectrographic analysis. He concluded from these data that the ionic conductivity in nominally pure ThO_2 results not from intrinsic Frenkel defects but from the

Figure 6.13. Ionic Component of Conductivity at 1273 K as a Function of ThO₂ and ThO₂-YO_{1.5} Compositions. (After Bauerle, 1966. Reprinted by permission of American Institute of Physics.)

aliovalent impurities that are introduced inadvertently. Thus, the lower valent cation impurities in so-called *pure* thoria cannot be neglected as contributors to ionic conductivity.

The n-type conduction region, which is expected to occur only at very low oxygen partial pressures, went undetected by Lasker and Rapp (1966) and by Bauerle (1966). Bransky and Tallan (1970) did detect this region but only to a limited extent and only at the highest temperatures explored. Bransky and Tallan (1970) made electrical conductivity and thermoelectric power measurements simultaneously on very pure ThO₂ (<75 ppm total metallic impurities and <15 ppm nonmetallic impurities) at temperatures ranging from 1273 to 1873 K at oxygen partial pressures of 1 to 10⁻²² atmosphere. Total conductance results plotted as a function of oxygen partial pressure

Figure 6.14. Total Conductance of ThO_2 as a Function of Oxygen Partial Pressure at 1273–1873 K. (After Bransky and Tallan, 1970. Courtesy, American Ceramic Society.)

Figure 6.14) show the three regions characteristic of the three different conduction mechanisms at the highest temperature only.

At the higher oxygen partial pressures (10^{-3} to one atmosphere) there is a $(P_{\text{O}_2})^{1/5}$ dependence, corresponding (according to results of thermoelectric power measurements) to positive hole conduction. The characteristic pressure-independent ionic conductivity region is observed at lower oxygen partial pressures. The width of this ionic conduction region decreases with increasing temperature. Bransky and Tallan (1970) suggest that this decrease is caused by the rapid increase in n-type electronic conduction with increasing temperature. At low oxygen partial pressures ($<10^{-8}$ atmosphere) but at high temperatures ($T \geq 1673$ K) there is a region of n-type electronic conductivity. Bransky and Tallan (1970) interpret the data as following a $(P_{\text{O}_2})^{1/6}$ dependence.

The measurements of Hammou et al (1971) of the electrical conductivity of nominally pure ThO_2 are in qualitative agreement with the results of Bransky and Tallan in showing the n-type region at the higher temperatures (1586 to 1788 K) but at much higher oxygen partial pressures. The data for the other regions are qualitatively similar to those previously reported by other investigators.

An attempt to obtain a more exact delineation of the boundaries of the various conduction regions in undoped ThO_2 was made by Choudhury and Patterson (1974). In this work, conductivity (AC), measurements were made under reducing conditions at temperatures from 1073 to 1373 K on polycrystalline disks fabricated from pure (99.94 percent) ThO_2 powder. The results are shown for two separate ThO_2 batches in Fig. 6.15. The $(P_{\text{O}_2})^{1/4}$ branch resulting from p-type conduction is seen at the higher pressure region. Similarly the P_{O_2} -independent ionic conductivity is shown by the horizontal region in the intermediate pressure range. The rising branch at the lowest oxygen pressures could not be determined with any precision. Choudhury and Patterson (1974) noted that the platinum leads invariably failed before equilibrium could be attained under such extreme reducing conditions, and concluded that the n-type conductivity region could not be established with any certainty from AC conductivity measurements alone.

Choudhury and Patterson (1974) showed Arrhenius-type plots of ionic conductivity in which they compared their data with those of Lasker and Rapp (1966) and Bauerle (1966). The Lasker and Rapp data were the minima of the reported isotherms for the total electrical conductivity; the Bauerle data was a single point at 1273 K which fell on the ionic conductivity line that represented the Lasker and Rapp data. Choudhury and Patterson (1974) expressed the sets of data by the following expressions:

$$\log \sigma_{\text{ion}} (\text{batch 1}) = 1.9 - 44.3 \times 10^3 / 4.575 T$$

$$\log \sigma_{\text{ion}} (\text{batch 2}) = 1.7 - 41.6 \times 10^3 / 4.575 T$$

$$\log \sigma_{\text{ion}} (\text{Lasker and Rapp}) = 1.3 - 34,000 / 4.575 T$$

Effects of calcia dopant on the electrical behavior of thoria were examined by a number of authors, including, among others, Steele and Alcock (1965), Mehrotra et al (1973) and Maiti and Subbarao (1976a and 1976b). Although no direct density measurements similar to those made on Y_2O_3 -doped ThO_2 by Subbarao et al (1965) and by Wimmer et al (1967) have been made on CaO -doped ThO_2 , it is very likely that electrical neutrality is maintained in ThO_2 - CaO by

Figure 6.15. Total AC Conductivity as a Function of Oxygen Partial Pressure for Two Batches of ThO_2 Specimens. (Choudhury and Patterson, 1974; Courtesy, American Ceramic Society.)

formation of oxygen vacancies. Wachtman (1963) assumed oxygen vacancies associated with Ca^{+2} ions to explain internal friction and dielectric loss peaks in ThO_2 -1.5 mole percent CaO .

Mehrotra et al (1973) measured the total conductivity (AC) of ThO_2 and CaO -doped ThO_2 in air at 873 to 1673 K and reported that conductivity increases steadily with composition at each temperature up to 7 mole percent CaO and then decreases. They suggested a solubility limit in ThO_2 of somewhere between 5 and 10 mole percent CaO from X-ray diffraction measurements; they had observed an extra peak corresponding to that for CaO in a 10 mole percent CaO sample but not in a 5 mole percent CaO specimen. However, there are still some uncertainties concerning the solid solubility limits for CaO in ThO_2 (see discussions in Chaps. 4 and 8).

Mehrotra et al (1973) explained the observed lower conductivities of ThO_2 - CaO in comparison to those for ThO_2 - Y_2O_3 in terms of some impurity-defect interaction. They reasoned that the association of the Ca^{2+} ion with O^{2-} vacancies is more probable than that of the $(\text{Y}^{3+}\cdot\text{O}^{2-})$ complex and that the movement of the oxygen anion is easier in ThO_2 - Y_2O_3 than in ThO_2 - CaO because the interionic spacing between the Th^{4+} and Y^{3+} ions is more than that between the Th^{4+} and Ca^{2+} ions.

Maiti and Subbarao (1976b) measured the electrical conductivities of ThO_2 doped with 1 to 15 mole percent CaO over the temperature range 873 to 1673 K at oxygen partial pressures from 1 to 10^{-25} atmosphere. A typical plot of electrical conductivity as a function of oxygen partial pressure (Fig. 6.16) shows two regions. In the first region, at the higher oxygen partial pressures, electrical conductivity decreases with decreasing P_{O_2} with a slope of 1/5 for the "pure" and the slightly CaO -doped ThO_2 ; the slope decreases to 1/8 for the more heavily doped materials. In the second region, at low P_{O_2} , conductivity is independent of oxygen partial pressure. The P_{O_2} values for the beginning of the second region are functions of both the impurity content and the temperature.

The results of transport number determinations made by Maiti and Subbarao (1976b) at two temperatures (1073 and 1273 K) are shown in Fig. 6.17. The value of the oxygen ion transport number, t_{ion} , increases with decreasing P_{O_2} and becomes unity when the conductivity becomes independent of pressure. The addition of CaO increases the oxygen ion transport number at each oxygen partial pressure. With the addition of 7 mole percent CaO , the conductivity becomes fully ionic below about 10^{-6} to 10^{-8} atmosphere.

The n-type conductivity is generally viewed as electronic in origin. However, Fujimoto and Tuller (1979) suggest that this may not be the case for ThO_2 doped with a multivalent cation such as cerium. The total electrical conductivity for ThO_2 doped with 2 mole percent Ce was found to show what appeared to be a p→n transition, i.e., the ionic

plateau region in the plot of conductivity versus P_{O_2} was absent. The onset of n-type conduction ($\sigma \propto (P_{\text{O}_2})^{-1/2}$) shifted to a higher oxygen partial pressure with increasing temperature. Fujimoto and Tuller (1979) attribute this n-type conduction not to enhanced electron generation but to pure ionic conduction, since ionic transport number measurements showed that t_{ion} reached a value of unity at oxygen partial pressures $\leq 10^{-8}$ atmosphere at 1273 K.

Figure 6.16. Electrical Conductivity of $\text{ThO}_2\text{-CaO}$ Solid Solutions as a Function of Oxygen Partial Pressure at 1273 K. (After Maiti and Subbarao, 1976b. Reprinted by permission of The Electrochemical Society, Inc.)

Figure 6.17. Ionic Transport Numbers for ThO₂-CaO Solid Solutions as a Function of Oxygen Partial Pressure at (a) 1073 K and (b) 1273 K. (After Maiti and Subbarao, 1976b. Reprinted by permission of The Electrochemical Society, Inc.)

The effect of higher oxygen pressures (0.2 to 500 atmospheres) on the total conductivities (AC) of $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solutions was investigated by Iqbal and Baker (1971). Two compositions (1.5 and 15 mole percent $\text{YO}_{1.5}$) were studied over the temperature range 1073 to 1373 K. Results (see Fig. 6.18) show that the conductivity is proportional to $(P_{\text{O}_2})^{1/4}$ at moderate pressures, but, at the highest pressure and for those samples containing the lower amount of yttria, conductivity is proportional to $(P_{\text{O}_2})^{1/2}$. This increase in proportionality at the higher pressures is difficult to explain. Iqbal and Baker suggest, as possibilities, the formation either of a large number of anion defect complexes of the type that could accommodate an O_2 molecule, or of positive holes from the formation of additional thorium vacancies.

Activation energy values for electrical conductivity, as determined by various authors for nominally pure ThO_2 or for ThO_2 doped with CaO or Y_2O_3 , are in most cases in the range of 1.0 to 1.5 eV. However, these values vary not only with composition and oxygen partial pressure, as is expected for different conduction processes, but also with temperature range, i.e., there are breaks in the Arrhenius-type plots. Also, it is not always clear whether the stated activation energies are for p-type hole conduction (ΔH_p), ionic conduction (ΔH_i), n-type electron conduction (ΔH_n), or mixtures of these.

For nominally pure ThO_2 , Bransky and Tallan (1970) reported activation energies of 1.0 and 0.9 eV, respectively, for p-type and ionic conductivities. They also estimated a value of about 3 eV for n-type conduction, which according to their measurements begins to appear at very low oxygen partial pressures above 1573 K. Hammou et al (1971) obtained activation energies for p-type conduction of 0.89 to 1.03 eV for temperatures below 1423 K and 0.79 to 0.91 eV for temperatures above 1473 K. Mehrotra et al (1973) reported what appears to be p-type conduction activation energies of 0.95 eV above 1373 K and 1.32 eV below 1373 K. Choudhury and Patterson (1974) reported ionic conductivity activation energies of 1.80 and 1.92 eV (41.6 and 44.3 kcal/mol) from their work and 1.47 eV (34.0 kcal/mol) from the work of Lasker and Rapp (1966). Maiti and Subbarao (1976b) showed three values for the activation energy for what seems to be ionic conduction: 0.99 eV at "low" temperature (873–950 K); 1.80 eV at "intermediate" temperature (950–1200 K); and 1.28 eV at "high" temperature (1200–1673 K).

In the case of ThO_2 doped with Y_2O_3 there seems to be reasonable agreement among the few sets of data on the activation energies derived from electrical conductivity measurements. Lasker and Rapp (1966) obtained a value of 1.2 eV from the "partial" ionic conductivity activation energy for $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solutions having $\text{YO}_{1.5}$ contents from 1.5 to 25.0 mole percent. For the 0.84 mole percent $\text{YO}_{1.5}$ composition an activation energy of 1.46 eV was found. Steele and Alcock (1965) reported values of 1.4 and 1.0 eV, respectively, for the

Figure 6.18. Conductivities of ThO_2 -1.5 and of ThO_2 -15 Mole Percent $\text{YO}_{1.5}$ as Functions of Oxygen Pressure and Fugacity. (After Iqbal and Baker, 1971. Reproduced with permission of the British Ceramic Society.)

1.0 and 15 mole percent YO_{1.5} compositions. Their values for p-type conductivity activation energies were independent of composition and were about 1.1 eV. Wimmer et al (1967) reported a value of 1.0 to 1.1 eV for the 13 mole percent YO_{1.5} composition.

For the CaO-doped ThO₂, Mehrotra et al (1973) reported activation energies ranging from 1.06 to 1.26 eV above 1373 K and 1.21 to 1.31 eV below 1373 K. Maiti and Subbarao (1976) observed three temperature regions with different activation energies: (1) a high-temperature region (1200 to 1673 K) where conductivity is attributed to dissociated vacancies, (2) an intermediate region (950 to 1200 K) where associated vacancy-impurity complexes dominate, and (3) a low temperature region (873 to 950 K) where grain boundary effects appear to become significant.

An estimate for the activation energy for electron conduction (ΔH_n) in nominally pure ThO₂ was made by Etsell (1972) on the assumptions that

$$\Delta H_n + \Delta H_p = E_g,$$

where

E_g = energy gap between the conduction band and the valence band,

and that

$$\Delta H_p = 1 \text{ eV}.$$

Etsell chose a value of 5 eV for E_g from the optical absorption data of Bates (1967) and therefore obtained 4 eV for ΔH_n , a value considerably higher than the 3 eV estimated by Bransky and Tallan (1970) from their electrical property measurements. Note, however, that if the Childs et al (1972) value for the energy gap (5.82 eV, see Chap. 3) is chosen, ΔH_n becomes 4.8 eV, increasing the discrepancy between the observed and the estimated values for ΔH_n , the activation energy for n-type electron conduction.

6.3.4 Electrical Conductivities of ThO₂-UO₂ Solid Solutions

The electrical conductivities of ThO₂-UO₂ solid solutions were measured by Lee (1973) as functions of oxygen partial pressure over the temperature range 1073 to 1473 K. One series of measurements was performed in a stream of hydrogen, and a second series was made in atmospheres of CO/CO₂ gas mixtures.

The experimental data obtained from the first series are given in the Arrhenius plot shown in Fig. 6.19. The electrical conductivities of UO₂ and UO₂-rich thoria-urania solutions are similar, showing essentially a single activation energy and a decrease in conductivity with

Figure 6.19. Electrical Conductivities of ThO_2 , UO_2 , and $Th_{1-y}U_yO_2$ as Functions of Temperature. (After Lee, 1973. Courtesy, Journal of Nuclear Materials.)

a decrease in UO_2 content. The ThO_2 -rich thoria-urania solutions show two regions of different activation energies, whereas the data for ThO_2 suggest a single activation energy. The activation energy values for all the compositions as given by Lee (1973) are shown in Table 6.4.

Some results from the second set of experiments are shown in Fig. 6.20, a plot of conductivities at 1273 K of the various compositions as a function of oxygen partial pressure. Again, the plots of the data for the UO_2 -rich thoria-urania solutions have similar shapes. At low oxygen pressures, where presumably the compositions are not oxidized, the conductivities show pressure-independent regions. The conductivities increase rapidly with increase in pressure and

Figure 6.20. Electrical Conductivities of ThO_2 , $(\text{Th}_{1-y}\text{U}_y\text{O}_{2+x})$ and UO_{2+x} as Functions of Oxygen Partial Pressure at 1273 K. (After Lee, 1973. Courtesy, Journal of Nuclear Materials.)

TABLE 6.4—ACTIVATION ENERGIES (eV) FOR ELECTRICAL CONDUCTIVITY OF $\text{Th}_{1-y}\text{U}_y\text{O}_2$ SOLID SOLUTIONS*

Composition	Region 1	Region 2
ThO_2	—	1.90
$\text{Th}_{0.85}\text{U}_{0.15}\text{O}_2$	0.40	1.59
$\text{Th}_{0.75}\text{U}_{0.25}\text{O}_2$	0.42	1.27
$\text{Th}_{0.5}\text{U}_{0.5}\text{O}_2$	0.29	—
$\text{Th}_{0.25}\text{U}_{0.75}\text{O}_2$	0.26	—
UO_2	0.24	—

*Lee (1973)

appear to level off at the highest oxygen partial pressures. For $\text{Th}_{0.75}\text{U}_{0.25}\text{O}_{2+x}$, conductivities are unlike those for the UO_2 -rich compositions but resemble that of ThO_2 , which shows the characteristic $(P_{\text{O}_2})^{1/4}$ dependence at high oxygen pressures (p-type conductivity) and the pressure-independent region at low oxygen pressures (ionic conductivity). The width of the ionic conductivity region decreases with increasing UO_2 content.

According to Lee (1973), the electrical conductivities for the urania-rich hyperstoichiometric solid solutions are proportional to $(P_{\text{O}_2})^{1/2}$ in the range of $0.01 < x < 0.1$. With increase in the amount of ThO_2 , the pressure dependence of the conductivity decreases, becoming proportional to $(P_{\text{O}_2})^{1/4}$ for ThO_2 . Lee interprets the p-type conduction at high oxygen partial pressures of ThO_2 and ThO_2 -rich solutions as resulting from the incorporation of excess oxygen into oxygen vacancies.

6.3.5 Ionic Conductivity and Diffusion

Oxygen ion diffusivity and ionic conductivity in ThO_2 are related through the general equation for the electrical conductivity of a charged species (Eq. (6.4), namely $\sigma_i = C_i Z_i e \mu_i$). The Nernst-Einstein equation relates diffusion (D_i) and mobility (μ_i) of the charge carrier by the expression

$$D_i = \frac{k T \mu_i}{Z_i e} \quad \text{Eq. (6.13)}$$

On combining Eqs. (6.4) and (6.13), the following expression is obtained:

$$D_i = \frac{k T \sigma_i}{C_i (Z_i e)^2} \quad \text{Eq. (6.14)}$$

Using this equation the following assumptions are made:

1. The charged species is the doubly-charged oxygen anion (O⁻²) having an ionic transport number equal to one.
2. The self-diffusion coefficient for the oxygen ion is equal to the diffusion coefficient defined by Eq. (6.13). This implies that diffusion is random, i.e., the correlation factor, *f*, that relates random diffusion to tracer atom diffusion in a cubic crystal, is equal to unity.
3. The product *Tσ_i* has the same temperature dependence as *D_i*. Using these assumptions Eq. (6.14) is transformed, for application to oxygen ion diffusivity and conductivity in ThO₂, to the expression

$$D_o^s = \frac{k T \sigma_{\text{ionic}}}{4 C_o e^2} \quad \text{Eq. (6.15)}$$

where

- D_o^s* = oxygen ion self-diffusion coefficient, m²/s
k = Boltzmann's constant = 1.38 × 10⁻²³ J/K
T = temperature, K
σ_{ionic} = ionic conductivity, S/m
C_o = number of oxygen ions per unit volume
 = 4.56 × 10²⁸/m³
e = 1.602 × 10⁻¹⁹ C.

The electrical conductivity data (Lee, 1973) for ThO₂ from Fig. 6.19 are replotted as log *σT* versus reciprocal temperature in Fig. 6.21. The activation energy for ionic conductivity is 192.6 kJ/mol (2.0 eV), in good agreement with the Ando et al (1976) reported value of 208.8 kJ/mol (2.2 eV) for the high temperature portion of the oxygen ion diffusion data. This good agreement supports the third assumption outlined above.

Shown in Fig. 6.22 is a comparison of the diffusion coefficients calculated from various electrical conductivity measurements with the measured oxygen ion diffusion coefficients; this plot is similar to that shown by Ando and Oishi (1981). The diffusion coefficients calculated from the Lee (1973) electrical conductivity data agree in magnitude as well as in activation energy with the high-temperature

Figure 6.21. Electrical Conductivity of ThO_2 versus Reciprocal Temperature. (After Lee, 1973.)

measurements of Ando et al (1976); those calculated from the Lasker and Rapp (1966) conductivity data agree in magnitude, but not in activation energy. Also shown on the plot are diffusion coefficients calculated from other sets of conductivity data.

6.4 THERMAL CONDUCTIVITY OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

6.4.1 Introduction

Since there are many reviews, assessments, and critiques of the thermal conductivity of oxide ceramic nuclear fuels, the book editors have chosen only to summarize highlights of previously published reviews. For thorough examinations of the data for UO_2 , the reader is referred to Brandt et al (1976), Fink et al (1981a), and Hyland (1983); for reviews of the data for ThO_2 and $\text{ThO}_2\text{-UO}_2$ solid solutions, to Belle et al (1967), Berman et al (1972), and Belle and Berman (1982).

Figure 6.22. Comparison of Calculated (Lasker and Rapp, 1966; Lee, 1973; Choudhury and Patterson, 1974) with Measured (Ando et al, 1976) Oxygen Ion Diffusion Coefficients in Thoria.

Heat transport through materials is described by two properties: thermal conductivity λ (under steady-state conditions) and thermal diffusivity α (under transient conditions). The two properties are related by the expression

$$\lambda = \alpha \rho C_p \quad \text{Eq. (6.16)}$$

where, for the material in question,

ρ = density

C_p = specific heat at constant pressure.

It is possible to determine thermal conductivities at very high temperatures, where direct steady-state measurements of thermal conductivity are very difficult, from thermal diffusivity measurements if the density and the specific heat are known or can be measured. However, thermal conductivity as determined from Eq. (6.16) is a derived quantity and therefore is subject not only to the errors of the individual measurements but to the deficiencies of the particular models or equations chosen to fit the data.

6.4.2 Heat Transfer in Oxide Ceramics

In crystalline solids, heat can be transported by at least three different mechanisms: (1) transport by phonons (lattice conduction, λ_r), (2) transport by photons (radiant heat transfer, λ_r), and (3) transport by electrons (electron conduction, λ_e). Phonons, which are quantized elastic waves in a crystal, are analogous to photons, which are quantized electromagnetic radiations. The relative contribution of each mechanism to the overall thermal conductivity depends on certain fundamental properties of the solid. Moreover, each contribution is temperature dependent, with each mechanism having a different functional dependence. For dielectric solids, such as the oxide ceramics, the lattice contribution to the thermal conductivity is predominant in the low to medium temperature range. At high temperatures, radiation and electronic contributions to thermal conduction can occur. An additional factor complicating the thermal conductivity of polycrystalline oxide ceramics such as ThO_2 and UO_2 is the effect of porosity.

(a) Lattice Conduction (Transport by Phonons)

According to kinetic gas theory, above the Debye temperature the lattice thermal conductivity for an ideal lattice can be expressed by

$$\lambda_r = 1/3 C_v V L \quad \text{Eq. (6.1)}$$

where

λ_r = lattice thermal conductivity, W/m·K

C_v = specific heat at constant volume, J/m³·K

V = velocity of sound in solid, m/s

L = mean free path of scattered waves (the phonon wavelength), m.

Above the Debye temperature, the thermal conductivity of electric insulators decreases with increasing temperature. Since an increase in temperature increases the atomic vibrational frequency, an in-

crease in the wave scattering is anticipated. This wave scattering has been shown to be due to phonon interactions (Peierls, 1929). Thermal energy is transferred by the *umklapp process*, in which two phonons interact to form a third. According to the theory, the lattice thermal conductivity should be inversely proportional to the absolute temperature. However, with increasing temperature the phonon wavelength is also decreased. When the phonon wavelength becomes less than the mean distance between scattering centers, the lattice thermal conductivity reaches a minimum value. For crystalline solids the minimum distance between scattering centers is the interatomic distance. Therefore, the minimum value of the lattice conductivity can be estimated from Eq. (6.18), where the phonon mean free path L is replaced by the lattice parameter, a_0 , i.e.,

$$(\lambda_r)_{\min} = 1/3 C_v V a_0 \quad \text{Eq. (6.18)}$$

Addition of impurity atoms can affect phonon scattering and thus present an additional resistance to the lattice conductivity. The total thermal resistivity can then be expressed as

$$R_r = A + BT \quad , \quad \theta_D < T < T_0 \quad \text{Eq. (6.19)}$$

where

$$R_r = \text{lattice thermal resistivity} = \frac{1}{\lambda_r}$$

A = athermal impurity contribution

B = temperature coefficient of thermal resistivity

T = temperature, K

θ_D = Debye temperature, K

T_0 = temperature, K, at which $L = a_0$.

The factor B of the temperature dependent term is unique for each material and characterizes the *intrinsic* contribution from anharmonic phonon-phonon interactions. The A term characterizes phonon scattering by various kinds of lattice imperfections and is related to the influence of impurities and microstructural features such as grain size. Although the value of A is expected to increase with increasing impurity content, the particular functional dependence on concentration is not known.

(b) Radiant Heat Transfer (Transport by Photons)

Just as the vibrational energy in solids is responsible for phonon conduction, so the higher frequency electromagnetic radiation energy is responsible for photon conduction. Although the latter fraction of

the total energy is small, it can become important at high temperatures because it is proportional to the fourth power of temperature. The resulting radiation contribution to the thermal conductivity can be important for an electrically nonconducting solid which is transparent to infrared radiation. The radiant energy contribution to the thermal conductivity is given by the expression (Kingery et al, 1976)

$$\lambda_r = \frac{16\sigma_s n^2 T^3 L_r}{3} = \frac{16\sigma_s n^2 T^3}{3k} \quad \text{Eq. (6.20)}$$

where

λ_r = the radiant energy contribution to thermal conductivity

L_r = the mean free path of the radiant energy, m

k = extinction coefficient, m^{-1}

σ_s = Stefan-Boltzmann constant = $5.6697 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$

n = index of refraction

T = temperature, K.

This equation for the radiation contribution is strictly valid for an extinction coefficient that is independent of wavelength, i.e., the material is a "gray absorber". It is also assumed that the refractive index is independent of wavelength and that both properties are independent of temperature. The effectiveness of the radiant energy transfer process depends on the mean free path of the radiant energy. For opaque materials ($L \approx 0$) energy transfer by this process is negligible. Similarly, if the mean free path is long compared with the size of the system, the interaction of energy with material is negligible, and radiation energy transfer is a surface or boundary phenomenon. It is only when the mean free path reaches macroscopic dimensions which are small, compared with the sample size, that the photon conduction process within the material is significant.

The absorption and scattering of photons in the visible and near-infrared region of the spectrum determine the photon conductivity. For materials with low values of the extinction coefficient k , photon conduction becomes important at low and intermediate temperatures; for materials with high values of the extinction coefficient or substantial scattering, photon conductivity does not become significant until very high temperatures are reached. In general, for sintered oxides the photon energy transfer process only becomes important at temperatures greater than about 1800 to 2000 K.

(c) *Electron Conduction (Transport by Electrons)*

Thermal transport by electrical charge carriers can also contribute to thermal conduction at high temperatures. This contribution is given by the Wiedemann-Franz law

$$\lambda_e = L\sigma T \quad \text{Eq. (6.21)}$$

where

λ_e = electronic component to the thermal conductivity, W/m·K

L = Lorenz number, V²/K²

σ = electrical conductivity, S/m

T = temperature, K.

For conduction by one charge carrier, as in an extrinsic semiconductor,

$$L = 2\left(\frac{k}{e}\right)^2,$$

where

k = Boltzmann's constant

e = electronic charge.

If, however, the material is an intrinsic semiconductor, equal numbers of holes and electrons are generated, and both carriers contribute to electrical and thermal conduction. In this case, the relationship between electrical and thermal conductivity has the form (Drabble and Goldsmid, 1961),

$$\lambda_e = 2\left(\frac{k}{e}\right)^2 T(\sigma_n + \sigma_p) + \left(\frac{k}{e}\right)^2 T\left(\frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p}\right)\left(\frac{E_g}{kT} + 4\right)^2 \quad \text{Eq. (6.22)}$$

where

σ_n = electrical conductivity arising from electrons

σ_p = electrical conductivity arising from holes

E_g = the band gap of the semiconductor, i.e., the gap between the valence and conduction bands.

The first term in Eq. (6.22) is the separate Wiedemann-Franz contribution from the electrons and holes; the second term is the ambipolar or combined electron-hole component.

6.4.3 Effect of Porosity on Thermal Conductivity

Attempts to evaluate the decrease in thermal conductivity due to porosity have been made by Eucken (1932) and by Loeb (1954). Loeb derived an equation for the thermal conductivity of a two-phase body; if pores are treated as a second phase with zero conductivity, Loeb's equation becomes

$$\lambda_p = (1 - P)\lambda_{100} \quad \text{Eq. (6.23)}$$

where

λ_p = conductivity of composite containing porosity P
 λ_{100} = conductivity of fully dense specimen
 P = volume fraction of porosity.

This equation applies to heat flow parallel to cylindrical pores. For other geometries, λ_p was expected to be less than the value indicated by the equation.

Porosity corrections in terms of the volume fraction of a second phase were derived by Maxwell (1891) for two specific geometrical arrangements: random distribution of randomly sized cylinders and spheres. These relationships, given in Eqs. (6.24) and (6.25), respectively, were subsequently applied to multiphase systems by Eucken (1932):

$$\lambda_p = \lambda_{100} \left(\frac{1 - P}{1 + P} \right) \quad \text{Eq. (6.24)}$$

$$\lambda_p = \lambda_{100} \left(\frac{1 - P}{1 + P/2} \right) \quad \text{Eq. (6.25)}$$

Many authors have related measured thermal conductivity to porosity by proportionality coefficients inserted into Eqs. (6.23) and (6.24). Thus, the Loeb equation has been used in the form

$$\frac{\lambda_p}{\lambda_{100}} = 1 - \alpha P \quad \text{Eq. (6.26)}$$

and the Maxwell-Eucken equation in the form

$$\frac{\lambda_p}{\lambda_{100}} = \frac{1 - P}{1 + \beta P} \quad \text{Eq. (6.27)}$$

Belle et al (1967) investigated this porosity correction problem by using computer simulation of bodies with various shapes, sizes, and

distributions of pore space. On the basis of these simulations, the authors concluded from curve fits of computer results that, for uniform ellipsoidal pores of zero conductivity and mutually perpendicular axes x , y , and z , x being the axis perpendicular to heat flow, the coefficient β in the modified Maxwell-Eucken equation, Eq. (6.27), can be defined as:

$$\beta = \frac{1/x}{1/y + 1/z} \quad \text{Eq. (6.28)}$$

Marino (1971) studied the case of spheroidal pores with axial ratio ϵ , the unique axis being randomly oriented. He came to the conclusion that Eq. (6.28), with its assumption of zero conductivity of the pores and parallel pore axes, was not realistic. He presented mathematical relationships permitting the evaluation of the Maxwell-Eucken coefficient β in terms of ϵ , and also of the ratio γ between the conductivities of pores and matrix.

In oxide ceramic fuel, as fabricated, the gas in the pores is generally hydrogen with an admixture, in the low percentage range, of CO and CO₂ originating from the decomposition of the organic binders and lubricants used in fabrication. Evaluation of γ is difficult; it must be calculated recursively, since it depends on the conductivity of the matrix, which can only be determined if a porosity correction is made. As an appropriate starting point, after exploratory calculations, Berman et al (1972) assumed that $\gamma = 1.5 \times 10^{-5} T$, where T is in kelvins, and the matrix consists of thoria or thoria-urania. They fitted the available measurements to various models of the porosity correction by using the sum of squares of the residuals as a guide to the quality of the fit. They came to the conclusion that the model of Marino (1971) was the most satisfactory and found $\epsilon = 0.1637$ as the best fit value for the coefficient. However, the authors cautioned that this conclusion should not be interpreted to mean that the pores are randomly oriented oblate spheroids with that axial ratio. Rather, it could be thought of as an indication that the pores actually present in a sintered, high-density polycrystalline oxide—pores that are far from uniform, spheroidal, or smooth-surfaced—impede heat flow as much as the same volume of flattened spheroids with the axial ratio of 0.1637.

With this information Berman et al (1972) used the Marino (1971) model and calculated, recursively, an appropriate value of β for each thermal conductivity determined from the measurements of Springer et al (1967) and Springer and Lagedrost (1968) on ThO₂-UO₂ compositions. As expected, there was some variation with temperature and to a slight extent with composition; however, β in most cases clustered closely around the mean value of 1.15. Berman et al (1972) assessed the magnitude of the error that could be introduced by the assumption

that β is constant and concluded that, for high-density materials, the error in the thermal conductivity value is considerably smaller than the measurement error. Accordingly, they selected, as a consensus value, $\beta = 1.15$, and regarded this value as a constant for high-density oxide ceramics fabricated by cold pressing and sintering.

6.4.4 Consensus of Thermal Conductivity Data for UO_2

Brandt et al (1976) presented a mean correlation curve of thermal conductivity versus temperature for UO_2 . They used data from a number of sources, including thermal conductivities calculated from thermal diffusivity measurements as well as data from direct thermal conductivity measurements. The data from the thermal conductivity measurements were those by Godfrey et al (1964), Stora et al (1964) and the round-robin measurements reported by Conway and Feith (1969). The thermal diffusivity data included the round-robin measurements reported by Conway and Feith (1969), the round-robin measurements reported by Bates (1970), and the measurements by Weilbacher (1972 and 1974).

Brandt et al (1976) reported the following expression as a best fit of the experimental data for UO_2 :

$$\lambda_T = \frac{1}{0.0439 + 2.16 \times 10^{-4} T} + 0.112T \exp[-1.18/(kT)] - 4.18 \times 10^5 \exp[-3.29/(kT)] \quad \text{Eq. (6.29)}$$

where

λ_T = thermal conductivity, W/(m·K)
 $k = 8.6144 \times 10^{-5}$ eV/K (Boltzmann constant).

In this equation, the first two terms are, respectively, the phonon conduction and the electron conduction contributions. The third term is that proposed by Weilbacher (1972) and represents the decrease thermal conductivity resulting from dislocations created at the higher temperatures. The Brandt et al (1976) equation, plotted in Fig. 6.23, summarizes the conductivity-temperature behavior of unirradiated, polycrystalline, stoichiometric UO_2 corrected to theoretical density; it shows a minimum thermal conductivity of 2.2 W/m·K occurring around 1970 K with increases to 3.4 W/m·K at 2773 K and to 3.7 W/m·K at 3023 K. The values above 2773 K used in this consensus curve were calculated from a set of thermal diffusivity measurements reported by Weilbacher (1972).

Fink et al (1981a) used a different model to fit essentially the same data base. The only data excluded in their analysis were some data of Bates (1970) that were judged to be suspect because of uncertainties

Figure 6.23. Comparison of Recommended Thermal Conductivity Values for Urania of Theoretical Density.

in stoichiometry. Since there was evidence for a phase transition for UO_2 at 2670 K from the enthalpy measurements (Fink et al, 1981b; also see Chap. 5), Fink et al (1981a) suggested a similar transition with temperature for thermal conductivity. The equations for the thermal conductivity of UO_2 were therefore made to conform with the enthalpy and heat capacity equations, i.e., a nonlinear equation based on phonon and electron contributions was used below the transition temperature of 2670 K, and a linear equation was used above the transition temperature. The authors also concluded that there was no statistical justification for the dislocation term recommended by Weilbacher (1972). However, they found that a CT^2 term in the denominator of the phonon part of the thermal conductivity equation improved the data fit in the temperature region between 1300 and 2100 K, and so they included this term in their equation. Cabannes

(1976) reported that such an additional term not only improved the fit for some oxide ceramic data, but he also related the theoretical significance of this term to Pomeranchuk (1941).

The thermal conductivity equation used to fit the data below 2670 K was constrained to agree with the linear equation at the point of juncture, 2670 K, to preclude discontinuities in the calculated values of the thermal diffusivity. The equations recommended by Fink et al (1981a) are:

For $298.15 \text{ K} \leq T \leq 2670 \text{ K}$,

$$\lambda_T = \frac{1}{A + BT + CT^2} + DTe^{-E/kT} \quad \text{Eq. (6.30)}$$

For $2670 \text{ K} \leq T \leq 3120 \text{ K}$,

$$\lambda_T = 4.1486 - 2.2673 \times 10^{-4} T \quad \text{Eq. (6.31)}$$

where

$$A = 6.8837 \times 10^{-2} \text{ m} \cdot \text{K/W}$$

$$B = 1.6693 \times 10^{-4} \text{ m/W}$$

$$C = 3.1886 \times 10^{-8} \text{ m/W} \cdot \text{K}$$

$$D = 1.2873 \times 10^{-1} \text{ w/M} \cdot \text{K}^2$$

$$E = 1.1608 \text{ eV}$$

$$k = 8.6144 \times 10^{-5} \text{ eV/K (Boltzmann constant)}$$

$$T = \text{temperature, K}$$

$$\lambda_T = \text{thermal conductivity, W/m} \cdot \text{K}.$$

The plot of these equations is also shown in Fig. 6.23. In contrast to the Brandt et al (1976) analysis, the Fink et al (1981a) analysis shows a decrease in the thermal conductivity following the maximum at 2670 K. According to Fink et al (1981a) the equation presented by Brandt et al (1976) fits the low temperature data better, but the Fink et al (1981a) equations are a better fit overall. The relative standard deviation for the Fink et al (1981a) fit is given as 6.23 percent, whereas that for the Brandt et al equation is 7.34 percent.

Also shown in Fig. 6.23 is a plot of the equation recommended by Hyland (1983) for the thermal conductivity of UO_2 for the temperature range 2000 to 3120 K. This equation, according to Hyland, has a limit of error of $\pm 0.3 \text{ W/m} \cdot \text{K}$ and is based on sounder theoretical considerations than all other previously reported equations. In his analysis, Hyland (1983) evaluated the separate contributions (λ_r , λ_v , and λ_e) and arrived at the following equation:

$$\lambda_T = (2.3 \pm 0.4) + 2.25 \times 10^5 T^{-1} \exp[(-1.242 \times 10^4)/T] \text{ W/m} \cdot \text{K} \quad \text{Eq. (6.32)}$$

The first term is the sum of the lattice (2.1 ± 0.3 W/m·K) and radiation (0.2 ± 0.1 W/m·K) contributions, and the second term is the evaluation of the electronic contribution to the thermal conductivity. Note that the Hyland (1983) expression for λ_e differs in form from the Brandt et al (1976) and the Fink et al (1981a) expressions in that T is replaced by $1/T$.

The lattice contribution to the thermal conductivity of UO₂ for the temperature range 2000 to 3120 K (2.1 ± 0.3 W/m·K) was obtained by valuating the expression valid for lower temperatures, namely,

$$\lambda = \frac{1}{0.0375 + 2.165 \times 10^{-4} T} \text{ W/m}\cdot\text{K} ,$$

at 2000 K and assuming that λ has a constant value from $T = 2000$ K to the melting temperature, 3120 K.

The value of 0.2 ± 0.1 W/m·K for the radiation contribution to the thermal conductivity of UO₂, λ_r , was obtained by using Eq. (6.20), and values of extinction coefficients were estimated for these higher temperatures from room temperature data.

In evaluating the electronic contribution to the thermal conductivity of UO₂ Hyland (1983) pointed out that the expression for λ_e (Eq. (6.22)) was originally derived for a conventional semiconductor in which electrons and holes move in energy bands and is therefore not really applicable to UO₂. According to Hyland (1983), UO₂ in its ground state is an insulator characterized not by filled valence and empty conduction bands but by the existence of localized electrons. It becomes a semiconductor because of the thermally induced disproportionation reaction of the cation sublattice,

The electrical carriers, the extra electron and hole on the U³⁺ and U⁵⁺ ions, are treated as small polarons. Thus, according to Hyland (1983), Eq. (6.22) should be modified by replacing E_g , the semiconductor band gap, with U , the energy required for the disproportionation reaction (Eq. (6.33)). Since the electrons and holes individually neutralize each other as a result of the assumed hopping nature of their transport, only the so-called ambipolar contribution remains, and Eq. (6.22) becomes

$$\lambda_e = \left(\frac{k}{e}\right)^2 T \left(\frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p}\right) \left(\frac{U}{kT}\right)^2 \quad \text{Eq. (6.34)}$$

Hyland (1983) evaluated this general expression for the specific case of UO₂ by setting $\sigma_n = \sigma_p$. This assumption (the conductivities of the

electrons and holes are equal) is consistent with the observed behavior of the thermoelectric (Seebeck) coefficient for UO_2 at high temperature. The equation then becomes

$$\lambda_e = \frac{1}{4} \left(\frac{U}{e} \right)^2 \frac{\sigma}{T} \quad \text{Eq. (6.35)}$$

Equation (6.35) evaluates quantitatively to the second term in Eq. (6.32) on inserting values for $\sigma[2600 \exp(-1.07 \text{ eV}/kT)]$ from the data of Killeen (1980) and for $U(1.96 \text{ eV})$ from the data of Hyland and Ralph (1983).

6.4.5 Thermal Conductivity Data for ThO_2 and $\text{ThO}_2\text{-UO}_2$

(a) Introduction

Peterson and Curtis (1970) compiled data on the measurements of the thermal conductivity of ThO_2 to about 2000 K. They attributed the considerable scatter among the several sets of data to "variations in porosity and other structural features of the specimens". Touloukian et al (1970) summarized essentially the same data for ThO_2 and made no recommendation for best values. They also reported thermal conductivity data (Kingery, 1959) for various compositions in the $\text{ThO}_2\text{-UO}_2$ system.

In a review paper primarily concerned with theory, Slack (1979) calculated the temperature dependence of the minimum value of the thermal conductivity of ThO_2 up to its melting temperature, which he reported as 3573 K, and compared this calculated curve with measured conductivities (Fig. 6.24). The experimentally derived curve was a composite of values from several sources that were subsequently corrected for porosity. Indeed, it was this curve, showing a leveling off of the ThO_2 thermal conductivity near 2300 K to a temperature-independent value of about $2.5 \text{ W/m}\cdot\text{K}$, that suggested to Hyland (1983) that the lattice contribution to the thermal conductivity of UO_2 should show a similar leveling off at the homologous temperature. As discussed in Sect. 6.4.4, Hyland (1983) assumed the minimum value for UO_2 ($2.1 \text{ W/m}\cdot\text{K}$) to occur at about 2000 K and to be constant up to the melting point of UO_2 , i.e., 3120 K.

The first systematic attempt to correlate thermal conductivity, temperature, and composition for the $\text{ThO}_2\text{-UO}_2$ system was made by Berman et al (1972). They used results of thermal expansivity, thermal diffusivity, and specific heat measurements to about 2000 K of Springer et al (1967) and Springer and Lagedrost (1968) and calculated thermal conductivities by Eq. (6.16). A decade later Belle and

Figure 6.24. Thermal Conductivity versus Temperature for ThO_2 up to the Melting Point (M.P.). The Measured Value (Solid Line) Approaches the Calculated Minimum (Broken Line) above 1700 K. (Slack, 1979. Reprinted by permission of Academic Press, Inc.)

Berman (1982) updated the thermal conductivity correlation to about 3400 K to take advantage of enthalpy measurements to this temperature. In this work Belle and Berman (1982) assumed that expressions developed for density and thermal diffusivity data could be extrapolated to these higher temperatures. They also assumed that the $\text{ThO}_2\text{-UO}_2$ solid solution system can be treated as ideal (see Chap. 5). The results of their analysis are outlined below.

(b) The Calculational Model

Belle and Berman (1982) calculated molar densities of the thoria-urania solid solutions by evaluating the molar volume of the two components at the temperature of interest, then finding the value for the solid solution by linear interpolation. Similarly, they calculated heat capacities for the $\text{ThO}_2\text{-UO}_2$ solid solutions from mole

averages of the heat capacities of ThO_2 and UO_2 on the assumption that, below the transition temperatures, the heat capacity for this system obeys ideal solution behavior.

Thermal diffusivity data for ThO_2 and $\text{ThO}_2\text{-UO}_2$ solutions were taken from several sources: Berman et al (1972), Weilbacher (1972), Murabayashi et al (1969), Murabayashi (1970), Faucher et al (1970), and Ferro et al (1970). Where thermal conductivity measurements were available, as in the case of ThO_2 data from Koenig (1953) and Pears (1963), corrected thermal diffusivities were calculated using the density and heat capacity equations. In all cases, Belle and Berman (1982) calculated thermal conductivities by using Eq. (6.16); they corrected the resulting values for porosity using the Maxwell-Eucken expression with a constant value of 1.15 for the β coefficient. In the case of ThO_2 , the resulting thermal conductivities were fitted to the lattice conductivity equation,

$$\lambda_t = \frac{1}{A + BT},$$

using least-squares statistical techniques. The equation reported by Belle and Berman (1982) for the thermal conductivity of 100 percent dense ThO_2 for the temperature range 298 to 2950 K is the following:

$$\lambda_o = \frac{1}{0.0213 + 1.597 \times 10^{-4} T} \quad \text{Eq. (6.36)}$$

The fitted equation for the thermal conductivity of thoria is represented by the solid line in Fig. 6.25; the dashed line represents the equation that was recommended by Berman et al (1972). Figure 6.25 also shows the measured thermal conductivities of Koenig (1953) and Pears (1963); the latter set of data was not used in the statistical assessment.

For UO_2 contents up to 30 mole percent in the $\text{ThO}_2\text{-UO}_2$ system, Belle and Berman (1982) used a model in which the A and B terms Eq. (6.19) were defined in terms of M, the mole fraction of UO_2 , as follows:

$$A = \frac{1}{A_o + A_1 M}$$

$$B = B_o + B_1 M + B_2 M^2$$

where

A_o and B_o = values for pure ThO_2 .

Figure 6.25. Thermal Conductivity of 100 Percent Dense Thoria from 298 to 2950 K for $\beta = 1.15$. Points Shown are Those Listed in Appendix B of Belle and Berman (1982) Including Those (Pears; also 2973 K Determinations of Weilbacher) Excluded from Curve Fitting. Broken Line is Curve Recommended by Berman et al (1972).

The fitted equation for the solid solutions was constrained to fit the coefficients given for thoria; i.e., when M , the mole fraction of UO₂, was set equal to zero, the equation was reduced to the fitted equation for thoria. The best-fit coefficient values obtained are:

$$A_1 = -112.072$$

$$B_1 = 6.736 \times 10^{-4}$$

$$B_2 = -2.156 \times 10^{-3}$$

The fitted equations for the thermal conductivities of 100 percent dense thoria and thoria-urania solid solutions from room temperature to the transition temperatures are represented by the solid lines in Figs. 6.26, 6.27, and 6.28. The equation given by Fink et al (1981a) for UO_2 is shown as a dashed line in these illustrations. The data points shown were divided into three compositional groups for clarity of representation.

At temperatures up to approximately 1500 K, thoria has a thermal conductivity approximately 50 percent higher than urania. As urania is introduced into solid solution in the thoria, however, the thermal conductivity declines sharply toward the urania values. The process is substantially complete by the time a composition of ThO_2 -30 mole percent UO_2 is reached.

Implicit in this empirical fit of the data is the assumption that, at least up to the transition temperatures, thermal conduction is essentially by phonons in ThO_2 and in ThO_2 - UO_2 solid solutions of low UO_2 content. The radiant heat transfer contribution is significant at high temperatures for pure ThO_2 if it is assumed that the extinction coefficients reported by Chan and Ma (1981) and discussed in Chap. 3 are

Figure 6.26. Thermal Conductivities, Corrected for Porosity, of ThO_2 through ThO_2 -6 Mole Percent UO_2 .

Figure 6.27. Thermal Conductivities, Corrected for Porosity, of $\text{ThO}_2\text{-UO}_2$ Solid Solutions with 10 to 13 Mole Percent UO_2 .

true values. However, these coefficients were estimated from room-temperature absorption spectra for single-crystal material and are therefore not representative. Considerable uncertainty exists in evaluating or measuring extinction coefficients at high temperatures.

The electron conduction contribution is also unlikely for pure ThO_2 , since this oxide is principally an ionic conductor at high temperatures. In the case of low UO_2 content $\text{ThO}_2\text{-UO}_2$ solutions, there may be some electronic conduction contribution, but this is accounted for in the model, in which it is assumed that the solid solution is intermediate in character between the two end members.

(c) Extrapolation to Higher Temperatures

Belle and Berman (1982) used the following procedure to extrapolate the thermal conductivity of ThO_2 beyond the 2950 K transition temperature. They first obtained an expression for the thermal diffusivity up to the transition temperature of 2950 K from the thermal conductivity, heat capacity, and density expressions using Eq. (6.16).

Figure 6.28. Thermal Conductivities, Corrected for Porosity, of ThO₂-UO₂ Solid Solutions with 20 to 30 Mole Percent UO₂.

The resulting values were fit to the diffusivity equation, $\alpha = \frac{1}{A + BT}$, with results as follows:

$$\alpha = 1/(-34191.1 + 561.28 T) \text{ m}^2/\text{s} \quad \text{Eq. (6.37)}$$

On the assumption that there is no discontinuity in the diffusivity, at the transition temperature, Belle and Berman (1982) used Eq. (6.37) to extrapolate thermal diffusivity values for thorium from the transition temperature of 2950 K to 3400 K, the highest temperature for which heat capacity data were available from enthalpy measurements. The results are shown in Fig. 6.29. Also shown in Fig. 6.29, as a dashed line, is a plot of an equation proposed by Weilbacher (1972) for the thermal diffusivity of thorium. It is in satisfactory agreement with the data and with Eq. (6.37).

Figure 6.30 shows calculated values represented by the solid line for the thermal conductivity of 100 percent dense thorium from

room temperature to 3400 K. There is a sudden increase in the thermal conductivity at the 2950 K discontinuity, from 2.03 to 3.05 W/m·K,—an increase of 50 percent, which represents the change in heat capacity occurring at that point. The value of 2.03 W/m·K is the minimum value encountered over this temperature range. At temperatures above the discontinuity, after the sudden increase, the thermal conductivity apparently continues to decrease with higher temperature at about the same rate as it had before the transition.

The minimum thermal conductivity is encountered at 2950 K, not at around 2300 K as suggested by Slack (1979).

Belle and Berman (1982) estimated the minimum value of ThO₂ thermal conductivity from Eq. (6.18), by assuming (1) that phonon velocity can be approximated by $(E/\rho)^{1/2}$, where E is Young's modulus and ρ is the density; (2) that the equation giving the temperature variation of E can be extrapolated to higher temperatures; and (3) that the minimum value for the phonon mean free path can be approximated by the lattice parameter a_0 . The calculated minimum value of thermal conductivity for ThO₂ at 2950 K is 2.07 W/m·K as compared with the value of 2.03 W/m·K from Fig. 6.30.

The thermal conductivity of urania, according to equations given by Fink et al (1981a), is plotted as the dashed line in Fig. 6.30. At the UO₂ transition temperature, 2670 K, there is a change of slope accompanied by a small increase in thermal conductivity. The minimum value of the thermal conductivity does not occur at the transition temperature, as it does for ThO₂, but occurs within a segment of the smooth curve at about 1970 K. The lowest value reached is 2.19 W/m·K. The lowest value for UO₂ estimated from UO₂ data and Eq. (6.18) is 2.37 W/m·K. These estimates for minimum values of thermal conductivity for both ThO₂ and UO₂ are uncertain because elastic constant data needed to convert C_p to C_v were obtained by extrapolating measurements at lower temperatures to much higher temperatures. However, neutron scattering measurements at high temperatures on UO₂ by Clausen et al (1984) suggest that such an extrapolation may be reasonable.

Although both ThO₂ and UO₂ show the expected decrease in thermal conductivity with temperature according to the expression $\lambda = \frac{1}{A+BT}$, differences in thermal conductivity behavior are apparent at the higher temperatures. For UO₂ there is an upswing in thermal conductivity which occurs following a minimum reached at around 1970 K. This increase is gradual and uniform to about 2670 K at which temperature a second gradual decrease sets in. For ThO₂, on the other hand, the decrease in thermal conductivity is uniform to a much higher temperature. At about 2950 K, however, there is a precipitous increase followed by a second uniform decrease in thermal conductivity with temperature.

Figure 6.29. Data and Fitted Equations for the Thermal Diffusivity of Thoria. The Dashed Line Indicates the Equation Recommended by Weilbacher (1972).

In the case of UO_2 , the upswing in thermal conductivity around 1970 K is satisfactorily explained in terms of the electronic contribution. On the other hand, the precipitous increase in the thermal conductivity of ThO_2 at a much higher temperature (2950 K) is not the result of an electronic contribution but is associated with the large increase in heat capacity resulting from a discontinuity in the enthalpy-temperature curve. The origin of the enthalpy anomaly in ThO_2 , and therefore of the heat capacity anomaly, probably is not electronic.

Figure 6.30. Thermal Conductivities of Thoria and Urania, Corrected for Porosity, Extended to Higher Temperatures.

As discussed in Chap. 5, views have varied over the years concerning both the origin of the enthalpy anomaly in UO_2 and its possible effect on thermal conductivity. Young (1979) and Harding et al (1980) suggested that electronic defects make a major contribution to the specific heat, and Browning (1980) felt that the arguments were strong in favor of attributing the increase in thermal conductivity to electronic processes. Browning (1983) was convinced that the UO_2 enthalpy data are anomalous only for temperatures greater than 2500 K and that the onset at 2500 K of a diffuse, structural transition is responsible for the excess enthalpy at these temperatures. Hyland and Ralph (1983) pointed out that whatever is the mechanism responsible for the anomalous enthalpy it does not contribute to the thermal conductivity in any significant manner.

It may be as Williams (1982) suggests for SrCl_2 that thermal conductivity can be increased as a result of the enhancement of anion mobilities associated with the formation of some *superionic* state. Whether the Bredig (1972) transitions for ThO_2 and UO_2 (see Chap. 5) represent such states is unknown.

6.5 SUMMARY

The predominant lattice disorder in ThO_2 is due to oxygen ion vacancies and interstitials. Since these defects are responsible for transport properties, oxygen ion diffusivity is considerably greater than thorium ion diffusivity. Similarly the transport number for the oxygen ion is much greater than for the thorium ion.

Thoria is a mixed ionic-electronic conductor whose electrical properties depend on temperature, oxygen partial pressure, and, for nominally pure ThO_2 , on impurity content. Indeed, it is not certain whether "truly pure" ThO_2 is an intrinsic ionic conductor. However, calculated oxygen ion diffusion coefficients derived from electrical conductivity and oxygen ion transport numbers agree with measured values.

Doped ThO_2 and solid solutions of ThO_2 with other oxides behave as mixed conductors with electron hole conduction at oxygen partial pressures near one atmosphere. They become exclusively oxygen ion conductors in the lower range of oxygen partial pressures. At very low oxygen partial pressures there is some evidence of n-type conduction.

Thermal conductivity information on ThO_2 at high temperatures suggests that the phonon conduction term is the only significant contribution for temperatures up to the transition temperature. However, this information is based on heat capacity data and on an extrapolation of some thermal diffusivity data. There is a need for corroborative data from direct thermal conductivity measurements. The behavior of the ThO_2 - UO_2 solid solutions appears to be intermediate between the two end members.

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Chapter 7

MECHANICAL PROPERTIES OF ThO_2 AND ThO_2 - UO_2

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7.1 INTRODUCTION

Sintered bodies of thoria-base fuel for nuclear technology have satisfactory mechanical properties. It is possible to produce these bodies to high density, close tolerances, good uniformity and acceptable yield even to very stringent specifications. The material is reasonably resistant to chipping and breaking, and has adequate mechanical strength to maintain physical integrity during typical fabrication procedures. In this chapter is summarized the available information on the mechanical properties of ThO_2 and ThO_2 - UO_2 at room temperature and at fuel operating temperatures. Most of the available data were obtained on pellets of sintered, polycrystalline material derived from the calcination of thorium oxalate or, in the case of ThO_2 - UO_2 solutions, from mixed powders. Exceptional materials, such as single crystals and sol-gel products, are noted in the text.

7.2 ANISOTROPY

Since the crystal structure of ThO_2 is cubic, there should be no differences among the properties of the material in the three mutually perpendicular axial directions. There are, however, an infinite number of other directions, and lines traveling along these directions through the crystal structure would encounter densities and arrangements of atoms differing from those found along an axial direction. The properties of ThO_2 may therefore, at least theoretically, differ with direction.

The literature contains only one reference to measurements of directional variation of mechanical properties of ThO_2 . This is the work done by Macedo et al (1964), who determined the elastic constants at room temperature of single crystal ThO_2 prepared by arc-melting. Table 7.1 lists these determinations, together with similar single-crystal data for UO_2 (Wachtman et al, 1965), and also values calculated from these data for the

TABLE 7.1—SINGLE-CRYSTAL ELASTIC CONSTANTS FOR ThO₂* AND UO₂† AND DERIVATIVE VALUES FOR 100% DENSE POLYCRYSTALLINE MATERIAL

	ThO ₂	UO ₂
Measured on Single Crystals		
C ₁₁ (GPa)	367	396
C ₁₂ (GPa)	106	121
C ₄₄ (GPa)	79.7	64.1
Derived from above Measurements		
Anisotropy Factor	0.61	0.47
Young's Modulus (GPa)		
[100] Direction	320	338
[111] Direction	210	175
Values Calculated for 100% Dense Polycrystalline Material		
Young's Modulus (GPa)	249.7	230.5
Shear Modulus (GPa)	97.2	87.5
Bulk Modulus (GPa)	193.0	212.7
Poisson's Ratio (μ)	0.284	0.317

*Macedo et al (1964)

†Wachtman et al (1965)

anisotropy factor and *Young's modulus*. For cubic materials, the only nonzero tensor quantities are those designated C₁₁, C₁₂, and C₄₄. The anisotropy factor is defined as

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad \text{Eq (7.1)}$$

The degree of anisotropy is greater for UO₂ than for ThO₂. The fact that the anisotropy factors are less than 1 indicates that the elastic moduli will be at a minimum in the [111], or octahedral direction, and will be a maximum in the [100], or cube direction. The maximum amount of variation to be expected in the elastic properties due to anisotropy or preferred orientation should be such that the value in the octahedral direction is 61 percent of that in the cube direction for ThO₂, 47 percent of that in the cube direction for UO₂. Calculated values for Young's moduli based on the single-crystal measurements are given in Table 7.1. They show somewhat less than the maximum permitted amount of variation; for ThO₂, the octahedral value is 66 percent of the cube value, and for UO₂, it is 52 percent.

Table 7.1 also lists the values of the various moduli for randomly oriented, fully dense polycrystalline bodies calculated from the single-crystal data using the Voigt-Reuss-Hill approximation (see Hill, 1952). These calculations are discussed by Wolfe and Kaufman (1967). For Young's modulus and the shear modulus, this calculation is approximate; upper and lower bounds can be calculated, and the values given in Table 7.1 are the means of these two bounds. For the bulk modulus, however, the calculation is exact.

Thoria used in nuclear applications is polycrystalline. There have been no indications that thoria is strongly subject to mechanisms that would inadvertently create a strong degree of preferred orientation. Furthermore, cubic materials have a large number of equivalent directions in their structures; even highly oriented polycrystalline samples would therefore not be expected to show directional variation in properties as great as those observed in single crystals.

Significant directional variations in properties have not been much observed, but it is possible for them to occur. It is unlikely, but possible, for the properties of a polycrystalline sample to vary from those given below, due to directional effects. The mechanical properties discussed in the remaining sections of this chapter have been determined on polycrystalline material which is randomly oriented in a crystallographic sense.

7.3 TEMPORARY DEFORMATION

7.3.1 Elastic Properties

A convenient SI unit for expressing the elastic constants (Young's modulus E , the shear modulus G , and the bulk modulus K) is the gigapascal, abbreviated GPa. (1 GPa = 10 kilobars, 10^{10} dyne/cm², or 0.145×10^6 psi.) Poisson's Ratio, μ , is dimensionless; it is equal to $(E/2G)-1$ for isotropic materials or for randomly oriented cubic polycrystalline materials that behave isotropically on a macroscopic scale.

For purposes of this section, reference conditions are defined as those applicable for pure, polycrystalline, randomly oriented thorium dioxide, at a temperature, T , of 298 K and with a value of P , the volume fraction of porosity, equal to zero. Values of the elastic constants for the reference conditions are given; then, insofar as information is available, data are given for the correction of these reference values for the effects of porosity, temperature, and composition as these factors vary from the standard reference conditions.

Data on the elastic properties of thoria were reviewed, summarized, and evaluated by Wolfe and Kaufman (1967). They presented consensus values and equations, which are given in the following sections.

(a) *Young's Modulus*

Wolfe and Kaufman (1967) reexamined a comprehensive set of measurements by Spinner et al (1963a and b) in assessing the factors contributing to variation in Young's modulus for thoria. The value proposed by Wolfe and Kaufman (1967) for reference conditions, E_r , is 249.1 GPa. For values of P , the volume fraction of porosity, in the range from 0.06 to 0.4, Wolfe and Kaufman (1967) fitted the Spinner et al (1963a and b) data the equation

$$E[298, P] = E_r(1 - 2.21 P) \quad \text{Eq. (7.2)}$$

Values for Young's modulus at other temperatures may be derived from the equation

$$E[T, P]/E[298, P] = 1.0230 - 1.405 \times 10^{-4} T \exp(-181/T) \quad \text{Eq. (7.3)}$$

Equation (7.3) is stated by Wolfe and Kaufman (1967) to be valid for polycrystalline thoria over the temperature range from 298 to 1300 K. At temperatures above 1300 K, the values of E in polycrystalline material decrease gradually below the result obtained by evaluating Eqs. (7.2) and (7.3), due to grain-boundary relaxation. The differences increase with increasing temperature. The variations of the elastic moduli with temperature are discussed further below and in Sect. 7.3.3.

Spinner et al (1963a), in their own evaluation of their data, fitted the porosity correction to a quadratic form,

$$E[298, P] = E_r(1 + aP + bP^2) \quad \text{Eq. (7.4)}$$

with the values of the fitted coefficients a and b differing somewhat depending on the range of porosities considered. For this mathematical model, they suggested a value of $E_r = 261.0$ GPa. This porosity correction is discussed further in Sect. 7.3.2.

Values of 238.4 and 241.5 GPa were given for ThO_2 with 0.5 weight percent CaO added (Lang and Knudsen, 1956; Wachtman and Lam, 1959). For thoria with $P = 0.08$, a room-temperature value of 137.3 GPa was cited (Ryshkewitch, 1960); correction of this value to reference conditions using Eq. (7.1) gives 167 GPa. This measurement must be regarded as almost certainly too low.

Equation (7.3) was found to describe satisfactorily the temperature dependence for all the sets of data examined, up to 1300 K for dynamic measurements. A few sets of data (Fig. 7.1) departed from the calculated equations in the region between 1000 and 1300 K, but these were static measurements, and were not considered representative by Wolfe and

MODULUS	M_r , GPa	MATERIAL	%P	METHOD	REFERENCE
○ E	137.3	ThO ₂	8	STATIC	RYSHKEWITCH (1960)
△ G	98.1	ThO ₂	1.7	STATIC	WYGANT (1951)
□ E, G	238.4, 93.0	ThO ₂ -5w/o CaO	1.0	DYNAMIC	LANG & KNUDSEN (1956)
--- E	241.5	ThO ₂ -5w/o CaO	3.2	DYNAMIC	WACHTMAN & LAM (1959)
— E, G	261, 100.6	ThO ₂	(a)	DYNAMIC	SPINNER ET AL (1963 a, b)
--- E	226	UO ₂	(b)	DYNAMIC	OLSEN (1976)
(a) 3.7-39.4% POROSITY, EXTRAPOLATED TO 0 USING EQ. 7-4					
(b) COMPUTER FIT TO DATA OF OTHERS					

Figure 7.1. Variation of Elastic Constants with Temperature for ThO₂, ThO₂-0.5 w/o CaO, and UO₂.

Kaufman (1967). At higher temperatures, the available data showed that the values of E fell below the predictions of Eq. (7.3), and that this shortfall increased with temperature. However, the amount of the shortfall differed considerably among the various investigations, and appears sensitive to microstructural factors.

(b) Shear Modulus

On the basis of the results of Spinner et al (1963a and b), Wolfe and Kaufman (1967) recommended a consensus value for the shear modulus, under reference conditions, of $G_r = 96.9$ GPa. Other values quoted are 98.1 and 93.0 GPa (Wygant, 1951; Lang and Knudsen, 1956). Ryshkewitch (1960) mentions a very much lower value of 59 GPa. For correction of the reference value for the effects of porosity, Wolfe and Kaufman (1967) give the linear equation

$$G[298, P] = G_r(1 - 2.12 P) \quad \text{Eq. (7.5)}$$

Correction of the shear modulus for the effect of temperature takes the same form as Eq. (7.3):

$$G[T, P]/G[298, P] = 1.0230 - 1.405 \times 10^{-4} T \exp(-181/T) \quad \text{Eq. (7.6)}$$

Wolfe and Kaufman (1967) present a graph on which both $E[T, P]/E[298, P]$ and $G[T, P]/G[298, P]$ are plotted together as a function of temperature. The comparable behavior of the two moduli is demonstrated. Up to a temperature of 1300 K, both adhere closely to the ratios calculated from Eq. (7.3) or (7.6), except for the questionable data previously mentioned. Above 1300 K, both moduli depart from those ratios in a comparable manner. The graph is reproduced as Fig. 7.1.

(c) Bulk Modulus

Wolfe and Kaufman (1967) give the values of 192.8, 193.0 and 215.3 GPa for K_r , the bulk modulus under reference conditions (Table 7.2). Lang and Knudsen (1956) give an additional value of 182 GPa. A consensus value of 193 GPa is suggested. No data are available on the change of bulk modulus as a function of temperature; reasonable engineering judgment would suggest, however, that it would behave in a manner comparable to Young's modulus and the shear modulus, and therefore, at least as a first approximation, the ratios generated by Eq. (7.3) or (7.6) may be applied. Since the bulk modulus is simply the adiabatic compressibility expressed as a reciprocal, it is a property of 100 percent dense material; a correction of the bulk modulus, or the compressibility, for the effects of porosity would not be appropriate, or of any general applicability.

TABLE 7.2—ROOM TEMPERATURE ELASTIC MODULI FOR 100% DENSE POLYCRYSTALLINE ThO₂

	A*	B†	C‡
Young's Modulus E (GPa)	249.7	261.0	249.1
Shear Modulus G (GPa)	97.2	100.6	96.9
Bulk Modulus K (GPa)	193.0	215.3	192.8
Poisson's Ratio (μ)	0.284	0.297	0.285

*Calculated by Macedo et al (1964) from single-crystal measurements.

†Extrapolated to zero porosity by Spinner et al (1963a).

‡Extrapolated to zero porosity by Wolfe and Kaufman (1967).

(d) Poisson's Ratio

Poisson's ratio, μ , is equal to $(E/2G)-1$ for randomly oriented polycrystalline materials that behave isotropically on a macroscopic scale. It is a dimensionless quantity, and since E and G behave comparably with regard to temperature, the ratio is not a function of temperature for thoria. Poisson's ratio may be calculated by evaluating Eqs. (7.2) and (7.5) for E and G, respectively, and using the resulting quantities in the equation for μ given above.

Table 7.2 summarizes various values proposed for the elastic properties of thoria under reference conditions. The consensus values recommended by Wolfe and Kaufman (1967) for application to typical nuclear fuel are listed in Column C. These were used in the calculation of Table 7.3, which contains sample evaluations, using Eqs. (7.2) through (7.5), for Young's modulus, E, and the shear modulus, G, for various temperatures and porosities, and the corresponding Poisson's ratios.

7.3.2 Effect of Microstructure

The elastic constants E, G, and K are stated in terms of force per unit area. For 100 percent dense material, the area would be that of the cross-section of the specimen; for porous material, such as polycrystalline thoria, the reduced cross sectional area must be taken into account when calculating the elastic behavior.

TABLE 7.3—ELASTIC CONSTANTS OF POLYCRYSTALLINE ThO_2 (GPa)
FOR VARIOUS TEMPERATURES AND POROSITIES*

Temperature (kelvin)	P = 0.02	P = 0.04	P = 0.06	P = 0.08
Young's Modulus				
298	238.1	227.1	216.1	205.0
400	235.0	224.1	213.3	202.4
500	231.9	221.1	210.4	199.7
600	228.7	218.1	207.5	196.9
700	225.4	215.0	204.6	194.2
800	222.2	211.9	201.6	191.3
900	218.9	208.8	198.6	188.5
1000	215.6	205.6	195.7	185.7
1100	212.3	202.5	192.7	182.8
1200	209.0	199.3	189.7	180.0
1300	205.7	196.2	186.7	177.1
Shear Modulus				
298	92.8	88.6	84.5	80.4
400	91.6	87.5	83.4	79.4
500	90.3	86.3	82.3	78.3
600	89.1	85.1	81.2	77.2
700	87.8	83.9	80.0	76.2
800	86.6	82.7	78.9	75.1
900	85.3	81.5	77.7	73.9
1000	84.0	80.3	76.6	72.8
1100	82.7	79.0	75.4	71.7
1200	81.4	77.8	74.2	70.6
1300	80.1	76.6	73.0	69.5
Poisson's Ratio, All Temperatures (Dimensionless)				
	0.283	0.280	0.277	0.274

*Wolfe and Kaufman (1967)

In dynamic resonance measurements, such as those of Spinner et al (1963a and b), the elastic moduli are calculated from determinations of fundamental resonance frequencies of ultrasonic signals. Equations for converting the observed frequencies to values of the elastic constants are given by Spinner and Tefft (1961). Such equations always include a term for the density of the sample on which the measurements are made. The resulting values of the elastic constants are therefore valid for the true cross section of the solid material, after an appropriate reduction has been

made for the porosity present. The variation of the constants themselves as functions of the porosity P , as shown in Eqs. (7.2) and (7.5), is in addition to the correction already incorporated.

Wolfe and Kaufman (1967) reviewed the quadratic model proposed by Spinner et al (1963a), Eq. (7.4), as well as their own linear model, Eqs. (7.2) and (7.5), for the effect of porosity on the elastic moduli. No theoretical justification was given by Spinner et al (1963a) for the P^2 term of Eq. (7.4). Kingery et al (1976), summarizing earlier work on bodies with two phases of different elastic properties, stated that the extreme case of void space can be "adequately represented" by an expression such as Eq. (7.4), assuming closed porosity and a continuous matrix. However, on examining the data of Spinner et al (1963a and b) on thoria, Wolfe and Kaufman (1967) found that the inclusion of a P^2 term did not substantially improve the quality of fit of the data to the equations. Also, the reference values obtained from the linear model were closer to those calculated from the single-crystal data of Macedo et al (1964) for which porosity is not a consideration. A mathematical model higher than the first order therefore appears to be unjustified. A similar problem was discussed in Chap. 4 concerning the generalization of Vegard's Law to a large class of properties, collectively described as "Property X", that could be considered quasilinear in their variation with composition. Even when higher-order terms were known to exist in the theoretical equation, they could be regarded as insignificant in dilute solutions. It appears, from the available data, that the elastic constants of thoria may be considered as part of such a class of quasilinear "X" properties. Void space may be considered as a component of the material, just as vacant lattice positions were so considered in Chap. 4.

However, the variation in the elastic properties calculated from the "P" term may not, in fact, be entirely due to porosity. Other microstructural features, such as grain size, uniformity, and configuration, as well as pore size and distribution, vary in a manner closely associated with the total amount of porosity, and it is not possible to deal with the effects of these various factors independently.

Grain size and configuration certainly are important factors in controlling the departure of the elastic constants from the fitted equations at temperatures above 1300 K. The differences seen among the various investigations may be ascribed to these factors. The fact that the differences are minimized below 1000 K indicates that microstructural factors other than total porosity are of limited significance in this region.

Wolfe and Kaufman (1967) point out that, for $P = 1$, i.e., 100 percent porosity, the elastic moduli are necessarily zero, and the empirical porosity corrections in the above equations are clearly not applicable. Indeed, the equations should not be used outside of the range of data on which they are based; the data of Spinner et al (1963a and b) included values of P up to 0.4.

7.3.3 Effect of Temperature

In discussing the temperature dependence of the elastic moduli of a polycrystalline solid, Wolfe and Kaufman (1967) noted the following features: (1) As a consequence of the Third Law of Thermodynamics, the derivative of an elastic modulus with respect to temperature approaches zero at 0 K; (2) at elevated temperatures, both in metals and nonmetals, the elastic moduli decrease approximately linearly with increasing temperature; (3) at still higher temperatures, the elastic moduli begin to decrease more rapidly than the linear extrapolation.

On the basis of these observations, Wachtman et al (1961) proposed that the temperature dependence of Young's modulus could be fit to an equation of the form

$$E = E_0 - BT \exp(-T_0/T) \quad \text{Eq. (7.7)}$$

where

E_0 = Young's modulus at absolute zero

B = empirical parameter

T_0 = empirical parameter, i.e., a characteristic temperature.

According to this formulation, Young's modulus of thoria at absolute zero would be 204.16 GPa, and the characteristic temperature T_0 would be 181 K. Equation (7.7) is recast in relative form as Eqs. (7.3) and (7.6).

Spinner et al (1963b) observed that the temperature dependence of the shear modulus was the same as for Young's modulus. Equation (7.7) could therefore be rewritten with the terms G and G_0 in place of E and E_0 . The appropriate value for G_0 , the shear modulus at absolute zero, would in this case be 79.4 GPa. At temperatures above 1300 K, the moduli decrease below the values defined by Eq. (7.7), and the amount of this shortfall increases with increasing temperature. This is ascribed to grain boundary relaxation on the basis of the following observations: (1) It is not observed in single crystals; (2) in polycrystalline materials, it is associated with internal friction peaks (Chang, 1961).

This relaxation consists of sliding along grain boundaries. Increases in grain size and increases in the rate of loading (or, in sound-velocity techniques, the frequency of vibration) should minimize the shortfall effect.

Zener (1941) derived an equation for E/E_{calc} , the maximum fractional shortfall to be expected, assuming a solid with uniform grains and viscous grain boundaries:

$$\frac{E}{E_{\text{calc}}} = 0.5 \left(\frac{7 + 5\mu}{7 + \mu - 5\mu^2} \right) \quad \text{Eq. (7.8)}$$

where

E_{calc} = the evaluation of E resulting from Eq. (7.3) or (7.7)

μ = Poisson's Ratio.

In Table 7.1, the value of μ for high-density thoria is shown as varying slightly about a value of 0.28; use of this value in Eq. (7.8) would result in $E/E_{\text{calc}} = 0.61$. This upper limit on the effects of grain boundary relaxation is in accord with the observations in Fig. 7.1.

7.3.4 Effect of Composition

No data are available on the effect of variations of stoichiometry, or of UO₂ additions, on the elastic moduli of ThO₂. Several workers have investigated the elastic moduli of ThO₂ with 0.5 weight percent CaO added, and there is no evidence that the addition of CaO affected significantly the values obtained. Wolfe and Kaufman (1967) present data showing a 30 percent decrease in Young's modulus of hyperstoichiometric UO_{2+x} as x increases from 0 to 0.06; on further increases, no additional change was observed. Anderson and Nafe (1965) proposed, primarily on the basis of empirical surveys, that the bulk moduli of crystalline solids can be correlated with specific volume, regardless of whether a change in volume results from temperature, pressure, or compositional effects. Unit cell size behaves in a precisely analogous way, and the approximation represented by Vegard's Law, as discussed in Chap. 4, would be appropriate. Certainly, if the elastic moduli behave in a quasilinear manner with regard to macroscopic void space (Sect. 7.3.2), they should also do so if the component being introduced is an actinide or lanthanide, the oxides of which normally form extensive solid solutions with thoria. Therefore, the reference values E_r , G_r , and K_r for ThO₂-UO₂ solid solutions can be estimated on the assumption that they vary linearly with molar composition.

Wolfe and Kaufman (1967) also examined the porosity correction for Young's modulus in polycrystalline UO₂, and arrived at an equation

almost precisely analogous to Eq. (7.2); the best-fit coefficient of the P term was 2.277 rather than 2.21, as it is for ThO_2 . Olsen (1976) reported a value of 2.62 for this coefficient. Olsen (1976) also investigated the temperature dependence of Young's modulus in UO_2 . The resulting curve is shown in Fig. 7.1; the slope is about 30 percent less than for ThO_2 . The value of Young's modulus for polycrystalline UO_2 extrapolated to zero porosity, E_r , was found to be 223.4 GPa by Wolfe and Kaufman (1967) and 226 GPa by Olsen (1976); the corresponding value for ThO_2 is 249.1 GPa. Fritz (1976) gives the following reference values for polycrystalline UO_2 : $E_r = 221$ GPa, $G_r = 83$ GPa, and $K_r = 209$ GPa. These measurements are in good agreement with the values for UO_2 in Table 7.1, based on single-crystal measurements.

The elastic moduli for ThO_2 - UO_2 solid solutions, at a given temperature and porosity, can be estimated by the following procedure. The corresponding moduli for pure ThO_2 are determined by using the equations given by Wolfe and Kaufman (1967). For pure UO_2 , the moduli are determined by using the corrections of Olsen applied to reference values of Olsen (for E_r) or Fritz (for K_r or G_r). Vegard's Law is then applied to estimate the value for the solid solution.

7.4 PERMANENT DEFORMATION

Thoria fails by brittle fracture in tension while still in the range of elastic deformation. However, for compressive and shear stresses, a region of ductile behavior becomes significant at temperatures higher than half the melting point on the absolute scale, i.e., above 1800 K. Grain size and strain rate are significant variables determining the amount of deformation under any given conditions, and the point at which failure occurs. There is additional discussion of these phenomena in Sect. 7.6, below.

Diffusional creep, generally speaking, refers to the movement of material by diffusion under the action of a potential gradient set up by the applied stress. Plastic deformation refers to the yielding of the material along glide planes, in glide directions. Both phenomena result in the permanent deformation of the sample. However, creep is largely characterized by a time dependence (although it may be a function of crystallographic direction as well); plastic deformation may be characterized largely by its relationship to slip planes (although it may also exhibit a time, or at least a strain rate, dependence). Clearly, the experimental separation of these two phenomena can be accomplished only partially. However, it is useful to consider creep as the time-dependent component

of the permanent deformation, and as such it is minimized in experiments conducted over a relatively brief time span. The available information on the permanent deformation of thoria is presented in this section.

7.4.1 Slip

The glide planes and directions in thoria would be expected to be comparable to those in other fluorite-type oxides. Wolfe and Kaufman (1967) reviewed the work done on single crystals of such materials, including some investigations on thoria itself (Edington and Klein, 1966; Gilbert, 1965). In all such work, there is a consensus that the principal plane along which slip occurs is the cube face, or $[100]$. Edington and Klein (1966) observed etch pits and slip lines on thoria deformed above 1200 K, and also reported some evidence of secondary slip on the $[110]$ planes, which truncate cube edges, and the $[111]$ planes, which truncate corners. Slip directions of $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ have been reported, with the cube face and cube direction being the most commonly observed. However, Gilbert (1965), who examined thoria platelets from rolled, thoriated tungsten-rhenium alloy by electron micrography, did not observe gliding along cube planes.

7.4.2 Plastic Deformation

Theoretically, it is appropriate to assume that plastic deformation, strictly so called, in polycrystalline ThO_2 occurs by the yielding of individual grains along the slip planes, and in the slip directions, described above, and that the resistance to plastic deformation is in part defined by the frequency of occurrence of grains in an appropriate orientation such that a component of the applied force is in the proper direction for this yielding.

Virtually the only data available in which plastic deformation of polycrystalline ThO_2 can be distinguished from creep is that of Morgan et al (1968), which is presented as Figs. 7.2 and 7.3. In these figures, the curves marked by the "+" symbols represent low-density pellets (91 percent theoretical) fabricated from sol-gel thoria powders subjected to a strain rate of 0.042 hr^{-1} at 1723 K. At 69 MPa, it was found that deformation continued to increase with time without any further increase in stress. The horizontal slope of this curve in Figs. (7.2) and (7.3) represents a region in which the deformation must be assigned primarily to creep. This result is plotted with other creep measurements in Fig. 7.4 and discussed further in Sect. 7.4.3.

Figure 7.2. Plastic Deformation of ThO₂ Pellets at a Strain Rate of 0.042 hr⁻¹ (Morgan et al, 1968; Courtesy, Oak Ridge National Laboratory. Operated by Union Carbide Corporation for the Department of Energy.)

The other curves, in Figs. 7.2 and 7.3 were obtained from measurements on pellets that were fabricated from oxalate-derived ThO₂ powders. They fail to attain a horizontal slope, and therefore plastic deformation is an important component of the total observed permanent strain.

The curve marked by circles in Fig. 7.3 shows the behavior of oxalate-derived thorium high-density pellets (98 percent of theoretical) at 1723 K, a reasonably typical fuel operating temperature. The straight portion of the curve indicates that strain increases linearly with applied stress until it reaches a value of 0.9 percent at 138 MPa. The initial slope in material with a lower density (94.4 percent of theoretical, i.e., 2.8 times the porosity) is approximately 4.1 times as great. Over the region of plastic deformation, therefore, it may be estimated that the strain varies linearly with stress, and as $P^{1.37}$ with porosity.

Figure 7.3. Plastic Deformation at 1723 K of ThO_2 of Various Densities (Morgan et al, 1968; Courtesy, Oak Ridge National Laboratory, Operated by Union Carbide Corporation for the Department of Energy.)

Figure 7.2 shows that temperature is also a factor. At higher temperatures, creep becomes an increasing component of the total permanent deformation.

7.4.3 Creep Deformation

At low strain rates, any observed permanent deformation may be ascribed almost entirely to creep, which may therefore be measured independently of plastic deformation. The creep data for ThO_2 most nearly applicable to nuclear fuel is that of Poteat and Yust (1966). They performed compressive creep tests on samples of high-density ThO_2

Figure 7.4. Steady-State Creep of ThO₂.

(97.5 percent of theoretical) with a grain size averaging 10 μm and typical pore diameters on the order of 1 μm. Temperatures ranged from 1703 K to 2063 K and stress levels from 27 to 76 MPa. Wolfe and Kaufman (1967) obtained measurements on 98.5 percent dense ThO₂ with a grain size of 15 μm and a pore size of 1 μm; these data are closely comparable to the data of Poteat and Yust (1966).

The two sets of values are plotted in Fig. 7.4. The combined set of data was used in a statistical study to determine the nature and magnitude of factors affecting the creep rate. Curve-fitting computer techniques were used to fit the data to the equation

$$\ln \dot{\epsilon}_s = \ln A + n \ln \sigma - Q/(RT) , \quad \text{Eq. (7.9)}$$

which is a transformation of the classical creep equation:

$$\dot{\epsilon}_s = A \sigma^n \exp[-Q/(RT)] \quad \text{Eq. (7.9a)}$$

where $\dot{\epsilon}_s$ equals the steady-state creep rate in hr⁻¹, σ equals stress in MPa, and the best fit values for the other coefficients are as follows:

Term	Value	Standard Deviation
$\ln A$	14.75	1.58
n	1.47	0.23
Q	404 kJ/mol	23.4

The value of 404 kJ/mol for the activation energy of creep in 10–15 μm ThO₂ may be compared with the value of 380 kJ/mol reported by Armstrong et al (1962) for 96.1 percent dense stoichiometric UO₂ with a grain size of 6 μm . The difference between the two materials is consistent with the ratio of their absolute melting temperatures. On the assumption that the predominant mechanism for creep in both ThO₂ and UO₂ is diffusional or Nabarro-Herring creep, the activation energies for creep should be similar to those for volume diffusion of the slower diffusing ion, i.e., Th⁴⁺ in ThO₂ and U⁴⁺ in UO₂. The activation energies for volume diffusion of cations in ThO₂ and UO₂ are, respectively, 626 and 540 kJ/mol (see Chap. 6), somewhat greater than the values for the respective creep activation energies. The Nabarro-Herring creep mechanism is probably not the only mechanism for transfer of material; other diffusion-controlled mechanisms may also contribute.

Poteat and Yust (1966) expressed the opinion, based on graphical examination of subsets of the data, that the exponent n in Eq. (7.9) was a function of temperature. However, computer-aided attempts to fit the entire collection of their data to mathematical models of n that included thermal and athermal terms were not successful. Poteat and Yust's value

for the activation energy Q was 469 kJ/mol in contrast to the value of 404 kJ/mol obtained from the computer-aided calculation. On the basis of the supposed difference from UO₂ and temperature dependence of n , Wolfe and Kaufman (1967) postulated various distinctive creep mechanisms: cation diffusion, the collection of dislocations at grain boundaries, and the formation of necklace-type porosity. The present reexamination indicates that no such explanation is needed; there are apparently no large differences in the general nature of creep in the two oxides. The difference in activation energies may be attributable to the difference in the melting points as discussed above.

Wolfe and Kaufman (1967) also examined thoria with a considerably larger grain size: oxalate-derived material that had an average grain diameter of $220\text{ }\mu\text{m}$ as a result of annealing for four hours at 2073 K . These results are also plotted in Fig. 7.4, as the filled symbols. The data from these coarse-grained samples were fit to an expression of the form of Eq. (7.9), and the following best-fit values of the coefficients were obtained:

Term	Value	Standard Deviation
$\ln A$	21.10	2.22
n	4.36	0.24
Q	724 kJ/mol	45

In Fig. 7.4, evaluations of Eq. (7.9) for fine-grained material are shown as solid lines, and for coarse-grained material as dashed lines. The coarse material exhibits a stress-dependence exponent three times as large, and an activation energy twice as large, as the $10\text{--}15\text{ }\mu\text{m}$ thoria. For any given temperature, the two lines would intersect in the general vicinity of the right side of the graph, i.e., at a stress value comparable to the fracture strength of the material. However, over most of the ranges of temperature and stress for which steady-state creep has been investigated in thoria-base oxide fuels, the coarse-grained material exhibits less creep under comparable conditions.

In Sect. 7.4.2, a portion of the profile obtained for sol-gel material (Figs. 7.2 and 7.3) was ascribed to creep. The corresponding creep rate is plotted in Fig. 7.4, together with the value that would be calculated from Eq. (7.9) using the coefficients for $10\text{--}15\text{ }\mu\text{m}$ grain size. The sol-gel material apparently has a creep rate almost two orders of magnitude higher than Poteat and Yust's sintered, oxalate-derived material, other things being equal. However, Fig. 7.4 also shows another set of results: that of Morgan and Hall (1966). Their results, on sintered, oxalate-derived thoria, were nearly an order of magnitude lower than the value that would be predicted from the equation, using the same $10\text{--}15\text{ }\mu\text{m}$ coefficients.

It therefore appears that the creep rate is sensitive to the frequency of occurrence of grain boundaries in the material, but there are probably other factors as well, which might make a difference amounting to an order of magnitude or more in the observed result. Among these factors may be the general condition of the grain boundaries: the smoothness of their configuration, their uniformity, and the occurrence of precipitates in the grain boundary region. Morgan and Hall (1966), and also Poteat and Yust (1966), examined their samples photomicrographically after the

creep tests. Both observed a large number of cracks along grain boundaries, in the direction of the applied stress, and extending a large fraction of the diameter of the adjacent grains, i.e., that portion of a grain boundary that was oriented close to the stress direction was likely to have been opened. It was postulated that creep occurs largely by dislocation slip along the grain boundaries. These boundaries consist of regions of good fit, capable of sustaining high stress, and weaker regions of poor fit. A migration of the dislocations occurs in such a way as to equalize the stress.

7.4.4 Effect of Composition

(a) Effect of UO_2 Additions

Wolfe and Kaufman (1967) measured the steady state creep of ThO_2 -9.8 mole percent UO_2 with an average grain size of $30\text{ }\mu\text{m}$. Results are plotted in Fig. 7.5, where they are compared to values that would be predicted from the coefficients for pure thoria with a grain size of $10\text{--}15\text{ }\mu\text{m}$. The data appear simply to have been shifted downward by an amount comparable to the interval between a pair of lines as drawn on the graph; the measurements are about one-third the values that would be predicted for pure thoria, or alternatively, those that would be expected at a temperature about 100 K lower. The stress exponent n and the activation energy Q appear to have been little affected by the addition of the urania. It is convenient to express the observed results in terms of a *multiplication factor* by which the pre-exponential coefficient A appears to have changed as a result of the change in composition. In the case of Fig. 7.5, the multiplication factor is approximately 0.33.

Figure 7.6 shows the steady-state compressive creep rate measurements of Wolfe and Kaufman (1967) on ThO_2 -9.8 mole percent UO_2 in material with an average grain size of $120\text{ }\mu\text{m}$. The lines drawn on the figure represent the fitted equation for pure thoria using the coefficients for a grain size of $220\text{ }\mu\text{m}$. Once again, values for n and Q are comparable, while the coefficient A has undergone a multiplication factor amounting, in this case, to about 0.2.

For the coefficients n and Q , the material (pure thoria or ThO_2 -9.8 mole percent UO_2) appears to display one set of values ($n = 1.47$, $Q = 404$) for grain sizes of 10 , 15 , and $30\text{ }\mu\text{m}$, and another set of values ($n = 4.36$, $Q = 724$) for 120 and $220\text{ }\mu\text{m}$. There appears to be a transition, in terms of Fig. 7.4, between the solid lines and the dashed lines, in the neighborhood of $100\text{ }\mu\text{m}$. These sets of lines can be translated upward or downward by the multiplication factor, which affects the coefficient A , and which is a function of composition. However, the slope and spacing of the lines are maintained during the translation, at least to a first approximation.

Figure 7.5. Steady-State Creep Rate for ThO_2 -9.8 Mole Percent UO_2 with an Average Grain Size of $30 \mu\text{m}$ (Wolfe and Kaufman, 1967).

(b) Effect of CaO Additions

The thorium used in the creep study of Poteat and Yust (1966) was reasonably pure; it contained 25 ppm Ca, 8 ppm Mg, and 40 ppm C, and the amounts of Si, Fe, and S were below the limits of detection. Morgan and Hall (1966) characterized their thorium as containing about 350 ppm of various impurities. Further details were not given, but it may be assumed that Ca was an important impurity.

The effect of larger amounts of CaO additions on the creep rate of ThO_2 was also investigated by Morgan and Hall (1966). The fabricated specimens of $\text{ThO}_2 + \text{CaO}$ contained CaO in amounts from 0.45 to 8.10 mole percent. These were subjected at 1673 and 1738 K to compressive stresses ranging from 3 to 55 MPa.

Figure 7.6. Steady-State Creep Rate for ThO_2 -9.8 Mole Percent UO_2 with an Average Grain Size of $120 \mu\text{m}$ (Wolfe and Kaufman, 1967).

The grain size in these samples increased from 4 to $8 \mu\text{m}$ before the experiments to around $20 \mu\text{m}$ after their conclusion. The appropriate

coefficients of the creep equation to be used for comparison purposes would, in this case, be those of fine-grained material. No comparable increase in grain size was observed in thoria without the calcia additions.

Initial stresses were 3 or 5 MPa. They resulted in very high initial creep rates, on the order of 300 times the value that would be predicted from the fine-grained coefficients. These very high initial rates may be attributed to transient creep. As the test proceeded, this degree of enhancement declined, and the stress was periodically increased in order to maintain a creep rate within the limits of detection.

The initial multiplication factor, of approximately 300, was comparable for the different levels of CaO content. However, the rate of decline of the multiplication factor was greatest for materials with low CaO content. At

100 hours, the multiplication factor was about 10 for material with 3.84 mole percent CaO, and 15 for material with 6.16 mole percent CaO. After 700 hours, the only material run for this length of time (3.84 mole percent CaO) showed a multiplication factor of approximately 3.

This enhancement is in contrast to the effect of CaO on the creep rate of UO_2 , as observed by Armstrong and Irvine (1964). They found that CaO additions caused a decrease in the creep rate of that material.

The enhancement of the sinterability of thorium by calcia additions discussed in Chap. 8. If it is assumed that comparable mechanisms are operative in the case of creep, then the enhancement of creep may be due to decreased grain boundary viscosity as a result of the segregation of calcium at the grain boundaries.

(c) *Effect of Stoichiometry in UO_{2+x}*

Creep in UO_{2+x} was discussed by Seltzer et al (1971) and by Bretheau et al (1979). Large effects were noted on variation of stoichiometry. The multiplication factor varied as x^2 , where x is the oxygen excess in formula units. The activation energy Q varied from 380 kJ/mole, for $x = 0$, to 225 kJ/mole for $x = 0.1$, in polycrystalline material.

7.4.5 Hot Pressing

Hot pressing, or pressure sintering, in which a uniaxial load is applied for a specified time to a pellet in a restrained die at elevated temperatures, approximates the actual conditions in a fuel rod. Understanding of the process taking place under controlled hot-pressing conditions is therefore useful in interpreting the complex pore-closure behavior observed in low-density ceramic fuels on irradiation. In-reactor densification is discussed in Chap. 9; both that process and pressure sintering may be regarded as creep testing under a confining pressure. The rate controlling process should be comparable to that observed in compressive creep tests of the type described in the previous section.

Accordingly, it should be possible to write an equation:

$$P/P_0 = \exp(-Bt) \quad \text{Eq. (7.10)}$$

where

P_0 = present porosity

P = porosity at time t hours in the future

B = densification rate, in fraction of the present porosity disappearing per hour.

The coefficient B should be related directly to the steady-state compressive creep rate $\dot{\epsilon}_s$, also in units of hr^{-1} , which may be calculated for the prevailing conditions of temperature and pressure using Eq. (7.9).

Measurements of the densification of ThO₂ and ThO₂-UO₂ under hot-pressing conditions were obtained by Wolfe and Kaufman (1967) and are listed in Table 7.4. Also given are determinations of the densification rate B , calculated using Eq. (7.10), and evaluations of the steady-state compressive creep rate of fine-grained pure thoria at the same conditions of temperature and pressure, calculated using Eq. (7.9). The coefficients for fine-grained material are appropriate because the grain-boundary intercepts of the hot-pressed material are given as being 100 μm or less. Geometric densities were used in the calculation of the coefficient B ; the "Initial Density % T.D." column corresponds to $100(1 - P_0)$.

Equation (7.9) was generated using data obtained from pure thoria. Figures 7.5 and 7.6 showed that compositional variation was among the factors affecting the creep rate. It was convenient to express this effect as a multiplication factor, to be applied to the pre-exponential coefficient A . By comparing the observed densification rate with the creep rate as calculated from Eq. (7.9), a ratio is generated which may be termed the apparent multiplication factor; these ratios are listed in Table 7.4 for each sample. For compositions other than pure thoria, such a factor would incorporate the effects of compositional variation. It would also incorporate, in the values both for ThO₂ and ThO₂-UO₂ solid solutions, effects attributable to the fact that the densities of the densification samples were lower than those on which the creep rate data were obtained. The factor would also reflect the different nature of the densification and the steady-state compressive creep tests.

The determinations at the lowest pressure (6.90 MPa) are clearly aberrant; they are marked with a dagger in the table and are not considered further. For the remaining measurements, the apparent multiplication factors for each composition were averaged. They show a systematic mean variation with composition, from 1.33, for pure thoria, to 2.68 for ThO₂-11.76 mole percent UO₂. For ThO₂-24.28 mole percent UO₂, however, the n value of the apparent multiplication factor was found to be 0.30.

A major portion of the apparent multiplication factor may therefore be ascribed to compositional variation, although the nature of this effect must be considered subject to future elucidation, particularly in the compositional region above 12 mole percent UO₂. If it is assumed that this effect could be taken into account, the steady-state compressive creep equation would generally predict the densification rate within an order of magnitude. This is an adequate degree of precision; the porosity is only a minor fraction of the total volume of the fuel, the densification accounts for only part of the porosity, and uncertainties in the densification rate account for only a small part of that quantity.

TABLE 7.4—RELATIONSHIP BETWEEN HOT PRESSING AND CREEP RATE
IN ThO₂ AND ThO₂-UO₂*

Mol% UO ₂	Temp. (K)	Pressure (MPa)	Time (min)	Initial Density (%T.D.)	Measured Densifi- cation Rate (hr ⁻¹)	Calculated Creep Rate (hr ⁻¹)	Apparent Multipli- cation Factor	Mean
0.00	2223	34.48	101	83.06	0.03839	0.15243	0.252	1.33
0.00	2293	34.48	81	83.26	0.02888	0.29686	0.097	
0.00	2393	34.48	140	83.46	0.13895	0.71896	0.193	
0.00	2223	34.48	60	83.92	0.15291	0.15243	1.003	
0.00	2323	34.48	30	83.35	0.26141	0.39018	0.670	
0.00	2193	37.23	60	81.74	0.25854	0.12662	2.042	
0.00	2193	37.23	60	81.74	0.25854	0.12662	2.042	
0.00	2193	37.23	61	83.37	0.03553	0.12662	0.281	
0.00	2193	39.30	63	81.59	0.21045	0.13709	1.535	
0.00	2093	42.75	60	83.73	0.02552	0.05388	0.474	
0.00	2183	54.13	61	80.97	0.42289	0.19829	2.133	
0.00	2303	54.13	61	77.20	0.86735	0.63160	1.373	
0.00	2223	68.95	90	82.97	0.34107	0.42227	0.808	
0.00	2073	68.95	60	83.40	0.21864	0.08699	2.513	1.88
0.00	2233	68.95	60	83.72	0.71802	0.46565	1.542	
0.00	2423	68.95	60	83.72	1.42640	2.56026	0.557	
1.96	2093	6.90	172	83.13	0.03659	0.00369	9.926†	
1.96	2103	6.90	180	84.89	0.01651	0.00412	4.010†	
1.96	2093	33.79	120	83.15	0.07030	0.03813	1.844	
1.96	2088	75.16	120	84.33	0.23315	0.11682	1.996	
1.96	1993	75.85	120	84.67	0.07065	0.03910	1.807	
4.89	2093	6.90	167	85.61	0.01013	0.00369	2.747†	
4.89	2098	6.90	166	84.84	0.02466	0.00390	6.331†	
4.89	2088	33.79	120	84.19	0.08419	0.03607	2.334	2.41
4.89	1993	75.16	120	84.44	0.10630	0.03858	2.248	
4.89	1993	75.16	120	84.44	0.10630	0.03858	2.755	
8.82	2093	6.90	167	83.73	0.05630	0.00369	15.273†	
8.82	2093	6.90	180	84.72	0.02892	0.00369	7.846†	
8.82	2093	34.48	120	84.19	0.14374	0.03928	3.660	
8.82	2093	73.78	120	84.09	0.28154	0.12018	2.343	
8.82	1993	74.47	120	84.01	0.07728	0.03806	2.031	
11.76	2098	6.90	180	84.62	0.00370	0.00390	0.951†	2.67
11.76	2098	6.90	180	84.35	0.01082	0.00390	2.778†	
11.76	2093	34.48	120	82.85	0.16175	0.03928	4.118	
11.76	1993	74.47	120	84.39	0.05837	0.03806	1.534	
11.76	2093	75.85	120	84.17	0.29586	0.12516	2.364	

*Data from Wolfe and Kaufman (1967).

†Omitted from mean because of low pressure.

TABLE 7.4— (CONTINUED)

Mol% UO ₂	Temp. (K)	Pressure (MPa)	Time (min)	Initial Density (%T.D.)	Measured Densifi- cation Rate (hr ⁻¹)	Calculated Creep Rate (hr ⁻¹)	Apparent Multipli- cation Factor	Mean
24.28	2098	6.90	120	83.95	0.00722	0.00390	1.852†	
28	2433	33.79	120	85.28	0.06406	0.97416	0.066	
28	2263	34.48	38	85.23	0.07554	0.22422	0.337	
24.28	2438	34.48	60	85.25	0.14180	1.04543	0.136	
24.28	2098	34.48	120	84.99	0.01625	0.04151	0.392	
24.28	2193	64.12	120	85.37	0.12781	0.28154	0.454	
24.28	2433	65.50	120	85.25	0.14260	2.57807	0.055	
24.28	2083	66.88	120	85.07	0.06158	0.09308	0.662	
24.28	2273	67.57	360	85.21	0.04179	0.66264	0.063	
24.28	2083	67.57	120	85.40	0.07208	0.09449	0.763	
24.28	2268	68.26	20	85.27	0.24607	0.64168	0.383	
24.28	2183	68.61	120	85.30	0.06106	0.28096	0.217	
24.28	2433	68.95	60	85.40	0.24042	2.77998	0.086	
24.28	2263	68.95	48	85.28	0.09800	0.62115	0.158	
24.28	2248	68.95	120	85.58	0.05531	0.53833	0.103	
24.28	2173	68.95	239	85.28	0.10967	0.25551	0.429	
24.28	2183	68.95	21	85.46	0.13685	0.28304	0.483	
24.28	2193	68.95	120	85.33	0.06974	0.31324	0.223	
24.28	2193	68.95	300	84.17	0.05374	0.31324	0.172	
24.28	2183	68.95	120	85.53	0.07638	0.28304	0.270	
24.28	2173	68.95	120	85.27	0.02720	0.2551	0.106	
24.28	2083	69.64	240	85.28	0.04047	0.09877	0.410	
24.28	1983	69.64	120	85.03	0.02570	0.03050	0.843	
24.28	1993	69.64	120	85.78	0.01427	0.03449	0.414	
24.28	2183	69.64	86	84.79	0.08476	0.28721	0.295	
24.28	2193	69.64	120	84.32	0.0397	0.31785	0.107	
24.28	2193	70.33	120	85.21	0.03392	0.32249	0.105	

The relationship between creep rate and densification has been examined theoretically by Murray et al (1958). They assumed, for purposes of calculation, that sintering takes place according to a highly idealized model proposed by Mackenzie and Shuttleworth (1949) which in turn assumes that the porous fuel approximates a Bingham Solid. It is convenient to refer to this approach as the Murray Model.

Among the assumptions of this model are the following: (1) Hydrostatic pressure; (2) spherical, uniform pores uniformly distributed in a continuous, uniform matrix; (3) a uniform contraction, during the densification process, of both the pore radius and the spacing between the pores, such that a fixed ratio between the two is maintained; (4) a constant number of pores; (5) low surface tension compared to the applied hydrostatic pressure; (6) pressures and temperatures in the range where viscous flow takes place.

Under these conditions, it was shown that the multiplication factor, aside from the effects of change of composition, should be 0.75. The factors actually found for pure thoria had a mean value of 1.33; a reasonable consensus value for the multiplication factor would be 1. For approximate calculations, a multiplication factor need not be used, and the steady-state compression creep rate can be taken as equivalent to the densification rate.

7.5 FRACTURE

Some workers in the fields of mineralogy, crystallography, and ceramics regard the phenomena of cleavage and fracture as mutually exclusive. However, thoria fractures by cleaving; the resulting surfaces are crystallographically controlled, and must technically be classed as cleavages. In a typical rupture of sintered thoria, the surface follows successive cleavage planes in stepwise fashion, with typical step widths in the range of tens or hundreds of nanometers.

Campbell et al (1959) investigated fracture surfaces in a commercial single crystal of ThO_2 , and found that they corresponded principally to $\{100\}$ planes. Gilbert (1965) examined particles of thoria in "thoriated" tungsten alloy. This material had a composition of W-5 wt% Re-2.2 wt% ThO_2 . It was reduced 92 percent by hot-rolling at 1873 K; during this procedure, the thoria particles, originally approximately spherical and 2 μm in diameter, were deformed plastically. The resulting alloy sheets, approximately 1 mm in thickness, were formed into tensile specimens and tested to failure at room temperature; during this procedure, the flattened thoria bodies fractured. Examination of shadowed replicas of the fracture surface by transmission electron micrography showed that the principal cleavage surfaces in the thoria corresponded to the $\{111\}$ plane. This corresponds to the well-developed cleavage observed macroscopically on the isostructural compound fluorite, CaF_2 . Also observed were $\{110\}$ and $\{100\}$ planes, although somewhat less frequently.

In conjunction with his determination of fracture surface energy (see Chap. 5) Matzke (1980) obtained a value for the fracture toughness of sintered thoria at room temperature, i.e., its resistance to crack growth. This value is $1.07 \text{ MPa m}^{1/2}$ ($\text{MN m}^{-3/2}$).

7.6 HARDNESS

The hardness of a material is a measure of its resistance to deformation. For most purposes, it is determined from the load and the size of the indentation impressed into the material by means of a hard indenter.

There are a number of ASTM Standards defining the methods of performing the recognized, reproducible tests that have been developed. (See listing under "ASTM" among the references for this chapter). Strict application of these standards would provide that only the Knoop, Vickers and Rockwell A scales may be used for brittle materials such as thorium and uranium oxides. Standard E-92, which first defines the Vickers scale, states that the scope of the standard "covers the determination of the

Vickers Hardness of metallic materials". However, in the course of defining the Knoop Hardness in Standard E-384, the ASTM document also redefines the Vickers Hardness, and makes no mention of any restriction to metallic materials. The two standards differ in the angles of the diamond indenter, and in the fact that the Vickers Hardness requires determination of the mean of the two diagonals of the rhombus-shaped indentation, while the Knoop Hardness is based only on the major diagonal; the resulting Knoop and Vickers Hardness Numbers should be quite similar, however.

The various scales have units of kg/mm^2 , where the numerator refers to the imposed load, and the denominator to the area of the indentation. However, the values on the various scales are not equal, because the results also depend on the indenter used, as well as the load and the rate of application of the load. Accordingly, although the units resemble superficially those used for pressure, it is not appropriate to transform them to the corresponding SI pressure unit (pascals).

6.1 Effect of Temperature

Wolfe and Kaufman (1967) reviewed the available hardness measurements on thoria, urania, and their solid solutions. Results are summarized in Fig. 7.7. In this graph, the log of the Vickers Hardness is plotted against the temperature, expressed as a fraction of the melting temperature on the absolute scale (the homologous temperature).

The results for the individual materials may be characterized as consisting of a series of straight lines on the semilog plot. The slope of these is relatively uniform and equivalent to a doubling of the area of the indentation for each temperature increment of 15 percent of the melting point. The data in Fig. 7.7 have been replotted from Wolfe and Kaufman (1967), using melting temperatures consistent with those recommended in Chap. 5. A doubling of the area of the resulting indentation is equivalent to changing the Knoop or Vickers Hardness Number to half its previous value. This temperature effect may be considered appropriate for sintered pure thoria, pure urania, and their solid solutions in the range examined, which extends from 0 to 30 mole percent urania.

Figure 7.7. Hardness Measurements on ThO_2 , UO_2 , and Their Solid Solutions at Room Elevated Temperatures Replotted from Wolfe and Kaufman (1967) Using Melting Temperatures Recommended in Chapter 5.

Belle and Berman (1978) reported some additional room-temperature measurements of thoria and related materials. All are given in terms of Knoop Hardness Numbers (KHN). These included determinations by Smid (1976) on 98 percent theoretical density thoria, of KHN 760, using a 1-kg load; and a determination by Wygant (1951) on ThO_2 -0.5 weight percent CaO, of KHN 640, using a 500-gram load. The leftmost points

plotted in Fig. 7.7 are room temperature determinations; they indicate a Vickers Hardness Number of approximately 700, intermediate between the values quoted (assuming the approximate equivalence of the Knoop and Vickers scales). Belle (1961) gives a consensus value of KHN 666 for stoichiometric UO_2 ; this is also in the range of values quoted above.

Wolfe and Kaufman (1967) also give some data obtained by mutual indentation tests on thoria. In these tests, sintered polycrystalline cylinders, 0.424 cm in diameter, were placed with their axes at right angles and their curved surfaces in contact, and a load was applied for 10 seconds. Areas of the resulting two indentations were determined, and their mean was taken; the Meyers Hardness Index was then computed as the load (in kg) divided by the mean area (in mm^2). The load, in these experiments, varied from 12 to 37 kg. Results are shown in Fig. 7.8.

The Meyers Mutual Indentation Test is not considered a standard hardness test by the ASTM; results are affected by sample and experiment design, as well as time and rate of application of the load. Results should be compared only within the same experiment or strictly comparable ones. No special significance should be attached, for example, to the fact that the Meyers "Numbers" shown in Fig. 7.8 are approximately half the Vickers "Numbers" shown in Fig. 7.7 for thoria at comparable densities and homologous temperatures.

The Meyers Test would be capable of demonstrating strain hardening if it were present; such strain hardening would cause a change in the value with load at any one temperature. No such systematic variations can be seen; the measurements at any one temperature, at various loads, are clustered closely together. The temperature dependence appears to be the same as that found in the Vickers Hardness tests of Fig. 7.7. Also, no significant difference could be observed between the Meyers Hardness values of the two batches of thoria examined, although these differed slightly in porosity and considerably in grain size. The Meyers Hardness values presented in Fig. 7.8 may be regarded as offering confirmatory information to the Vickers Hardness data of Fig. 7.7.

Effects of Composition and Porosity

In Fig. 7.7, the "x" and "+" marks are used to indicate pure thoria and pure urania, respectively, at the comparable densities of 95.0 and 95.3 percent of theoretical. The square and diamond marks are used for these two materials at another pair of comparable densities: 97.5 and 97.0 percent of theoretical, respectively. A comparison shows that, at comparable porosities and homologous temperatures, there is no significant difference between the Vickers Hardness Numbers of pure urania and pure thoria. Higher porosities are associated with lower hardness numbers; the

Figure 7.8. Mutual Indentation Hardness Measurements on ThO_2 (Wolfe and Kaufman, 1967).

91.6 percent dense UO_2 (circles) has a Vickers Hardness Number approximately 30 percent lower than the 95.3 percent dense UO_2 at a comparable temperature.

The solid solutions (filled-in circles and squares in Fig. 7.7) have Vickers Hardness numbers greater than pure urania or pure thoria at the same homologous temperature. The effect of composition on hardness at

Figure 7.9. Hot-Hardness Isotherms for $\text{ThO}_2\text{-UO}_2$ Compositions.

arious temperatures is summarized in Fig. 7.9. In all cases, the solid solutions are harder than the pure end members. The increase reaches a maximum in the composition range of 6–8 mole percent UO_2 , at 1273 K. At higher temperatures, the maximum in this composition range is not well defined, and the total increase in hardness is less.

The traditional Mohs Hardness Scale, used by mineralogists, establishes the position of a material in a standard series of minerals, such that the material will be scratched by all materials higher in the scale, and will scratch all materials lower in the scale. Frondel (1958) states that thoria-nite (naturally occurring thoria-urania; see Chaps. 1 and 9) has a Mohs Hardness of 6.5 to 7. Accordingly, it will scratch orthoclase (No. 6 in the Mohs Scale) and it will be scratched by quartz (No. 7). Quartz is the hexagonal form of SiO_2 stable at room temperature; orthoclase is ideal monoclinic KAlSi_3O_8 . It is understood that all determinations are made at room temperature.

Weast (1978) gives a table comparing hardness values on the Mohs and Knoop scales. The Knoop Hardness Number of orthoclase is given as 560, and that of quartz as 820. Figure 7.7 indicates that the Vickers Hardness (approximately equivalent to the Knoop Hardness) of thoria and urania is approximately 700 at room temperature. Apparently, there is good agreement between hardness determinations based on scratching and those based on indentation.

7.7 RUPTURE

Under certain conditions of loading, particularly with regard to temperature and state of stress, oxide fuel materials will fracture in a brittle manner with little prior plastic deformation. Bend tests on UO_2 (Tottle, 1965) and compression tests on ThO_2 (Yust and Poteat, 1965) showed that failure, in these particular modes of deformation, occurred by brittle fracture when the temperature was less than half the melting point on the absolute scale.

In the case of UO_2 , this is in agreement with evidence that insufficient slip systems are available below that temperature to permit continuous macroscopic flow in polycrystalline samples. However, under combined states of stress—those that cannot be characterized as pure shear or compression—plastic deformation can be observed at comparatively low temperatures. In indentation hardness tests, for example, plastic deformation is observed even at room temperature.

In the bend test, the stress at the most stressed fiber at failure is termed the modulus of rupture. In the brittle range, this value is sensitive to material and environmental conditions including temperature, state of stress, strain rate, porosity, grain size, specimen dimensions, surface conditions, and atmosphere. It is therefore not a simple matter to characterize the strength of a given fuel composition. However, Knudsen (1959), after reviewing the available data on ThO_2 and UO_2 , proposed that the effects of grain size and porosity on the modulus of rupture could be fit to an equation of the form

$$S = KG^{-a} \exp(-bP) \quad \text{Eq. (7.11)}$$

Figure 7.10. Bending Strength of Polycrystalline Thoria at Room Temperature, as a Function of Porosity and Grain Size (Knudsen, 1959; Chen, 1981).

S = modulus of rupture (MPa)
 G = mean grain diameter (μm)
 P = volume fraction porosity
 K = fitted coefficient
 a = fitted coefficient
 b = fitted coefficient.

Knudsen's data for the modulus of rupture of thoria in bend tests at room temperature are shown in Fig. 7.10, together with curves representing a fitted equation of the form of Eq. (7.11), with the coefficients shown in Table 7.5.

TABLE 7.5—FITTED COEFFICIENTS OF EQ. (7.11) FOR THORIA AT ROOM TEMPERATURE IN BEND TESTS

Coefficient	Value	Standard Deviation
K	440.963	38.720
a	0.3578	0.0258
b	4.0858	0.1901

The above coefficients represent a refitting of the data of Knudsen (1959) using a nonlinear least squares computer program. They are similar to values originally stated by Knudsen; however, he did not give values indicating the associated error.

Chen (1981) measured the modulus of rupture of polycrystalline thoria bars in which $P = 0.0245$ and $G = 45 \mu\text{m}$. Evaluation of Eq. (7.11) would predict a value of 102.2 MPa for this material. Chen found a mean value of 112.7 MPa, with a standard deviation of 18.3 MPa, for bars with a rectangular cross section; this is within the expected error variation of the predictive equation. However, for bars with chamfered edges, Chen found a considerably higher modulus of rupture: 128.1 MPa, with a standard deviation of 23.4 MPa. These data are also shown in Fig. 7.10.

Chen (1981) also examined bars of ThO_2 -0.59 mole percent CaO with $P = 0.0016$ and $G = 2 \mu\text{m}$. For these values, in pure ThO_2 , Eq. (7.11) would predict a modulus of rupture of 342 MPa, a value much too high. The conditions are outside the range of application of the equation. Chen did, however, find a considerably elevated modulus of rupture for these bars: 147.1 MPa for the bars as received, and 199.3 MPa for the bars as polished. Chen's results show that there are variables having a significant effect on the strength of the material that are not considered in Eq. (7.11). Among these is the condition of the surface of the specimen, which is related directly to the likelihood of initiation of a crack.

Chen (1981) found that the distribution of failures about the mean values corresponded to a Weibull distribution, i.e., the cumulative failure curve was a straight line when plotted on a coordinate of $\log(-\log S)$, where S is the fraction of samples surviving. Detailed discussion of the Weibull distribution is outside the scope of this work. It is based on a mathematical model in which failure occurs at a "weakest link". In this particular case, over most of the range of S , it corresponds in general

characteristics to the normal distribution, i.e., approximately two-thirds of the failures occur within one standard deviation of the mean values given.

Knudsen also determined the modulus of rupture at 1273 K for five of the thoria materials that had been examined at room temperature. Results are given in Table 7.6, together with the ratios between the strengths as measured at the two temperatures.

The available data are not sufficient for delineating fitted coefficients.

However, examination of Table 7.6 indicates that the strength of the material, on raising the temperature by about 980 K, changes by a factor of approximately $\exp(-P)$. This is equivalent to a statement that the value of the coefficient b , of Eq. (7.11), is approximately 5 instead of 4 at 1273 K. Grain size appears to have only a secondary effect on the changes observed.

A similar examination was conducted with UO₂, with and without titania additions (Knudsen et al, 1960). It was found that the coefficient b at room temperature was 3.17 and at 1273 K was 5.84; this compares rather closely with the thoria values of approximately 4 and 5. The value given for the coefficient a , at room temperature, was 0.119—considerably less than the thoria value of 0.358. It therefore appears that the temperature dependence is comparable in the two materials, and the grain size dependence is less in uranium. In the region of overlap of measured data in the two

TABLE 7.6—MODULUS OF RUPTURE OF THORIA
AT ROOM TEMPERATURE AND AT 1273 K*

Porosity (%)	Grain Diameter (μm)	Rupture Modulus (MPa)		Ratio S_{1273}/S_{RT}	$\exp(-P)$
		R.T.	1273 K		
6.7	25.1	110	117	1.06	0.935
	16.4	129	119	0.92	0.918
23.2	6.1	94	67	0.71	0.793
31.1	42.9	32	17	0.53	0.733
31.3	9.4	63	39	0.62	0.731

*Knudsen (1959)

studies, thoria was approximately 50 percent stronger than urania in brittle rupture in the bend test at room temperature. Results of two sets of tests run under comparable conditions are given in Table 7.7. However, in UO_2 , variations from stoichiometry constitute another variable that must be considered, and the available data are inadequate for the presentation of a predictive equation comparable to Eq. (7.11). In both thoria and urania, the strength at elevated temperatures was either approximately the same or somewhat less than at room temperature.

Chen (1981) measured the modulus of rupture of his ThO_2 -CaO sample at elevated temperatures. Although this material had very little porosity ($P = 0.0016$), the decrease in modulus of rupture observed at 1273 K was comparable to that for the highest-porosity sample in Table 7.6; the ratio S_{1273}/S_{RT} was 0.61. Once again, it is clear that the strength of these ceramic materials is affected by many factors, some of which are not readily identified, characterized, or controlled.

A random selection of 120 thoria pellets fabricated for the Light Water Breeder Reactor (LWBR) according to the methods described in Chap. 8 were subjected to destructive evaluations, which included a measurement of room-temperature crush strength. The mean grain diameter of these pellets was $20.4 \mu\text{m}$ and the mean porosity was 2.2 volume percent. Evaluation of Eq. (7.11) using these quantities results in a modulus of rupture of 137 MPa, which may be considered typical of LWBR thoria production pellets.

In tests made with the cylindrical ends of the pellets ground flat and the dished portions removed, the mean crush strength was 566 MPa, or 4.1 times the modulus of rupture. The compressive strength of thoria is therefore considerably greater than the resistance to the forces of torsion used in the rupture modulus test.

TABLE 7.7—BRITTLE RUPTURE OF URANIA AND THORIA IN BEND TESTS RUN AT ROOM TEMPERATURE UNDER COMPARABLE CONDITIONS

Material	Porosity (%)	Grain Diameter (μm)	Stren. (MPa)
UO_2	8	20	83
ThO_2	8.6	17.4	129
UO_2	5	59	76
ThO_2	5.3	53.1	110

Some variations of the compressive strength of the pellets from the mean value could be attributed to pellet size. The smallest pellets examined, with cross-sectional areas of 0.329 cm^2 , had a mean crush strength about 7 percent less than the mean for all the samples. The largest pellets, with cross-sectional areas of 2.787 cm^2 , had crush strengths about 9 percent larger than the mean. The difference may perhaps be attributed to the fact that the dimensions of the smallest pellets are approaching the region in which local weaknesses, or configurations causing stress concentrations, can compromise the integrity of the entire ceramic body.

7.8 THERMAL SHOCK

Fracture occurs in ceramics after a sudden change in temperature. This fracture, known as thermal shock, results from stresses that arise from nonlinear temperature gradients or any restraints to thermal expansion (Kington et al, 1976). These stresses are more significant in ceramics than in metals because there is a lack of ductility to relieve the stresses; consequently, cracking and fracture are more common.

When a uniform steady heat flow is disturbed by the presence of internal cracks and cracklike imperfections, with a thermal conductivity different from the matrix, there is local intensification of the thermal gradient at the precise location that is likely to coincide with a mechanical weakness. As a result, there may be catastrophic spreading of the imperfection. Internal cracks therefore aggravate the tendency of ceramics to fracture when thermally shocked.

A constant rate of temperature change can also lead to temperature gradients and thermal stresses. When the sample surface is cooled at a constant rate, a parabolic temperature distribution occurs. The surface temperature is lower than the average temperature, and central compressive stresses occur. When a sample is heated, these stresses are reversed. Tensile stresses are thus present during both heating and cooling. Since ceramics are much weaker in tension than under compression, failure is considered to occur once the thermal stress concentrations exceed the

the strength of the ceramic locally. In other words, it is assumed that under the influence of a complex system of stresses imposed on a solid body, its failure would result from overstressing its weakest kind of mechanical strength. In brittle materials, this is the tensile strength.

For purposes of evaluation, the case is considered of catastrophic cooling such that the surface is at room temperature. Equation (7.11) and Fig. 7.10 give values for the modulus of rupture under these conditions; failure can be expected if the stresses induced by the temperature change exceed these values.

The strain introduced by a temperature change from an elevated temperature T to room temperature can be calculated from the consensus equation for linear expansion (see Chap. 5):

$$\frac{L}{L_0} = \frac{L_0 + \Delta L}{L_0} = 0.9976 + 7.837 \times 10^{-6} T + 9.995 \times 10^{-10} T^2 \quad \text{Eq. (7.12)}$$

and

$$\frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \quad \text{Eq. (7.13)}$$

where $\Delta L/L_0$ is the fractional change in length between a higher temperature T and a lower temperature T_0 .

At room temperature, Young's modulus E , as given in Eq. (7.2a), is

$$E[298, P] = 249.1 (1 - 2.21 P) \text{ GPa} \quad \text{Eq. (7.2a)}$$

where P is the volume fraction of porosity.

Kingery et al (1976) give the maximum stress, such as would be developed at the surface of a pellet, as

$$\sigma_{\text{MAX}} = \frac{E \Delta L}{1 - \mu} \quad \text{Eq. (7.14)}$$

where μ is Poisson's ratio (Sect. 7.3.1(d); Table 7.3).

However, evaluation of σ_{MAX} by means of Eq. (7.14) leads to excessively conservative results, which indicate that cracking can happen if a typical body of thorium—a cylinder, for example—undergoes a sudden temperature change of as little as 60 K. Such a change would result in a maximum change in stress equal to the tensile strength. Because of thermal diffusivity, however, stresses are much less than the maximum calculated from Eq. (7.14). The mean stress can be calculated from the equation given by Kingery et al (1976) for pellets of equal radius and length:

$$\sigma_{\text{MEAN}} = \left(\frac{\sigma_{\text{MAX}}}{T - T_0} \right) \left(\frac{0.105 \text{ gr}^2}{\alpha} \right) \quad \text{Eq. (7.15)}$$

where

T = center temperature of the pellet, K
 g = rate of cooling, K/s
 r = pellet radius, m
 α = mean thermal diffusivity, m²/s.

Values of α can be calculated for the ThO₂ and ThO₂-UO₂ compositions from equations given in Chap. 6.

7.9 SUMMARY

For pure polycrystalline thoria, the mechanical properties in the region of elastic deformation may be regarded as well characterized. Values have been established for the various elastic moduli (Young's modulus, shear modulus, bulk modulus) and Poisson's ratio under reference conditions, and equations have been developed for the variations of these properties with porosity and temperature. Results are summarized in Table 7.2, and appear to be valid and internally consistent for temperatures up to 1300 K and porosities up to a volume fraction of 0.4. There is good agreement with values derived from measurements on single crystals of thoria. Values of these properties for urania are rather similar to those for thoria, and it may be assumed that those for thoria-uranium solid solutions vary linearly with molar composition between the two end members.

Likewise, the mechanical properties associated with eventual failure—strength and hardness—are moderately well characterized. Figure 7.10 summarizes the room temperature modulus of rupture of thoria as a function of porosity and grain size. Measurements are also available indicating a decrease in strength with increasing temperature. These relationships were also observed with UO₂. Under comparable conditions, the modulus of rupture of UO₂ was found to be about two-thirds the value for ThO₂. Hardness, as a function of temperature, porosity, and composition, is summarized in Fig. 7.7. To generalize: Resistance to deformation decreases with increasing temperature and porosity, and the effect of changing composition is secondary to these factors.

At temperatures less than half the melting point on the absolute scale, rupture occurs within the region of elastic deformation, and the phenomena associated with permanent deformation are not significant on a bulk scale, although they do occur to a limited extent, i.e., hardness indentations. These phenomena are not fully characterized. There appears to be a transition between fine-grained and coarse-grained behavior, occurring in the vicinity of a grain size of 100 μ m; the nature of this transition, its exact location, and the factors influencing it still remain to be explored.

Variation in composition within the fluorite-type solid solution can cause changes of an order of magnitude in the creep rate; the occurrence of a grain boundary phase, such as may be present in materials with CaO, can affect the rate by several orders of magnitude. Likewise, there are variations, not fully understood but perhaps amounting to an order of magnitude, between the compressive creep rate and the densification rate observed on hot pressing. Plastic deformation is also known to occur independent of creep, but cannot be readily quantified.

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- E-10 Brinell Hardness of Metallic Materials
 - E-18 Test for Rockwell Hardness and Rockwell Superficial Hardness
 - E-92 Test for Vickers Hardness of Metallic Materials
 - E-140 Standard Hardness Conversion Tables for Metals
 - E-384 Test for Microhardness of Materials
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Chapter 8

FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUELS

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8.1 INTRODUCTION

Fuel fabrication with ThO_2 and $\text{ThO}_2\text{-UO}_2$ in both particulate form and bulk is discussed in this chapter. Methods for the bulk thoria-base fuels were adaptations from the large body of manufacturing and service experience with UO_2 fuel pellets for PWR and BWR installations. One manufacturing procedure, termed the ADU process after the ammonium diuranate starting material, consists of calcining the ADU in a reducing atmosphere to produce UO_2 . Analogously, ThO_2 is the air calcination product of precipitated thorium oxalate. To fabricate $\text{ThO}_2\text{-UO}_2$ pellets, the two calcined oxides are comminuted, agglomerated with an organic binder, cold-pressed, and then sintered in hydrogen at 2063 K. This method, used to manufacture the fuel for the LWBR core, is termed the *LWBR Reference Process*.

Without calcia additions, the early attempts to develop the LWBR Reference Process for ThO_2 resulted in fuel pellets of comparatively low density (90 to 94 percent of theoretical). Sinterability was eventually improved through use of a more *active* powder, produced by an improved comminution procedure, and a higher sintering temperature.

Aside from the LWBR Reference Process, the most significant fabrication method for thoria-base fuels is the Sol-Gel Process, which results in high-density ThO_2 and $\text{ThO}_2\text{-UO}_2$ spheres used as fuels in β -cooled reactors. This process is carried out at comparatively low temperatures and results in a product with extremely small crystallite sizes. Sol-gel fuel has also been vibration-compacted inside metal cladding, and the resulting fuel elements have been irradiated as part of the experimental Kilorod project (Haws et al, 1965).

8.2 TYPES OF FUEL ELEMENTS

8.2.1 Sol-Gel Microspheres

Attempts to fabricate pellets from sol-gel material on a production scale have not consistently resulted in bodies with satisfactory

mechanical characteristics. However, it is possible to form the product of the Sol-Gel Process itself, such that it is available as high-density microspheres with diameters in the sub-millimeter range. This product can then be sized by sieving, and appropriate size fractions can be incorporated directly into fuel elements.

Microspheres are fabricated by permitting droplets of thoria hydrosol, dispensed at the top of a column of 2-ethylhexanol by a vibrating hollow needle, to fall through the column of liquid. The hydrosol loses water and assumes a spherical shape. After further heat treatment, the product is sieved to obtain the desired sphere size. For the HTGR application (see Chap. 1) the sol-gel thoria was fabricated as high density (99 percent of theoretical) particles, 400 μm in diameter.

Among the advantages claimed for the Sol-Gel Process are (1) use of a wet-chemistry route, thus avoiding dust-generating steps; (2) adaptability to shielded, remote operation, which is particularly important in reprocessing fuel containing ^{232}U ; and (3) use of temperatures no higher than 1423 K.

8.2.2 Vibratory-Packed Fuel Elements

Microspheres produced by the liquid column method were also used to prepare fuel rods by vibratory compaction. Manufacture of such rods was undertaken as the Kilorod project, and also in conjunction with the development of the sphere-pac fuel elements. In all cases, the procedure designs are adaptable to remote fabrication of recycled material, since this is one of the principal applications envisioned for this technique.

Recent work with the sphere-pac process (Haas et al, 1978) used sol-gel spheres of three different sizes. The fuel filler was composed as follows: 60 weight percent of spheres with a diameter of 800 μm ; 20 weight percent of spheres with a diameter of 200 μm ; and 20 weight percent with an average diameter of 30 μm . The two large sizes were blended and loaded into the fuel rod; the smallest microspheres were then packed into the void spaces using a low-energy vibrator (Suchomel et al, 1978).

On the basis of gamma scans of 1100 rods manufactured by an earlier variant of this process for the Kilorod project, approximately 100 were rejected due to low or nonuniform density. The remainder had densities between 88 and 91 percent of the theoretical value (Haws et al, 1965).

8.2.3 Metal-Clad Pellets

The LWBR Reference Process can be used to produce pellets of high density and complicated shape to close dimensional tolerances. Specifically, for LWBR, pellets of nine different compositions (ThO_2 and

eight $\text{ThO}_2\text{-UO}_2$ solid solutions) were manufactured to very detailed dimensional specifications, which were different for each type. The right circular cylindrical shape of the pellets was modified by dishes, chamfers, and tapers (Johnson and Crain, 1967; Johnson and Allison, 1981). The purpose of the dishes was to minimize axial growth; that of the chamfers was to aid in loading the long, hollow rods of cladding while minimizing chipping; and that of the tapers was to decrease the formation of bamboo-like bulges along the cladding as the fuel swelled during service.

A general description of LWBR is given in Chap. 1. Detailed descriptions of each of the pellet types, with all dimensions, are given by Connors et al (1979), together with specifications for the Zircaloy-4 cladding, which also differed in thickness for the various types of rods.

8.3 SOURCE MATERIALS

The occurrence of thorium and uranium among the minerals of the earth's crust is discussed in Chap. 1. Monazite, the principal ore of thorium, and the various types of uranium ores are first separated from the surrounding mineral matter by physical methods. The thorium-bearing monazite sand is concentrated in sluice boxes to reject lighter sands. The heavier sands are then separated by gravity concentration or by electrostatic or electromagnetic methods. The uranium ores are upgraded and comminuted by mechanical crushing and separating methods to reduce the material to a small size suitable for leaching. Flotation has been used to separate uranium ores into carbonate-rich and silicate-rich fractions for separate alkaline and acid leaching (Cordfunke, 1969; Hogerton, 1963).

Leaching is the key operation in the processing of thorium and uranium ores. Sulfuric acid is used to extract thorium from monazite and thorite (ThSiO_4). When monazite is digested in sulfuric acid, thorium, uranium, and the rare earths dissolve, and the mineral residue (gangue) is removed by filtration. In a contrasting caustic

leach process the gangue goes into solution, leaving the desired elements as oxide precipitates which are filtered, washed, and dried. Thorium is recovered from leach liquors by selective precipitation, filtration, and solvent extraction. The thorium precipitates are dissolved in nitric acid and extracted with tributyl phosphate. This treatment results in a purified thorium nitrate product suitable for reactor use (Cuthbert, 1958).

Due to the wide variety of uranium ores, many different techniques for extracting uranium have been developed. Most ores are leached with an acid (sulfuric, nitric, hydrochloric) to bring uranium into solution. After filtering off the solid residues, either solvent extraction or ion exchange is used to purify and concentrate the uranium (MacCready and Wethington, 1981). The uranium is recovered from

solution by precipitation as ammonium or sodium diuranate. Alkaline leaching is used for carbonate ores to avoid the troublesome and wasteful evolution of carbon dioxide. The alkaline leaching medium consists of a hot solution of sodium carbonate and bicarbonate. In the final refining steps, the impure diuranate salts are precipitated from the acid or alkaline leaching solutions; these precipitates are dissolved in nitric acid and extracted with tributyl phosphate to yield a purified uranyl nitrate solution (Cordfunke, 1969; Hogerton, 1963).

8.4 POWDER PREPARATION METHODS

Thorium and uranium oxide powders can be prepared by air pyrolysis or hydrogen reduction of precipitated thorium and uranium salts (oxalate, hydroxide, diuranate, carbonate, peroxide) and also by direct decomposition of the nitrates.

8.4.1 Pyrolysis of Thorium Oxalate

Thoria powder is produced commercially by calcining the precipitate of hydrated thorium oxalate. Thorium oxalate hexahydrate is precipitated on the addition of oxalic acid to a solution of a thorium salt, usually thorium nitrate, according to the following equation:

Pentahydrate, dihydrate, and monohydrate oxalate precipitates have also been reported (D'Eye and Sellman, 1955; White et al, 1981a).

Precipitation processes are generally complex and often nonreproducible with regard to particle shapes, sizes, settling times, and hydrates produced. Walton (1967) has discussed some of the factors involved, such as nucleation and cluster formation, crystal growth and crystal growth kinetics, induction periods, effect of impurities on growth rates, temperature coefficients of growth and precipitation, dissolution and aging of precipitates, and adsorption and surface exchange. Precipitation by direct mixing of reactants, the customary technique used for preparing thorium oxalate, is especially complicated; mixing can be inhomogeneous and can result in a wide spectrum of particle morphologies (Walton, 1967). In spite of these difficulties, however, many of the parameters controlling the particle size, shape, and texture of the precipitated thorium oxalate and the resulting calcined thorium dioxide have been identified. These are discussed below.

In most studies (Allred et al, 1957; Breysse et al, 1965; Hutchison and Lloyd, 1979; Kantan et al, 1958; Kinoshita et al, 1965a; White et al, 1981a) a slight excess of oxalic acid was added to a thorium nitrate

solution (*direct strike*). A significant variable in this procedure is the precipitation temperature, which affects surface area, bulk density, particle size, and size distributions not only of the precipitated thorium oxalate but also of the calcined ThO_2 powder. As shown in Figs. 8.1 through 8.3, lower precipitation temperatures result in greater surface areas, smaller particle sizes, and smaller bulk densities for the calcined thorium powder.

The degree of agitation (ultrasonic versus magnetic stirring), digestion time, and acidity also affect the size of the thorium oxalate crystals that are formed. Magnetic stirring during precipitation and longer digestion times favor formation of particles with improved filtering characteristics (White, 1979). The greater the acidity (free nitric acid) during precipitation, the denser the thorium oxalate precipitate (Grimaldi, 1961; Hutchison and Lloyd, 1979). A given amount

Figure 8.1. Surface Area of Calcined Thoria Powder as a Function of Precipitation Temperature of Thorium Oxalate. (Hutchison and Lloyd, 1979.)

Figure 8.2. Average Particle Size of Calcined Thoria Powder as a Function of Precipitation Temperature of Thorium Oxalate. (Hutchison and Lloyd, 1979.)

Figure 8.3. Bulk Density of Calcined Thoria Powder as a Function of Precipitation Temperature of Thorium Oxalate. (Hutchison and Lloyd, 1979.)

of thorium oxalate precipitated from 1.5 N acid is about half as voluminous as the same amount precipitated from a 0.5 N acid solution; the volume of the precipitate reflects the crystal size. The free nitric acid in the thorium nitrate solution affects the crystallite size by controlling the concentration of oxalate ions available to react with the thorium ions to form the thorium oxalate crystallites. Reducing the concentration of available oxalate ions by increasing the free acid

level favors the growth of these crystallites and thereby reduces the surface area of the powder.

Other precipitation parameters affecting the physical properties of the thorium oxalate precipitate and the resulting thorium oxide powder include pH, concentrations of the reactants, and rate and sequence of combining the reactants (Hart et al, 1979). The data of Breyse et al (1965) on the effect of several thorium oxalate precipitation parameters on the surface area of the derived ThO₂ powder are given in Table 8.1. The range of surface areas produced by the variation of a specific precipitation parameter indicates its importance and significance. The increase in ThO₂ powder surface area with increased temperature of precipitation may be due to the morphology,

TABLE 8.1—EFFECTS OF OXALATE PRECIPITATION PARAMETERS ON ThO₂ POWDER SURFACE AREA*

Precipitation Parameter	Surface Area (m ² /g)
pH of initial nitrate solution 2.2 to 0.7	33 to 36
Rate of addition 2.5 ml/min to 0.833 ml/min	12 to 25
Sequence of addition H ₂ C ₂ O ₄ to Th(NO ₃) ₄ (direct strike)	40
Th(NO ₃) ₄ to H ₂ C ₂ O ₄ (reverse strike)	34
Concentration of Th(NO ₃) ₄ solution 1.0 M (570 g nitrate/liter)	40
0.1 M	27
0.02 M	18
Excess of oxalic acid 0	28
20%	24
100%	19
Precipitation temperature 307 K	17
348 K	24
boiling	33
Time of digestion 0 hr	24
1 hr	28
4 hr	30

Breyse et al (1965), as compiled by Hart et al (1979): Oxalate calcined at 623 K.

internal porosity, or surface roughness of the powder particles. Hart et al (1979) suggest that this result is compatible with the thorium oxalate decomposition data of Beckett and Winfield (1951), who observed that the larger ThO_2 particles were composed of spongy thin plates (laminae) of oxide crystallites with a central hole lined by very thin projecting scales.

Finally, the temperature of calcination or decomposition of the thorium oxalate precipitate is a critical parameter in determining the properties of both the ThO_2 powder and final sintered body (Hepworth and Rutherford, 1964; Hey and Livey, 1969; Warren and Elyard, 1968). Low calcination temperatures favor a more *active* powder, consisting of porous particles and having a large surface area. However, if the calcination temperatures are too low, incomplete decomposition can occur and impurities, such as carbon from the oxalate, are retained in the thorium powder.

8.4.2 Pyrolysis of Other Thorium Compounds

Thoria powders have been made on a laboratory scale by precipitating and then calcining the hydroxide, carbonate, oxycarbonate, peroxide, formate, benzoate, and tannate of thorium (Bilinski et al, 1963; Correa and Costa, 1969; Cuthbert, 1958; Davis, 1965; Grimaldi, 1961; Harada et al, 1962; Hasty and Boggs, 1964; Kantan et al, 1958; Mentzen, 1968; Moorehead and McCartney, 1976; Moorthy et al, 1963, 1964, 1965). Although these preparations have not been studied as extensively as the thorium oxalate precipitation, the ThO_2 powder properties from the laboratory preparations differ widely, depending on various control parameters during the critical steps of precipitation and calcination. In some cases, processing is difficult because the preparations are gelatinous, as is the case for the thorium hydroxide and peroxide precipitates.

8.4.3 Direct Decomposition of Thorium Nitrate

Thorium dioxide can be prepared by direct thermal decomposition of thorium nitrate without an intermediate precipitate. The simplicity of the direct denitration route offers a potential advantage for producing thoria in a remote processing facility (Feraday, 1979, 1981). The results of experimental tests (El-Fekey et al, 1979 and 1982; Harada et al, 1962; Johnson, 1966; Kantan et al, 1958; Palmer et al, 1982; Pope and Radford, 1974a and 1974b), however, show that the direct denitration procedure consistently produces coarse powders of low ceramic quality. High integrity sintered bodies with densities greater than 90 percent of theoretical could not be made from these powders. Comminution processes (ball milling, micronizing, Majac milling) have been successfully used to increase the surface area and

reduce the particle size of nitrate-derived ThO_2 powders, thus making it possible to achieve high density sintered bodies (Johnson, 1966; Palmer et al, 1982). However, comminution methods complicate the simple denitration procedure and result in pickup of undesirable impurities (Clayton, 1976). The primary use of the denitration process is in the preparation of oxide for the Sol-Gel Process (Nelson, 1966).

1.4 Preparation of UO_2 Powders

Preparation procedures for producing natural and enriched UO_2 powders have been extensively reviewed (Brandberg, 1973; Clayton and Aronson, 1961; Fellows, 1961; Mathieu, 1978; Woolfrey, 1968). Some commercial methods are: (1) direct denitration of uranyl nitrate hexahydrate (UNH) to UO_3 followed by hydrogen reduction to UO_2 ; (2) hydrolysis of UF_6 and precipitation of either ammonium diuranate (ADU) or ammonium uranyl carbonate (AUC), either of which is then decomposed and reduced in hydrogen; and (3) decomposition and reduction of UF_6 by superheated steam and hydrogen.

The high purity urania ($^{233}\text{UO}_2$) powder used in the manufacture of $\text{ThO}_2\text{-UO}_2$ fuel for the Light Water Breeder Reactor (LWBR) was made by the ADU precipitation process (Frankhouser et al, 1967; Leitnaker et al, 1972; Lloyd, 1980; Parrott, 1980). Thoria was irradiated under special conditions such that the recovered $^{233}\text{UO}_2$ product contained not more than 10 ppm of the isotope ^{232}U impurity. The irradiated thoria was dissolved and an ion exchange purification process was used to remove the gamma-emitting alpha-decay daughters of ^{232}U in order to minimize the gamma-radiation field of the $^{233}\text{UO}_2$ during LWBR fuel manufacture. The ^{233}U , in the form of uranyl nitrate effluent from the ion exchange process, was precipitated as ADU with gaseous ammonia and reduced with hydrogen to $^{233}\text{UO}_2$.

1.5 Preparation of $\text{ThO}_2\text{-UO}_2$ Powders by Coprecipitation

Coprecipitation of thorium and uranium from the same solution offers a direct chemical route for preparing homogeneous $\text{ThO}_2\text{-UO}_2$ powders. The simplest method is to add ammonium hydroxide to a thorium-uranium solution. Thorium is precipitated as thorium hydroxide and uranium as ammonium diuranate. The mixed precipitate is usually calcined in air to $\text{ThO}_2\text{-U}_3\text{O}_8$ and reduced with hydrogen to $\text{ThO}_2\text{-UO}_2$, but it can also be decomposed directly by heating in a reducing atmosphere. Experimental details for three coprecipitation processes (mixed hydroxides, peroxides, and oxalates) are listed in Table 8.2. Tests indicate that the dioxides made from coprecipitated oxalates sinter to much higher densities than the dioxides made from coprecipitated hydroxides or peroxides (Gabaglio and Liscia, 1966).

TABLE 8.2—THORIUM-URANIUM COPRECIPITATION STUDIES

Formula	Precipitant	Calcination Temperature (K)	Reduction Temperature (K)	Reference
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	873	1573	Aronson and Clayton (1960)
$\text{Th}(\text{OH})_4 + \text{Na}_2\text{UO}_4$	NaOH	1273	---	Boekschoten and Kema (1968)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	1073	1273	Goto (1968)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	873	1073	Kanno et al (1982)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	1723	1923	Pope and Radford (1974a)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	1023	1923	Pope and Radford (1974a)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	873, 1023, 1273	1973	Radford and Bratton (1975)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	723—1073	---	Sata (1965)
$\text{Th}(\text{OH})_4 + (\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH	873—1273	1573—1773	Sata and Kiyoura (1961)
$\text{U}_x\text{Th}_{1-x}(\text{C}_2\text{O}_4)_2$	$\text{H}_2\text{C}_2\text{O}_4$	---	---	Brau et al (1965)
$\text{U}_x\text{Th}_{1-x}(\text{C}_2\text{O}_4)_2$	$\text{H}_2\text{C}_2\text{O}_4$	700, 973, 1173	773, 973, 1173	Cogliati et al (1962, 1963)
$\text{U}_x\text{Th}_{1-x}(\text{C}_2\text{O}_4)_2$	$\text{H}_2\text{C}_2\text{O}_4$	1173	1673—2073	Gabaglio and Liscia (1966)
$\text{U}_x\text{Th}_{1-x}(\text{C}_2\text{O}_4)_2$	$\text{H}_2\text{C}_2\text{O}_4$	1473	1473	Gilpatrick et al (1963)
$\text{U}_x\text{Th}_{1-x}(\text{C}_2\text{O}_4)_2$	$\text{H}_2\text{C}_2\text{O}_4$	623	1173	White et al (1981a)
$\text{Th}_2\text{O}_7 + \text{H}_2\text{UO}_5 \cdot \text{H}_2\text{O}$	H_2O_2	1173	1873	Gabaglio and Liscia (1966)
$\text{Th}_2\text{O}_7 + \text{H}_2\text{UO}_5 \cdot \text{H}_2\text{O}$	H_2O_2	623	873, 1973	McCart and Mailen (1981)

Several studies on the mixed thorium-uranium oxalate system have been made (Table 8.2). For a quantitative coprecipitation the uranyl (UO₂⁺⁺) ion must first be reduced to the uranous ion (U⁺). Brau et al (1965) observed that, when oxalic acid is added to a solution of thorium and uranium (U⁺) nitrate, a mixed oxalate of variable composition is precipitated. However, reversing the order of addition of the reagents, i.e., adding the solution of nitrates to a saturated alic acid solution, gave homogeneous mixed oxalate precipitates.

Precipitation of thorium-uranium (U⁺) oxalate was investigated by Cogliati et al (1963) to determine the effects of thorium-uranium concentration, oxalic acid to thorium-uranium ratio, precipitation time, and digestion time on the filterability of the precipitate. They observed the settling and filtering properties of nine precipitate batches and found that, with the exception of oxalic acid excess, the influence of the concentration variables was negligible. Increasing the excess of oxalic acid broke up the precipitated aggregates, and a sharp decrease in both the settling and filtering rates occurred. Although no detectable influence on settling rate was observed, the particle size, as well as filtering rate, increased with increasing precipitation temperature. The settling rate decreased as the digestion time increased, again due to a breakdown of the aggregates. As was noted in the thorium oxalate precipitation studies, the temperature of calcination or decomposition of the mixed oxalate precipitate is a key variable in determining the properties of both the ThO₂-UO₂ powders and the final sintered bodies.

3.4.6 Preparation of ThO₂-UO₂ Powders by Mechanical Mixing Methods

Since ThO₂ and UO₂ form a continuous series of solid solutions, simply mixing and milling the component powders followed by cold pressing and sintering are a quick, economical method of preparing homogeneous ThO₂-UO₂ (Johnson, 1978; Weinreich et al, 1977). A 1:1 mixed powder preparation, after pressing, will achieve a nearly homogeneous structure by diffusion in reasonable times at practical temperatures during sintering (Berman, 1972). Production of homogeneous, evenly dispersed ThO₂-UO₂ blends and complete solid solution formation require intimate mixing of highly active powders. Experimental details of various mechanical preparation methods and subsequent heat treatment for ThO₂-UO₂ are listed in Table 8.3

Early processes used a double-firing technique to ensure meeting homogeneity objectives (Cohen and Berman, 1966; Johnson and Train, 1967). Thoria and UO₂ powders were blended or milled in proper proportion to achieve the desired compositions, briquetted, and

TABLE 8.3—ThO₂-UO₂ MECHANICAL MIXTURE PREPARATION METHODS AND SUBSEQUENT SINTERING CONDITIONS

Mixing Method	Comminution	Sintering Conditions		Reference
		Temperature (K)	Time (hr)	
V-blender	ball milling	1943	1—16	Bassi et al (1966)
Slurry mix	planetary ball milling*	1998	12	Burke (1969a)
Slurry mix	planetary ball milling	2023	15	Davis and Hutchison (1966)
V-blender	ball milling	1973-2023	11	Johnson (1978)
Slurry mix	planetary ball milling	1973-2023	11	Johnson (1978)
Slurry mix	colloid milling	1973-2023	11	Johnson (1978)
V-blender	micronizing	1973-2063	11	Johnson (1978)
Slurry mix	homogenizer	1973-2023	11	Johnson (1978)
Slurry mix	Majac mill	1973	6, 12	Johnson and Crain (1967)
Dry mix	ball milling	1973	4	Matthews and Davis (1981)
V-blender	---	1923	3	Pope and Radford (1974b); Radford and Bratton (1975)
V-blender	blade mill	1973	2.5	Skinner (1965)
V-blender	micronizing	2063	11	Weinreich et al (1977)

*Of granules calcined at 2023 K.

calcined at 1973 K in hydrogen to form partial ThO₂-UO₂ solid solutions. The calcined briquettes were crushed, comminuted, pressed into compacts, and sintered in hydrogen at 2023 K. The second firing densified the compacts and completed the solid solution formation.

The next improvement was the development of a process which eliminated the initial calcination step and used a single firing to initiate and complete solid solution formation during compact densification. (A single-sinter method has cost-saving advantages in time and equipment and, in the case of ThO₂-²³³UO₂, reduces personnel radiation exposure.) Two major techniques for ThO₂-UO₂ powder comminution and mixing were investigated: In the first, the energy for grinding was supplied by a fluid stream (colloid milling, homogenizing, Majac milling, micronizing); in the second, grinding was done by the motion of solid dense milling media (conventional and planetary ball milling). Problems were encountered in achieving dense, pure, homogeneous compacts (Clayton and Rettger, 1963; Davis and Hutchison, 1966; Johnson, 1978). Only micronization was able to consistently produce a dense, pure, homogeneous product. The micronizer is a fluid-energy mill in which the ThO₂ and UO₂ particles are fluidized by air and injected into a rubber-lined chamber where the oxide

particles collide with each other, resulting in size reduction and mixing. Among the advantages of a micronizer are that the temperature is not appreciably raised during comminution and also, since very little wear of the equipment occurs, that contamination of the $\text{ThO}_2\text{-UO}_2$ mixture is minimized (Clayton, 1976).

The single-sinter method was used to manufacture the $\text{ThO}_2\text{-UO}_2$ fuel pellets for the LWBR core (Johnson, 1978; Weinreich et al, 1977).

The process consisted of micronizing mechanically blended mixtures

ThO_2 and UO_2 twice, followed by reblending. An organic binder was added to the $\text{ThO}_2\text{-UO}_2$ powder mixture to maximize the green density of the pressed compact. A CO_2 binder removal treatment at 1198 K was followed by sintering at 2023 to 2063 K in an atmosphere of hydrogen.

8.5 PARTICLE PREPARATION PROCESSES

8.5.1 Sol-Gel Methods

Detailed descriptions of various portions of sol-gel technology are given by Dean et al (1962), Haas and Clinton (1965), Haas et al (1966, 1967, and 1968), Kosianic et al (1968), Lackey and Selle (1978), Matthews and Swanson (1979), Meservey (1967 and 1968), Podo and Horsley (1966), and Wymer (1968). Matthews (1978) presents a useful summary of sol-gel techniques.

The Sol-Gel Process has been applied to thoria, urania, plutonia, zirconia, and various solid solutions of these materials; work has also been done on the carbides. This section reviews the process as it applies to ThO_2 and $\text{ThO}_2\text{-UO}_2$ solid solutions. Thoria-base sol-gel-derived fuels have been fabricated in several forms as outlined in the flow sheet (Fig. 8.4). Vipac (vibratory compacted) fuel consists of angular particles that are mixed and vibration-compacted into fuel elements (Freshley, 1972). Fuel in the shape of rods has been extruded from sol-gel-derived clays (Fitts et al, 1968). Sphere-pac fuel consists of a two- or three-size mix of nearly perfect spheres, vibration-compacted into fuel elements (Haas et al, 1967). Pellet fuel is pressed from finely ground sol-gel shards or from sphere-cal (calcined microspheres) particles (Tiegs, 1980).

The sol-gel process for oxides is composed of four basic steps:

1. Preparation of a stable oxide hydrosol
2. Conversion of the hydrosol to a gel by removal of water
3. Drying and calcining of the gel
4. Sintering into a high density fuel

In sol-gel shard formation, the first step is the conversion of thorium nitrate by steam denitration into an easily dispersible (peptizable) thorium oxide powder. The steam-denitrated ThO_2 powder is

Figure 8.4. Flow Sheet for Sol-Gel-Derived Thoria Fuel Forms. (Matthews, 1978.)

dispersed in dilute nitric acid to form a stable hydrosol. To prepare mixed uranium-thorium oxide, a uranium salt is added as the hydrosol is formed. The hydrosol is dried to a gel in shallow trays, and the gel fractures into polygonal fragments called shards. The gel is fired in air at 1423 K to densify the oxide. If uranium is present, U^{+6} is reduced to U^{+4} by continuing the calcination in an argon-hydrogen atmosphere.

In the sphere-pac process, thoria and thoria-urania hydrosols are introduced in the form of small droplets at the top of a tapered column which has an up-flow of an immiscible organic, usually a long-chain alcohol such as 2-ethyl hexanol. The droplets fall against a counter-current of the alcohol, which serves as a fluidizing medium and simultaneously removes water from the droplets. The water diffuses out of the droplets into the alcohol. A surfactant is dissolved in the organic phase in order to keep the hydrosol droplets from sticking to each other and wetting the column wall during their descent. The spheres collected at the bottom of the column have sufficient mechanical integrity to maintain their shape during the subsequent treatments of drying, calcination, and coating.

The sphere-cal process uses sol-gel-derived microspheres rather than powder as feed material for fuel pellet fabrication. Many variations of the sphere-cal process have been reported (Brambilla et al, 1970; Haas et al, 1981; Matthews and Hart, 1979 and 1980; Ringel and Zimmer, 1979; Tiegs et al, 1979 and 1980; Van der Bruggen et al, 1968). The basic sphere-cal procedure includes sol preparation, microsphere formation, gelation, drying, and calcining; this results in a product that can be pressed into pellets and sintered.

A solution containing thorium or uranium is dispersed into droplets and then solidified by a chemical precipitation reaction. The solidification or gelation of the droplets is accomplished by neutralizing the actinide metal nitrate solution with NH_4OH in a precipitation reaction. The gelation process is classified as external or internal by the way the precipitation is accomplished. In external gelation, the precipitation agent, NH_4OH , reaches the droplets from the outside, and the microspheres are aged in the ammonium hydroxide until gelation has been completed through their centers. In internal gelation, a water-soluble ammonia donor, e.g., hexamethylenetetramine, is mixed into the solution prior to droplet formation and precipitation is initiated by a temperature increase causing the donor to release the ammonia. Since the ammonia donor and the metal ions are dissolved in the same solution, the gelation occurs rapidly and uniformly throughout the drop. Urania microspheres are produced by external gelation, and $\text{ThO}_2\text{-UO}_2$ microspheres by either internal or external gelation.

Following gelation, the microspheres are dried to remove residual water and low boiling organics. In addition, calcination of the dried microspheres is necessary for controlled release of residual organics and, in the case of uranium-containing fuel, for reduction of U^{+6} to U^{+4} . Reduction is done in an argon-hydrogen gas mixture. Increased calcination temperature reduces the potential for reoxidation of the uranium-containing microspheres. However, the sinterability of the pressed microspheres is also reduced as calcination temperature increases. A prolonged calcination residence time (20 hours) at 873 K increases the oxidation resistance without appreciably reducing sphere sinterability (Tiegs, 1980).

8.5.2 Freeze-Dry Process

The freeze-dry process produces oxide powder directly from a nitrate solution in the form of sinterable, free-flowing granules. In this process, an aqueous metal salt solution or sol is sprayed through a nozzle at low pressure into liquid nitrogen or a bath of cold immiscible liquid in order to freeze the droplets rapidly. Water is removed by sublimation from the frozen particles in a heated vacuum chamber, and the resulting anhydrous compound, consisting of aggregated crystallites, is decomposed by calcination. Crystallite size in the final product can be varied by changes in the solution concentration, sphere-forming, or calcination steps.

High-density ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$ bodies have been fabricated on a laboratory scale from freeze-dried granules (Bowman, 1970; Burke, 1982b; White et al, 1981b). In this process for $\text{ThO}_2\text{-UO}_2$, droplets of a mixed thorium-uranyl nitrate solution are frozen by

spraying into a cooling bath, e.g., Freon 12 (dichlorodifluoromethane). The as-frozen granules are vacuum dried, decomposed in argon, and then calcined. The spheres thus produced are replicas of the frozen solution spheres and have a very low bulk density ($<1 \text{ Mg/m}^3$). Thoria granules prepared by the freeze-dried process are spherical in shape. A scanning electron micrograph (Fig. 8.5) shows that the granules are composed of leaf-like aggregates of very fine particles (Burke 1982b). The sponge-like structure of the granules and the fine particle size account for the low bulk density (0.9 Mg/m^3) and the high surface area ($10.4 \text{ m}^2/\text{g}$).

8.5.3 Mechanical Methods

Spheroidal particles of various $\text{ThO}_2\text{-UO}_2$ compositions were prepared by a self-abrasion process (Reeve and Jones, 1963). Thoria and UO_2 powders were mixed and hydrostatically pressed. The pressed

Figure 8.5. Scanning Electron Micrograph of Freeze-Dried Thoria Granules, X1000. (Burke, 1982b.)

compacts were crushed and sieved to yield particles of the desired size range for spheroidizing, which was accomplished by shaking the particles in an alumina crucible. The almost-perfect spheres were sintered in hydrogen for two hours at 1973 K. After sintering, the product consisted of a ThO₂-UO₂ solid solution with a small range of composition within particles, but high uniformity from particle to particle.

5.4 High Temperature Techniques

Spheroidal ThO₂ and ThO₂-UO₂ particles were prepared by a high-temperature flame denitration procedure (Haws and Haas, 1963). In this one-step process, thorium or uranyl nitrate solutions were sprayed into a high-temperature (~2500 K) flame. Aluminum nitrate was added to lower the melting point of the feed material sufficiently to allow melting in the flame. The actinide oxide product particles were about 1 μm in diameter.

Thoria crystals have been prepared by a method based on electrolysis of plasma (Kawabuchi and Magari, 1979). A plasma can be considered a gaseous electrolyte because it contains ions which are mobile through an applied voltage. Positive ions in a plasma are accelerated to a cathode, collide with its surface, discharge, and deposit on it. High purity ThO₂ powders were used as starting materials, and an anode was prepared from the oxide powder by cold pressing and vacuum sintering at 2173 K. Thoria crystals were deposited on a tantalum cathode from the ThO₂ plasma generated inside a hollow ThO₂ anode. The temperature of the cathode was over 2300 K during deposition. The deposition from the ThO₂ plasma onto the cathode was examined by varying the plasma current and the anode heating power, and by feeding argon and oxygen gases into the ThO₂ plasma. The deposit was a black oxide whose O/Th ratio was determined to be 1.64; it probably was a mixture of thorium metal and hypostoichiometric thoria. As oxygen pressure was increased, the deposit changed color from black through gray to white, and transparent crystals with stoichiometric composition were formed.

8.5.5 Large and Single-Crystal Processes

Finch and Clark (1965) summarized the state of the art in the growth of single crystals of thoria for research purposes. Macroscopic single crystals had been successfully grown in fluxes of borax, K₃PO₄, and Na₂CO₃-ThF₄. It was also reported that crystals exceeding 1 cm³ in volume were routinely produced in an electric arc furnace. The procedure consisted of packing sintered polycrystalline thoria, ground to sand size, and carbon electrodes and driving an arc through the

material. Finch and Clark characterized the resulting crystals as opaque, discolored red to black, and showing poor facial development.

Finch and Clark (1965) produced optically clear octahedra of thoria, 3 mm on an edge, in a flux of lithium ditungstate. Growth occurred primarily by solution transfer from polycrystalline thoria, at a temperature of 1525 to 1625 K, across a thermal gradient in the melted salt, to seeds in regions 20 to 75 degrees cooler. Crystals doped with 200 to 1000 ppm of various rare earths were also grown. Increased growth rates were obtained by adding 1 weight percent B_2O_3 to the flux.

Neeley et al (1967) grew optically clear cubes of thoria up to 5 mm on an edge, in fluxes involving a mixture of 7 weight percent ThO_2 , 15 weight percent Bi_2O_3 , and the balance PbF_2 , in platinum crucibles. Single crystals were grown from both lead and lead-free ($NaF-B_2O_3$) fluxes by Linares (1967).

Laszlo et al (1967) grew single crystals of thoria by focusing the sun's rays, by means of a 150-cm reflector, onto the end of a polycrystalline rod. Temperatures on the order of 4000 K were generated. The crystals formed on the edge of a crater, which represented the volume of vaporized material. The largest crystals were 2 mm long and were arrowhead- or barb-shaped, with octahedral faces forming the head of the arrow. Photomicrographs showed small optically clear regions in the crystals. The crystallized material was exceptionally pure, due to the vaporization step. Arc-grown ThO_2 crystals have also been produced (Ando et al, 1976; Ferris et al, 1964; Weinreich and Danforth, 1952).

8.6 CHARACTERIZATION OF ThO_2 AND ThO_2-UO_2 FEED MATERIAL

8.6.1 Physical Characterization Data

Many of the physical and chemical properties of the oxides of thorium and uranium are determined to a large extent by the method of preparation and the associated thermal or mechanical treatments. By modifying the properties of the parent compound, the temperatures of precipitation, decomposition and calcination, and the oxide comminution conditions, considerable control can be exercised over the chemical composition, particle shape, size and size distribution, and related characteristics of the ThO_2 , UO_2 , and ThO_2-UO_2 powders (Clayton, 1961; Garrett and James, 1970; Williams, 1963 and 1965). Final comminution and calcination steps can be critical in determining the powder characteristics. These powder characteristics can, in turn, influence the properties of the final sintered product as well as the behavior of the oxide during processing into solid fuel.

The standard methods of physical characterization of ThO₂ and ThO₂-UO₂ powders are listed in Table 8.4.

(a) Density

The theoretical densities of ThO₂ and UO₂ are 10.00 and 10.96 Mg/m³, respectively (Cohen and Berman, 1966). This ideal or ray density is calculated from the size of the unit cell and the atomic weights of its constituents, assuming that all lattice points are occupied. As discussed in Chaps. 3 and 4, ThO₂ and UO₂ form a continuous series of solid solutions; compositions, lattice constants, and theoretical densities are given in Table 3.2 of Chap. 3.

Densities of powders are generally expressed as either *bulk* or *tap* densities. The former term is applied to the weight of remaining powder poured into a measured volume after leveling and without applied compaction; the latter term is applied to the same procedure but with some compaction by tapping of the container. The measured bulk and tap densities for ThO₂ and ThO₂-UO₂ are low and in the range of 1 to 5.5 Mg/m³ (Table 8.4 references). For oxalate-derived thorium powders, as illustrated in Fig. 8.3, the bulk density increases with increasing precipitation temperature. As shown in Fig. 8.6, a large increase in the tap density of ThO₂ powder occurs on ball

Figure 8.6. Effect of Ball Milling on the Tap Density of ThO₂ Powder. (Matthews and Davis, 1979a.)

TABLE 8.4—PHYSICAL CHARACTERIZATION OF ThO₂ AND ThO₂-UO₂ POWDERS

<u>Density</u>	<u>Particle Morphology*</u>	<u>Particle Size Distribution</u>	<u>Surface Area</u>	<u>Crystallite Size</u>	<u>References</u>
----	TEM	sedimentation	gas adsorption	X-ray	Allred et al (1957)
----	SEM	sedimentation	gas adsorption	---	Burke (1982a)
bulk	SEM, TEM	sedimentation, electron microscopy	gas adsorption, sedimentation, electron microscopy	---	Clayton (1976)
bulk, tap	TEM	sedimentation	gas adsorption	X-ray	Kinoshita et al (1965a, 1965b)
tap	SEM	----	gas adsorption	---	Matthews and Davis (1979a, b; 1981)
bulk, tap	TEM, SEM	sedimentation	gas adsorption	---	Pope and Radford (1974a and 1974b)
----	SEM	----	gas adsorption	X-ray	White et al (1981a)

*TEM = transmission electron microscopy
SEM = scanning electron microscopy

milling. Tap density values increased from 2.7 Mg/m^3 to 3.5 Mg/m^3 after milling for eight hours, with little further increase after doubling the time to 16 hours.

Calcination also markedly increased the bulk density of comminuted thorium powder from 1.97 to 2.64 Mg/m^3 (Clayton, 1976), probably due to agglomeration of contacting particles during the heating treatments. Figure 8.7 shows that both bulk and tap densities for thorium increased with the calcining temperatures from 723 to 1723 K . Froese (1949) investigated the rate of change in particle density as a function of calcining temperature for ThO_2 prepared by the thermal decomposition of thorium hydroxide. He observed that sintering between particles did not occur below 1273 K , and from this inferred that crystal growth occurred only among closely joined crystallites.

(b) Morphology

The particle shape of ThO_2 and $\text{ThO}_2\text{-UO}_2$ powders has an important influence on their performance during processing. Particle

Figure 8.7. Effect of Calcination Temperature on the Density of Thorium-Base Powders. (Pope and Radford, 1974a. Courtesy, Journal of Nuclear Materials.)

contours can control flow characteristics of the powder and the manner in which the powder is packed, and thus the as-pressed and sintered density of the compact. In addition, particle shape affects the results of bulk density, particle size, and surface area measurements.

The exterior shapes of fine powder particles usually depend on their method or conditions of preparation. Thus, powders prepared by thermal decomposition retain the relic of the crystal shape of the starting material, with each individual particle being itself porous and composed of many small crystallites (Veale, 1972).

Both transmission and scanning electron microscopy have been used to determine the shape and surface properties of thorium powders (Table 8.4). The shape of thorium particles prepared via oxalate precipitation is usually square or rectangular plates or cubes, but other shapes have also been observed (Table 8.4 references; Monson and Hall, 1981). Representative transmission and scanning electron micrographs are shown in Figs. 8.8 through 8.10. The shape of the source salt, thorium oxalate, is that of a thin square plate (Allred et al, 1957; Breyse et al, 1965; Hey and Livey, 1969; Kinoshita et al, 1965a). Both square and rectangular plates as well as angular plate fragments are clearly evident in the micrographs. In general, electron micrographs of thorium powder exteriors are similar, regardless of calcining conditions (Clayton, 1976). Comminution, especially repeated micronizing, results in particle rounding and some particle breakup.

White et al (1981a) made scanning electron micrographs of thorium particles prepared under eight different oxalate precipitation conditions. Precipitation temperature had a strong effect on morphology. Oxide particles derived from oxalate precipitated at 343 K were square platelets, although particles from oxalate precipitates digested for six hours and ultrasonically agitated were, in some cases, rounded. Particles from 283 K precipitations, with mechanical agitation, approximated cubes. The morphology of thorium particles produced by a continuous precipitation method at 283 K was quite different. Individual particles were agglomerates composed of intergrown platelets. The morphologies of particles from two coprecipitated $\text{ThO}_2\text{-UO}_2$ powders were identical and similar to the morphology of ThO_2 particles derived from oxalate precipitated at the same temperature, agitation method, and digestion time.

(c) Surface Area

Gas adsorption techniques measure the total surface of powders accessible to a gas. Because of particle roughness and other irregularities on the external surface, as well as accessible pores and cracks on the internal surface, the powder particle is receptive to adsorption. Both external and internal surface areas are significant characteristics in the processing of ThO_2 and $\text{ThO}_2\text{-UO}_2$ powders. Sedimentation rates, resistance to flow of gases, bulk density, flow, and packing

Figure 8.8. Transmission Electron Micrographs of Thoria Powder Calcined in Air at 1311 K (above) and Recalcined in Hydrogen at 1473 K (below); 9000X. (Clayton, 1976.)

Figure 8.9. Scanning Electron Micrographs of Thoria Powder Calcined in Air at 1311 K (above) and Recalcined in Hydrogen at 1473 K (below); 10,000X. (Clayton, 1976.)

Figure 8.10. Scanning Electron Micrograph of 5 Pass-Micronized 1473 K Hydrogen-Recalcined Thoria Powder; 10,000X. (Clayton, 1976.)

properties are functions of the external surface. The total surface, as well as the effects of surface impurities and adsorbed gases, contributes to such chemical reactivity as rates of decomposition, oxidation, and solution.

Gas permeability and microscopic measurements also give estimates of the surface area of a powder, but these methods are accurate only when the powder is made up of smooth, nonporous particles of uniform shape. The surface areas determined by these two methods are lower than that measured by gas adsorption to the extent that the oxide powder does not conform to the ideal, uniform particle. Many oxide powder particles are composed of strongly bound agglomerates which can survive grinding (Clayton and Aronson, 1959; Williams, 1965). The size and distribution of these agglomerates can be measured by air and liquid sedimentation techniques. In the case of comminuted UO_2 , measurements of 2 to 5 μm were obtained. The gas adsorption technique applied to the same material gave a much finer measurement of 0.2 μm for the average particle size.

In general, the surface areas of ThO_2 and $\text{ThO}_2\text{-UO}_2$ preparations depend on the surface area of the material from which they are prepared, their thermal history, and any comminution treatments. Gas adsorption surface area values from 1 to 50 m^2/g have been reported for various crystalline ThO_2 powder preparations and from 80 to 150 m^2/g for thorium gels (Bannister, 1967, 1975; Mikhail and Fahim, 1967; Fahim et al, 1970). Calcination temperatures and calcination times are also important in determining the surface areas of ThO_2 and $\text{ThO}_2\text{-UO}_2$ powders and gels. Surface areas decrease with increasing temperature and time of calcination. The changes in gas adsorption surface area with calcination temperature are shown in Fig. 8.11 for ThO_2 and $\text{ThO}_2\text{-UO}_2$ powders. For nitrate-derived ThO_2 , the surface area decreased from 40 m^2/g at 723 K to <1 m^2/g at 1723 K, whereas for oxalate-derived ThO_2 the surface area decreased from 26.7 m^2/g at 873 K to 1.6 m^2/g at 1723 K. The $\text{ThO}_2\text{-UO}_2$ surface area values decreased from 20.3 m^2/g at 873 K to 1.9 m^2/g at 1273 K.

Clayton (1976) performed gas adsorption surface area measurements on oxalate-source ThO_2 powder samples that were recalcined in air (1273 to 1473 K) and in hydrogen (1273 to 1673 K). The recalcination times were corrected for the initial calcination of 8 hours. The

Figure 8.11. Effect of Calcination Temperature on the Surface Area of Thorium-Base Powders. (Pope and Radford, 1974a. Courtesy, Journal of Nuclear Materials.)

time-temperature-surface area data were computer-fitted to an equation developed by Allred et al (1957) for particle growth of oxalate-derived thorium powder that was calcined in air over the 923 to 1573 K temperature range. A best fit was made of the powder surface area to the calcination conditions by the equation

$$S = K t^{-A} \exp[-B/R] \exp[C/(RT)] \quad \text{Eq. (8.2)}$$

where

S = surface area, m^2/g

t = time, s

T = temperature, K

R = $8.3143 \text{ J/mol}\cdot\text{K}$

and the remaining symbols are fitted coefficients which were found to have the following values:

K = $0.6168 \text{ cm}^2/\text{g}\cdot\text{sec}$

A = 0.0713 (dimensionless)

B = $13.97 \text{ J/mol}\cdot\text{K}$

C = 50054 J/mol

These data included several different thorium batches, as well as results from both air and hydrogen atmospheres. It was shown that these factors did not cause significant differences in the fitted coefficients.

Equation (8.2) is based on data for thorium samples that had surface areas greater than $6 \text{ m}^2/\text{g}$ before the start of the heat treatment, and may be considered valid if this condition applies. The surface area of the starting material does not appear to be of primary importance provided that it is in excess of this value. The data covered the temperature range from 1273 to 1673 K, and times from 2 to 50 hours.

Calculated and measured values for the surface area are compared in Fig. 8.12. The temperature of calcination is the primary factor in determining the surface area; there is little further decrease in surface area after the first 10 hours of calcination. The constant A in Eq. (8.2) is considered to be characteristic of ThO_2 prepared by the thermal decomposition of thorium oxalate. The temperature dependent function, $\exp[C/(RT)]$, is typical for a rate process requiring an energy of activation, the constant C being equal to the enthalpy of activation for surface shrinkage. The relatively low value of the heat of activation (50 kJ/mol) is in accordance with growth taking place among well ordered groups of crystallites. The intercept B , being an entropy term, is characteristic of a particular thorium oxide preparation and should be determined for each new preparation.

Figure 8.12. Surface Area of Thoria Powders after Calcining. Contours Represent Evaluations of Equation (8.2). Symbols Represent the Number of Measurements Indicated by the Small Digits. Larger Digits Show Average of Measurements as Percent above or below Calculated Value. (After Clayton, 1976.)

The effect of comminution by micronizing on the surface area oxalate-derived ThO_2 powders is shown in Fig. 8.13. The results indicate that the largest increase in surface area occurs during the initial comminution and for powders calcined at the lower temperatures (1255 K). This suggests that higher temperature calcining renders the thoria particles stronger and less friable and, thus, more resistant to particle breakup.

Gas adsorption surface area measurements were also performed on green thoria pellets pressed without binder from a series of powders: calcined; calcined and micronized; recalcined; and micronized and recalcined. The purpose was to determine the degree of thoria particle fracturing on pressing. These results are compared in Table 8.5. Some

Figure 8.13. Effect of Micronizing on the Surface Areas of Calcined Thoria Powders. (Clayton, 1976.)

increase in surface area due to pressing is indicated; the magnitude of the increase tends to become smaller at the higher recalcining

TABLE 8.5—SURFACE AREAS OF CALCINED OXALATE-DERIVED ThO₂ POWDERS AND PRESSED PELLETS

Powder Treatment	Pellet Density (% theoretical)	Surface Area (m ² /g)		Surface Area Change (%)	Reference
		Powder	Pellet		
Air calcined at 973 K	---	17.5	26.1	+49.1	Hey and Livey (1969)
Air calcined (1255 K, 8 hr), micronized	60	8.20	11.89	+45.0	Busby and Clayton (1976)
		8.24	11.89	+44.3	
		8.33	11.89	+42.7	
Air calcined (1311 K, 8 hr)	59	5.55	6.79	+22.3	Busby and Clayton (1976)
		5.93	6.79	+14.5	
		6.02	6.79	+12.8	
		6.12	6.79	+10.9	
Air calcined (1311 K, 8 hr); air recalcined (1373 K, 48 hr)	60	2.82	3.69	+30.9	Busby and Clayton (1976)
		3.23	3.69	+14.2	
		3.27	3.69	+13.8	
Air calcined (1311 K, 8 hr); hydrogen recalcined (1373 K, 48 hr)	58	4.42	5.27	+19.2	Busby and Clayton (1976)
Air calcined (1255 K, 8 hr); micronized; hydrogen recalcined (1373 K, 48 hr)	62	4.77	5.50	+15.3	Busby and Clayton (1976)
		4.77	5.14	+7.8	
Air calcined (1255 K, 8 hr); micronized; air recalcined (1373 K, 53 hr)	59	3.39	3.87	+14.2	Busby and Clayton (1976)
		3.52	3.87	+9.9	
		3.85	3.87	+0.5	
		3.88	3.87	-0.3	
		3.95	3.87	-2.0	

temperatures. This agrees with the ThO₂ powder data which showed that ThO₂ particles recalcined at temperatures higher than their preparation-calcination temperatures were stronger and less friable than equivalent particles calcined at lower temperatures. As shown in Table 8.5, the ThO₂ particles calcined at 973 K have a higher surface area and, hence, are much more porous and weaker than those calcined at higher temperatures.

Surface area measurements were also made on green pellets pressed without binder from repeatedly micronized ThO₂ powders (Busby and Clayton, 1976). Results showed, in all but one case, that pressing did not cause additional breakup of particles, since the particle agglomerates and weaker particles were already broken up by the comminution process.

Surface areas have also been estimated from data on the emanation of thoron from sintered ThO₂, ThO₂-UO₂, and UO₂ as a function of temperature (Balek, 1982; Bussiere et al, 1961; Clayton and Aronson, 1963; Moorehead and McCartney, 1976; Skladzien, 1961). The emanation-derived surface areas for ThO₂ and ThO₂-UO₂ powders had markedly lower surface areas than those determined by gas adsorption. However, the values agreed in showing that surface areas of powders decrease with increasing calcining temperature.

(d) Particle Size and Size Distribution

Mean or average particle diameters are usually calculated on the assumption that the powder is composed of ideal, uniform spheres. Particles in a real powder generally have a variety of sizes and shapes, and differ in surface roughness and porosity. In many cases, the calculated average particle diameters may have little physical meaning. Electron microscopic determination of powder particle size can be an accurate direct method, but it is limited by irregularities in particle shapes and by the difficulty of obtaining a truly representative small sample. Surface area and average particle diameters can be

calculated from sedimentation techniques used in measuring particle size distributions. Both the sedimentation and electron microscopic methods should give a better indication of the physical size of powder particles than gas adsorption measurements, since the latter do not measure the internal surface area and the surface roughness of the particles. In practice, however, powders are rarely composed of particles of uniform size, but exist in a range of different sizes. It is useful, therefore, to determine the particle size distribution, i.e., the quantitative distribution of the particles among the various sizes.

Particle size distribution curves have been obtained for a number of ThO₂ powders by liquid sedimentation analysis,—a technique which measures only the external particle and agglomerate sizes and not the internal porosity. As shown in Fig. 8.14, the particle size distribution

Figure 8.14. Effect of Calcining Conditions on Sedimentation Particle Size Distribution of Thoria Powder. (Clayton, 1976.)

of oxalate-derived ThO_2 powders did not change drastically on calcining below 1473 K. At the higher calcination temperature of 1673 K, there was a noticeable increase in the coarse particle content ($\geq 5 \mu\text{m}$) and a corresponding decrease in the finer particles ($\leq 1 \mu\text{m}$). The bimodal particle size distribution of the as-calcined powders was effectively eliminated by the micronizing process, which broke up the larger agglomerates (Fig. 8.15). Several investigators (Allred et al, 1957; Clayton, 1976; Kinoshita et al, 1965a; Pope and Radford, 1974a) found that the particle sizes of oxalate-derived ThO_2 powders determined by sedimentation analyses agreed with electron micrograph values. They also observed that gas adsorption surface areas were much larger and decreased with increasing calcining temperature. Moreover, crystallite size, as measured by X-ray diffraction peak broadening, corresponded very closely to the particle sizes derived from adsorption measurements. This indicates that pores between the crystallites in each individual particle contribute significantly to the measured gas adsorption surface area. Since the electron micrograph and sedimentation data showed no increase in particle size with increasing calcination temperature up to 1473 K (Clayton, 1976), it is concluded that crystallite growth is confined to the individual particles. As the calcination temperature is increased, sintering takes place between the crystallites in the interior of the ThO_2 agglomerate with consequent decrease in the amount of porosity in the agglomerate and hence decrease in surface area. Additional evidence for high porosity levels in the oxalate-source ThO_2 particles produced by calci-

Figure 8.15. Effect of Micronizing on Sedimentation Particle Size Distribution of 1673 K Hydrogen-Recalcined Thoria Powder. (Clayton, 1976.)

nations at temperatures ≤ 1373 K was obtained by the systematic analysis of gas adsorption-desorption isotherms (Hey and Livey, 1969).

In summary, the predominant process in thorium calcination is particle densification and formation of agglomerates. The monocrystalline thorium oxalate precipitates retain their external plate shape on conversion to polycrystalline ThO_2 by calcining, with porosity located at the boundaries of the microcrystalline ThO_2 grains. This internal porosity renders the oxide friable, thus making it easier to comminute. As the calcination temperature is increased, the plate shape of the original thorium oxalate relic is retained and the internal porosity gradually sinters out as the ThO_2 grains grow within each particle; the powder surface area decreases and the particle strength increases, with the result that the ThO_2 powder becomes less tractable to comminution.

(e) Crystallite Size

A crystallite may be defined as a portion of a solid which coherently scatters X rays. It is a partial synonym for the term *grain*, but it is generally used where the average diameter of these entities is below one micrometer, or where it is not possible to observe the grain boundaries directly. X-ray peak broadening is the usual method used to determine thorium crystallite sizes, but they may also be measured with the electron microscope (Bannister, 1967). A diffuse X-ray

pattern with broad peaks indicates a low crystallinity or a small crystallite size, whereas a sharp diffraction pattern indicates a high degree of crystallinity and crystallite growth. Average crystallite sizes are calculated from the peak breadth measurements, and analysis of the peak profile permits the determination of crystallite size distribution. Allowance must be made for lattice strain, since strain also causes X-ray peak broadening (Bannister, 1973). This method is normally applicable to powders containing crystallites below about $0.3\text{ }\mu\text{m}$ in diameter.

For oxalate-derived ThO_2 , smaller crystallite sizes were measured in powders with smaller particle sizes (Allred et al, 1957; White et al, 1981a). As shown in Fig. 8.16, crystallite size increases with increasing calcination temperature; it also corresponds very closely to the particle size estimated from gas adsorption surface area measurements (Allred et al, 1957; Kinoshita et al, 1965a), indicating that the ThO_2 particles are porous and that the surface area measured by the gas absorption method is primarily the area of the internal crystallite surface. Although thorium particles calcined at a given temperature had different particle diameters due to different precipitation conditions (temperature, digestion time, etc.), they had similar crystallite sizes (Kinoshita et al, 1965a). The crystallite sizes of thorium powders

Figure 8.16. Effect of Calcination Temperature on the Crystallite Size of Thorium Powders. (Allred et al, 1957; Reprinted with permission from Journal of Physical Chemistry.)

prepared from thorium tannate, thorium benzoate, and thorium carbonate also increased significantly with increasing calcination temperature (Moorthy et al, 1963, 1964, and 1965).

Bannister (1967, 1968a, 1968b, and 1975) obtained good quantitative agreement for the crystallite size distribution in thorium gel by both electron microscopic and X-ray diffraction techniques. These results also agreed with estimates from gas adsorption surface area measurements. He concluded that thorium gel contains equiaxed, approximately spherical crystallites of ThO₂ with a narrow distribution of crystallite sizes.

8.6.2 Chemical Characterization Data

(a) Thermogravimetric and Differential Thermal Analyses

As shown in Table 8.6, thermal decomposition studies on thorium compounds, especially thorium oxalate, have been extensive. In thorium oxalate the amount of water, both chemically combined and adsorbed, varies depending upon preparation conditions, age, and storage environment. Thermal analysis results are also influenced by type of atmosphere (air, vacuum, CO₂, inert gas), heating rates, and sample packing.

Most thermal analysis data indicate that, on heating in air, the thorium oxalate hexahydrate loses water at 373 to 423 K to give the dihydrate, which then yields the anhydrous oxalate at 473 to 573 K. Finally, the anhydrous oxalate is decomposed into ThO₂ at higher temperatures, either directly or through a carbonate intermediate. The chemical reactions are as follows:

or

TABLE 8.6—THERMAL ANALYSES OF THORIUM COMPOUNDS

Compound	Formula	Analysis Method*	Reference
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 5.8 \text{ H}_2\text{O}$	TGA	Beckett and Winfield (1951)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA, DTA	Bussiere et al (1961)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	DTA	Claudel et al (1961)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2 \text{ H}_2\text{O}$	TGA	D'Eye and Sellman (1955)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA, DTA	Kinoshita et al (1965a)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA, DTA	Moorehead and McCartney (1976)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2 \text{ H}_2\text{O}$	DTA	Padmanabhan et al (1960)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA	Srivastava and Vasudeva Murthy (1965)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA	Warren and Elyard (1968)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	TGA	Wendlandt et al (1961)
Oxalate	$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	TGA	White et al (1981a)
Nitrate	$\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$	TGA, DTA	Bussiere et al (1961)
Nitrate	$\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$	TGA, DTA	Moorehead and McCartney (1976)
Nitrate	$\text{Th}(\text{NO}_3)_4 \cdot 6.8 \text{ H}_2\text{O}$	TGA	White et al (1981a)
Hydroxide	$\text{Th}(\text{OH})_4$	TGA, DTA	Moorehead and McCartney (1976)
Formate	$\text{Th}(\text{HCOO})_4 \cdot 3 \text{ H}_2\text{O}$	TGA, DTA	Mentzen (1968)

*TGA = thermogravimetric analysis

DTA = differential thermal analysis

Elemental carbon has been detected in the ThO₂ residues. The free carbon, which persists up to high temperatures (873 to 1173 K), can be formed by a CO disproportionation reaction, i.e.,

b) Chemical Analyses

Impurities and additives in ThO₂ and ThO₂-UO₂ powders, introduced both during preparation of the powders and during their subsequent processing, can affect the various stages of fabrication (agglomeration, pressing, sintering) as well as the properties of the sintered bodies (Clayton, 1976; Smid, 1976).

Adsorption of gases and vapors on fine oxide powder particles can influence their chemical properties (Williams 1963 and 1965). The adsorption of fluoride and silicate on ThO₂ was studied using infrared spectrophotometry, thermogravimetric analysis, and differential thermal analysis (Stuart et al, 1972). Surface properties and sintered densities were affected. Metallic impurities and carbon contents in thorium powder are routinely determined by emission spectroscopic and combustion techniques (Bukowski and Hollis, 1975).

Finally, considerable amounts of impurity can be introduced into thorium-base powders as a result of comminution processes (Burke, 1969a; Clayton, 1976). Iron introduced by wear of the stainless steel mill and balls is a major source of contamination of ThO₂ and ThO₂-UO₂ powders during milling. The rate of iron pickup in milled ThO₂-UO₂ powders is illustrated in Fig. 8.17. The iron content can be reduced by acid leaching (Burke, 1969a). Metallic contaminants are further reduced by high temperature hydrogen sintering. Because the reduction of powder particle size by the micronization process involves the collision of like particles against each other in a rubber-lined chamber, very little wear of the equipment occurs, and contamination of the product is minimized (Clayton, 1976).

8.7 FABRICATION OF ThO₂ AND ThO₂-UO₂ PELLETS

8.7.1 Cold Pressing and Sintering

(a) The LWBR Reference Process

A flow diagram for the LWBR reference fabrication process for ThO₂ pellets is shown in Fig. 8.18; the process is essentially the same for ThO₂-UO₂ pellets. Thorium oxalate is precipitated from thorium nitrate solutions and calcined to the oxide. It is at this stage that ThO₂ powder is then blended with UO₂ powder for fabrication of ThO₂-UO₂.

Figure 8.17. Effect of Ball Milling Time on the Iron Content of ThO₂-UO₂ Powders. (Burke, 1969a.)

For either ThO₂ or the solid solutions, the single oxide or the mixed oxides are micronized, and agglomerated (i.e., swirled with Carbowax 6M, a polyethylene glycol polymer with a molecular weight of approximately 6000) to form millimeter-size globules with a density of approximately 3.5 Mg/m³. A small amount of Sterotex, a die lubricant consisting of a glyceryl ester of stearic acid, is added, and the mixture is pressed into the desired shape (Weinreich et al, 1977; Burke et al, 1980). The resulting green pellets are approximately 62 percent of theoretical density. The wax and lubricant are removed during a presintering heat treatment in CO₂; the heating cycle is in stages such that the pellets are held at 720 K for 4 hours, then at 1200 K for 3 hours. Sintering then takes place at 2063 K for 11 hours in hydrogen. The product generally has a density greater than 96 percent of theoretical. After sintering is completed, the fuel is centerless ground to dimensional specifications.

Figure 8.18. Process Flow Diagram for Fabrication of ThO_2 Pellets. (Clayton, 1976.)

(b) Laboratory Methods

The LWBR Reference Process was developed for $\text{ThO}_2\text{-UO}_2$ fuel compositions containing less than 10 mole percent UO_2 . Laboratory studies, using the cold pressing and sintering technique, have been conducted over the entire $\text{ThO}_2\text{-UO}_2$ composition range (Cohen and Berman, 1966; Goldsmith and Brite, 1978; Handwerk et al, 1957; Kanno et al, 1982; Lynch, 1965; Matthews and Davis, 1981; Moh and Moorthy, 1971). The most successful fabrication methods used an intimate mix of highly active ThO_2 and UO_2 powders which yielded a homogeneous distribution of the components, promoted solid solution formation, and resulted in high density pellets (Cohen and Berman, 1966; Matthews and Davis, 1981).

Thermally stable ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$ fuel pellets have also been fabricated with a high density matrix and controlled amounts of internal porosity. The fabrication methods included pre-pressing (*slugging*) the oxide powder before forming the green pellet (Pope and Radford, 1976) and adding pore formers such as organic additives (Burke, 1969b; Honda et al, 1981; Hutchison and Johnson, 1966; Ramm and Webb, 1972; Williams et al, 1968) or volatile uranium and ammonium salts (Radford and Pope, 1977). Pellet densities were controlled reproducibly by varying the amount of pore former. To obtain crack-free pellets, the pore former should have the same compressibility as the matrix oxide and a small volumetric expansion during thermal decomposition (Honda et al, 1981). Both high-density ThO_2 pellets and low-density ThO_2 pellets with a high matrix density were made without organic binders by the slugging technique (Johnson, 1982; Radford and Pope, 1977). The major parameter in density control of ThO_2 pellets is powder surface area (Frankhouser, 1967; Hutchison and Johnson, 1966).

The sphere-cal process uses gel-derived microspheres rather than powder as feed material for fuel pellet fabrication. Lubricants and binders are not necessary for successful pelletizing. Fuel pellets with homogeneous microstructures and densities greater than 95 per cent of theoretical have been fabricated from uranium microspheres, but the technology has yet to be fully established for the preparation of high density ThO_2 and $\text{ThO}_2\text{-UO}_2$ pellets (Crain and Hutchison, 1966; Matthews and Hart, 1979, 1980; Robbins and Stradley, 1969; Tiegs, 1980; Tiegs et al 1979). Most ThO_2 and $\text{ThO}_2\text{-UO}_2$ microsphere batches were hard and compacted poorly. Sintered pellet microstructures contained remnant microspheres and shards, and the microspheres sintered individually rather than together. The best sintered $\text{ThO}_2\text{-UO}_2$ pellets were produced from microspheres formed by an external gelation process (Brambilla et al, 1970). These $\text{ThO}_2\text{-UO}_2$

microspheres were softer, compacted easily, and sintered together to produce a more homogeneous pellet structure (Tiegs, 1980; Tiegs et al, 1979).

The Advanced Water Breeder Applications (AWBA) program (see Chap. 1) explored modifications for thorium-base breeder cores based on LWBR technology. A major AWBA development was the fabrication of two-region duplex fuel pellets. Thorium-uranium and UO₂ annular pellets containing a high density ThO₂ central pellet were produced (Burke, 1982c; Johnson and Karichko, 1982).

An alternative fabrication technique for conventional ThO₂-UO₂ pellets consists in fabricating fertile ThO₂ into green or partially sintered pellets which are then enriched by impregnating them with a solution containing fissile ²³³U (Feraday et al, 1979; Hastings et al, 1982). The amount of enrichment absorbed during impregnation depends on pellet density, impregnation time, number of impregnations, solution concentration, and impregnation technique.

8.7.2 Other Methods

Ceramic fabrication techniques, such as hot pressing, isostatic pressing, and extrusion have been applied successfully for limited production of ThO₂ and ThO₂-UO₂ bodies. However, the only practical method used for large scale, close tolerance production of high density ThO₂ and ThO₂-UO₂ fuels has been cold pressing and sintering.

The hot-pressing behavior of sintered low density ThO₂ and ThO₂-UO₂ was investigated over a temperature range of 1873 to 2423 K (Kaufman, 1969). Both cold-pressed and isostatically pressed compacts were examined. The tests were conducted in a graphite punch-and-die assembly primarily under a reduced pressure of carbon monoxide. These conditions resulted in hypostoichiometric compositions, which caused formation of metallic thorium and uranium inclusions in the microstructure and also pellet darkening. Gardiner (1964) also fabricated low density ThO₂ pellets by the hot pressing technique. He studied the effects of time (20 to 900 seconds), temperature (1273 to 1873 K), and load (0 to 20.7 MPa) on the final densities (≤ 84.2 percent of theoretical) of the pellets. Temperature had the greatest effect on density.

The extrusion fabrication method does not have the length-to-cross section or the cross-sectional shape limitations inherent in the cold-pressing and isostatic-pressing processes. In general, extrusion of ThO₂ and ThO₂-UO₂ involves the preparation of a source powder incorporating a plasticizer, such as methyl cellulose, to form a mass capable of being extruded. This is then subjected to the extrusion operation, controlled drying, and high-temperature sintering in an air, inert gas, or hydrogen atmosphere. The factors affecting extrusion and sintering are the binders used, the powder particle size and

size distribution, the wetness of the mass to be extruded, and the extrusion force (Cogliati et al, 1967). The successful extrusion of long (7 cm), high-density (94 percent of theoretical) ThO_2 and $\text{ThO}_2\text{-UO}_2$ rods has been accomplished by several investigators (Cogliati et al, 1967; Gabaglio and Liscia, 1966; Miller and Liscia, 1963; Miller and O'Leary, 1962; O'Leary and Miller, 1962). High-strength, high-density (99 percent of theoretical) ThO_2 rods based on the Sol-Gel Process have been reported by Fitts et al (1968). The extrusion process required no extraneous binders or plasticizers.

The slip-casting process consists of making a stable water suspension of insoluble particles which, when poured into a plaster mold, becomes solidified by means of a liquid extraction mechanism. After a given setting-up time, the solid has sufficient rigidity and strength to be removed from the mold in the green state. A slip-casting procedure for producing very thin-walled ThO_2 bodies has been developed by Ullman et al (1966). Sintering at 2373 K provided ThO_2 bodies with a wall thickness of 0.6 mm and almost theoretical maximum density.

8.8 THERMODYNAMIC ASPECTS OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ FUEL FABRICATION

The chemical reactions that take place during the various heat treatments used in the LWBR Reference Process are reviewed in this section. These heat treatments include the pretreatment in carbon dioxide at temperatures up to 1198 K, the subsequent presintering and sintering in moist hydrogen at temperatures up to 2063 K, together with the temperature regions that are necessarily traversed in heating and cooling.

These operations were performed in furnaces with flowing atmospheres, within which the total pressure was about one atmosphere. The flow was sufficient to prevent concentrations of undesired gaseous products greater than 1 percent of the gaseous molecules present. Generally, the concentrations were far less, but this value can be used for calculations of the worst case.

During developmental work that preceded manufacture, progress of the reactions was monitored by examining the effluent gases by chromatography. Completion of a reaction was signaled by the disappearance of the gaseous product from the atmosphere that had been swept over the samples.

8.8.1 Pretreatment in Carbon Dioxide

Having performed their physical functions, the Carbowax and Sterotex additives are readily and quantitatively removed from the fuel. In large part, these additives are volatilized during the lower

temperature portion (around 700 K) of the CO₂ pretreatment. Chromatographic analysis of effluent gases show the presence of methane at or near room temperature and the presence of higher hydrocarbons at around 550 K resulting from thermal decomposition of these organic additives. Carbon monoxide and water vapor, also detected in the effluent stream at these temperatures, are probably Carbowax decomposition products, although they could have resulted from emical reactions such as

and

At the higher temperatures (870 to 1200 K) the main residue is elemental carbon, which is removed by oxidation to CO according to the reaction

In the preproduction experimental runs, it was possible to detect carbon monoxide in the effluent gases until temperatures as high as 1100 K were reached; this indicates that the reaction was still incomplete at that temperature, and that some carbon still remained in the sample. Nevertheless, if the CO₂ pretreatment were continued long enough, and if the carbon dioxide atmosphere of the furnace were swept at a sufficient rate such that the CO concentration was held to 1 percent of the total atmosphere (or less), it would be possible to remove the elemental carbon completely.

The CO to CO₂ ratio at which Eq. (8.8) reaches equilibrium at any given temperature is determined by the equilibrium constant

$$K_p = (P_{\text{CO}})^2 / (P_{\text{CO}_2}) \quad \text{Eq. (8.11)}$$

which is related to the standard free energy of the reaction by the equation

$$-\Delta G^\circ = RT \ln K_p \quad \text{Eq. (8.12)}$$

The values of K_p , and therefore the concentrations of gases involved in the reaction, can be calculated for equilibrium at various temperatures. For Eq. (8.10), from the reactions compiled by Kubaschewski and Alcock (1979),

$$\Delta G_T^\circ = 170.7 - 0.1745 T \text{ (kJ/mol)} \quad \text{Eq. (8.13)}$$

Table 8.7 represents evaluations of the CO to CO₂ ratio and the percentage of CO in the atmosphere at various temperatures in the pretreatment range, in equilibrium with CO₂ and elemental carbon. However, since the furnace atmosphere is continuously swept with fresh carbon dioxide, the concentration of CO is held to very much lower values, and Eq. (8.10) continues to be driven to the right; additional elemental carbon is oxidized to CO and swept out of the furnace, as long as any elemental carbon remains available.

However, the thermodynamic equilibria represented by Table 8 give no information on the rate at which the reaction proceeds. For economic reasons, the residual carbon is removed during the low temperature portion of the hydrogen sintering cycle, as described in Sec. 8.8.2.

The possibility of formation of thorium and uranium carbides during the CO₂ pretreatment was evaluated from the following reactions,

and

where An stands for either actinide (thorium or uranium). The equilibrium constant for these reactions is $K_p = (P_{\text{CO}})^2$.

The standard free energies for the formation of the actinide carbide (Eqs. (8.14) and (8.15)) were evaluated at 1198 K from the data given in the literature (Kubaschewski and Alcock, 1979; Holley and Storm, 1967) and are shown in Table 8.8 along with the calculated fraction of carbon monoxide in equilibrium in the furnace atmosphere at 1198 K. Only if the fraction of CO in the CO₂ atmosphere at a given temperature is less than these very low values—and at temperatures below 1198 K, they would be even less—would the reactions shown in

TABLE 8.7—CO TO CO₂ RATIO IN EQUILIBRIUM
WITH ELEMENTAL CARBON

Temperature, (K)	CO/CO ₂	Percent CO in CO + CO ₂ Atmosphere
900	0.49	32.9
950	1.05	51.2
1000	2.27	69.5
1050	5.03	83.4
1100	11.1	91.8
1150	23.9	96.0
1200	49.3	98.0

Eqs. (8.12) and (8.13) be driven to the right, resulting in the formation of carbides from oxides.

On the other hand, oxidation of any carbides initially present is far more likely, according to the following reaction:

For this reaction using uranium dicarbide, if one atmosphere of CO₂ is assumed, the corresponding equilibrium pressure of CO would be 4300 atmospheres at 900 K and 500 atmospheres at 1200 K. Corresponding values for thorium dicarbide are 7900 and 5200 atmospheres. At any lower concentration of carbon monoxide, the actinide carbides, if any are present, would be converted to oxides by the reaction of Eq. (8.16).

Figure 8.19 shows the CO to CO₂ and H₂ to H₂O ratios in equilibrium with stoichiometric UO₂. In calculating these equilibria, the equation used for the oxygen potential of stoichiometric urania was that recommended by Perron (1968), and cited in Table 5.17 of Chap. 5, namely,

$$\Delta \bar{G}_{\text{O}_2} = -502.5 + 0.1168 T \text{ (kJ/mol) .}$$

In the CO₂ pretreatment furnace, the concentration of CO is held below the equilibrium curve, and the concentration of CO₂ is therefore at a value higher than the one that would be in equilibrium with stoichiometric UO₂. Accordingly, if stoichiometric urania is present in the fuel, it can be oxidized by the furnace atmosphere. The subsequent hydrogen treatment is necessary to reduce the hyperstoichiometric oxide to the stoichiometric condition as well as to remove the residual carbon. During this stage, as shown by the dashed lines of Fig. 8.19, the furnace atmosphere is reducing in relation to any hyperstoichiometric uranium dioxide that formed during the CO₂ pretreatment.

TABLE 8.8—FRACTION OF CO IN CO₂ FURNACE ATMOSPHERE THAT WOULD PREVENT FORMATION OF ACTINIDE CARBIDES AT 1198 K

Actinide Carbide	ΔG° (kJ/mol)	CO/CO ₂
UC ₂	315.5	1.3×10^{-7}
ThC ₂	358.6	1.6×10^{-8}
UC	347.6	2.6×10^{-8}
ThC	456.5	1.1×10^{-10}

Figure 8.19. Ratios of Reduced to Oxidized Gases in Furnace Atmospheres in Equilibrium with Stoichiometric Uranium Dioxide.

Strictly speaking, the Perron equation is for pure urania rather than for thorium-uranium solid solutions. However, during the presintering stages the solid solutions have not yet formed; and even at later stages, during sintering, it is an acceptable approximation to assume that thorium acts as an inert matrix during the oxidation of the urania.

8.8.2 Presintering and Sintering in Hydrogen

At moderate temperatures, dry hydrogen reacts with residual carbon or actinide carbides to form methane. These reactions, however, are suppressed if the temperatures are increased to the presintering or sintering range. At or above 1200 K, equilibrium is reached when only a small portion (≤ 3 percent) is methane; clearly, dry hydrogen would not be adequate for the task of removing the remaining carbon.

In fact, however, some water vapor is always present, even if it is not deliberately added. The water vapor oxidizes the residual carbon according to the equation

for which the standard free energy of the reaction, ΔG_T° , varies with temperature according to the equation (Kubaschewski and Alcock, 1979)

$$\Delta G_T^\circ = 134.7 - 0.1425 T \text{ (kJ/mol)} \quad \text{Eq. (8.18)}$$

The H₂O to H₂ ratio in equilibrium with elemental carbon corresponds to the lowermost curve of Fig. 8.20, which is labeled "C OXIDIZES". In normal operating practice, however, the moisture content of the hydrogen is held above these values, and the water vapor oxidizes any residual carbon that may be present.

It must next be determined whether this necessary oxidation can take place without, at the same time, causing the unwanted oxidation above stoichiometry of any urania that can be present, as was the case in the CO₂ pretreatment. This oxidation above stoichiometry can occur in the region above the dashed line in Fig. 8.20.

In the hydrogen sintering cycle below 1550 K, it is impossible to reach this region. The fuel is heated in a boat fabricated from molybdenum metal. If the moisture content of the gas were increased toward the dashed line, it would first encounter the curve marked "Mo OXIDIZES". At this point, the water vapor would attack the molybdenum which, as long as any metal remained, would protect the urania from oxidation.

At temperatures above 1550 K, it is theoretically possible for water vapor to oxidize urania above stoichiometry in a molybdenum boat. However, Fig. 8.20 shows that the concentration of water vapor needed would be such that the furnace atmosphere would be more than half moisture; the water would condense out if any portion of the hydrogen supply system fell below a temperature of 350 K. In the case of the LWBR Reference Process the water vapor content of the hydrogen was held well below that level; the dew point was in the vicinity of room temperature. The concentration of water vapor is thus sufficiently low that the hydrogen will reduce to stoichiometry any oxidized urania that could be present.

Figure 8.20 shows a very considerable range of conditions with which the primary thermodynamic constraints of the hydrogen sintering operation in the lower temperature region are compatible: the removal of the last traces of carbon and the maintenance of urania stoichiometry. This range of compatibility extends upward to the conditions used for sintering.

Figure 8.20. Temperature Dependence of H_2O/H_2 at Equilibrium Conditions for Oxidation of Carbon, Molybdenum, and Uranium Dioxide during Presintering and Sintering in Hydrogen.

8.9 SINTERING OF ThO_2 AND ThO_2-UO_2

8.9.1 Introduction

Sintering has been defined as a process by which powders are consolidated into a polycrystalline mass by heating at temperatures below the melting point. During this consolidation, pores change size and shape, the amount of porosity decreases, the bulk density of the mass usually increases, the average grain size increases, and the

surface area decreases. As a consequence, the surface free energy decreases, and hence the free energy of the system decreases, providing the driving force for the sintering process.

Many theoretical models have been proposed in attempts to explain the complex process of sintering. Various material transport processes have been considered, including lattice diffusion, grain boundary diffusion, surface diffusion, evaporation-condensation, and viscoelastic and plastic flow. In the particular case of ThO_2 , sintering kinetics have been interpreted by a grain-boundary diffusion mechanism (Bannister 1975; Daniels and Wadsworth, 1965), by a volume diffusion model (Laha and Das, 1971) and by a plastic flow mechanism (Morgan and Yust, 1963; Morgan et al, 1963).

It is generally accepted that sintering takes place in the three stages described by Coble (1961). In the first or *initial* stage of sintering, pores form when individual particles are joined by necks at points of contact. These necks gradually broaden with consequent decrease in the void space. The total shrinkage is approximately 3 to 5 percent. Grain growth is not an important feature of this stage.

During the second or *intermediate* stage of sintering, densification and grain growth both take place. The pore phase is continuous and the pores are intersected by grain boundaries. The pores continue to shrink until a significant amount of closed porosity is formed. Although the average pore size can increase as a result of the coalescence of pores, the total porosity decreases. This process continues until the network of pores breaks up, first into a few interconnected pores on grain edges and then into isolated pores on grain corners.

The third or *final* stage of sintering begins when the pore channels change from continuous to discontinuous. The pores can all remain on grain boundaries (intergranular porosity), or they can become isolated from the grain boundaries (intragranular porosity). The latter condition results when a relatively few large grains grow very rapidly and become much larger than neighboring grains before all the porosity is removed. This phenomenon has been given various names: exaggerated grain growth, abnormal grain growth, discontinuous grain growth, and secondary recrystallization.

When the pores become essentially all intragranular, they can no longer diffuse to the exterior surface along grain boundaries. It becomes very difficult to densify the body any further. The density approaches asymptotically a value that is, in general, somewhat less than the theoretical maximum. To obtain high densities, it is necessary to delay the transition to the final stage. The primary means of doing this is to restrict grain growth, such that the moving grain boundaries are kept, so far as possible, from bypassing and isolating void space.

The driving force for *normal* grain growth is the reduction of the free energy of the system in which the total grain-boundary area is reduced. As Burke (1949, 1968) has described, the rate of normal or of continuous grain growth in a polycrystalline material is inversely proportional to the average diameter of the grains that are present, i.e.,

$$\frac{dD}{dt} = \frac{k}{D}, \quad \text{Eq. (8.1)}$$

or

$$D^2 - D_0^2 = kt, \quad \text{Eq. (8.20)}$$

where

D = the instantaneous diameter of the grain, μm
 D_0 = the diameter of the grain at $t = 0$, μm
 k = an empirical constant
 t = time, s.

According to the equation, grain growth should continue until the sample becomes a single crystal. Before this can happen, however, grain growth stops, and a limiting grain size is reached because second-phase inclusions are invariably present in the material. The ultimate grain size can be estimated from the approximation suggested by Zener (see Smith, 1948),

$$D_f = \frac{4d}{3f} \quad \text{Eq. (8.21)}$$

where

D_f = the limiting grain size, μm
 d = the average diameter of the second-phase inclusion, μm
 f = the volume fraction of the second-phase inclusion.

Grain growth can also be inhibited by the presence of pores. Nichols (1966, 1968) analyzed the kinetics of grain growth where grain boundary mobility is limited by pore mobility, and presented equations relating grain growth kinetics to the pore migration process. The equation for normal grain growth then takes the following forms:

$$D^3 - D_0^3 = kt$$

for vapor transport where the pore size and the gas pressure are controlled by surface tension;

$$D^4 - D_0^4 = kt$$

for volume diffusion, or for vapor transport when the pressure within the pore is constant;

$$D^5 - D_0^5 = kt$$

for surface diffusion.

The constant, k , is equal to $A \exp[-Q/RT]$, where Q is the activation energy for the particular process, e.g., volume diffusion, surface diffusion, or vapor transport.

3.9.2 Densification

The initial stage of sintering in ThO₂ was investigated by Morgan and Yust (1963), by Morgan et al (1963), and by Morgan and Hall (1967). In the work of Morgan and Yust (1963) thoria compacts with a green density of 4.75 Mg/m³ (47.5 percent of theoretical density) were used. These were heated to various temperatures up to 1973 K, at heating rates from 1.6 to 6 K per second. The resulting density was not a function of heating rate, but only of the temperature reached. Specifically, at the end of the heat-up cycle, samples heated to 1673 K (regardless of heating rate) had densified from 4.75 to 6.51 Mg/m³; those heated to 1773 K had reached 6.88 Mg/m³; and those heated to 1873 K had reached 7.20 Mg/m³.

These materials were then held at temperature for times up to 360 seconds. A gradual increase in density was noted, approaching asymptotically a value about 5 percent higher than the density at the end of the heat-up cycle. There was little significant increase after 300 seconds. For these short times at these comparatively low temperatures,

it may be assumed that the densification consists entirely of the initial stage processes. However, if the complete sintering process is considered, for the times and at the temperatures usually used, the initial stage may be considered essentially instantaneous on a time scale of minutes. The critical quantity associated with this stage is not the time, but the proportion of void space that is eliminated due to initial stage processes.

Morgan and Yust (1963) suggested that plastic flow, i.e., material transport by dislocation movement, makes the main contribution to the initial sintering of ThO₂. (Initial sintering was defined as that which occurs as the temperature of the specimen is being increased.)

They ruled out volume diffusion as the rate-controlling mechanism during initial densification because the temperature-dependent densification end point was independent of the heating rate, and the increase in densification rate with increase in temperature was much greater than that expected from diffusion kinetics.

Morgan et al (1963) extended their study of the initial stage of sintering in ThO_2 to include ThO_2 -CaO compacts containing 0.053 to 1.84 weight percent CaO. Calcia was introduced through coprecipitation of the oxalates from nitrate solution. The ThO_2 -CaO compacts (except those that contained "extremely small quantities" of additive) sintered more readily in the initial stages than did the ThO_2 compacts. As in the case for ThO_2 , the initial densification was interpreted to be a result of dislocation movement. Calcia, according to Morgan et al (1963), can create sites in the lattice where other impurity ions can segregate, thus reducing impurity segregation at dislocations, and hence facilitating dislocation motion.

Morgan and Hall (1967) reported additional information supporting the view that material transport by dislocation movement governs the initial kinetics of sintering in ThO_2 . On the assumption that isostatic pressing can generate dislocations, these authors isostatically pressed, at 310 MPa, partially sintered, cold-pressed powder compacts of ThO_2 and ThO_2 -1.4 weight percent CaO and then resintered them. Densification during the second heat treatment was compared with the densification attained without the intermediate isostatic pressing step. The small, but definite, density increase was attributed to the isostatic pressing. Thoria and ThO_2 -1.4 weight percent CaO compacts behaved similarly. Morgan and Hall (1967) suggested that dislocations are introduced into the partially sintered compacts during isostatic pressing which, on heat treatment, move; this movement of dislocations results in an additional densification that would not have occurred without the pressing step.

Progress of densification during the initial stage of sintering depends on the number and nature of the initial points of contact. The measures taken during the preparation of the feed material to ensure an active powder can have a significant effect only during this stage. An active powder is one that undergoes a very considerable portion of its densification in the initial stage. It is therefore one in which the powder particles have many points of contact capable of rapid development of substantial necks, and one also in which the development of these necks does not entrap void space.

The intermediate stage of sintering in thoria has been investigated by Harada et al (1962), Laha and Das (1971), and Smid (1976). Laha and Das (1971) studied the isothermal sintering and grain growth of ThO_2 and ThO_2 -CaO compositions (2.31, 4.25, and 8.8 mole percent CaO) at temperatures from 1573 K to 1873 K and for times up to 120 minutes. Laha and Das attempted to relate their measurements

to the theoretical expression derived by Coble (1961) for his intermediate-stage sintering model. The volume diffusion coefficients for Th⁺⁴ estimated by Laha and Das (1971) from their sintering results and the Coble model were several orders of magnitude greater than reported diffusion coefficient measurements. The volume diffusion coefficient for Th⁺⁴ was expressed as $D_v = 1.3 \times 10^{-1} \exp(-93,000/RT) \text{ cm}^2/\text{s}$; the activation energy was 93 kcal/mol 389 kJ/mol. The activation energies for the ThO₂-CaO compositions were found to be 234, 197, and 188 kJ/mol, respectively, for the 2.31, 4.25, and 8.8 mole percent CaO materials. These authors also reported that grain growth for all ThO₂-CaO compositions and for ThO₂ itself followed linear rather than quadratic kinetics (see Sect. 8.9.3).

Bannister (1975) combined isothermal sintering experiments in air at 873 to 1173 K with measurements of crystallite size distribution by electron microscopy and BET surface area in a study of the sintering of thoria gel. He found that the shrinkage rate of ThO₂ gel was too slow to be controlled by oxygen ion diffusion and too fast to be controlled by the volume diffusion of the thorium ion. He suggested, instead, that the crystallites in the thoria gel sinter by a grain-boundary diffusion mechanism. He reported the grain-boundary diffusion coefficient of Th⁺⁴ to be $D_b = 0.63 \exp(-94,000/RT) \text{ cm}^2/\text{s}$. The activation energy (94.0 kcal/mol or 393 kJ/mol) agreed with that reported by Laha and Das (1971) for volume diffusion.

Smid (1976) investigated the densification of thoria in hydrogen at 2023 K with 53 ppm of water vapor present. Four batches of pellets were prepared through the pretreatment step under laboratory conditions simulating the LWBR Reference Procedure. One pellet was removed from each batch, and its density determined, after various sintering periods from 0 to 22 hours. Results are shown in Fig. 8.21.

These results are fairly consistent over the four batches, even though a considerable range of initial densities was represented. There appears to be no clear relationship between initial density and minor differences in densification rate observed. The straight line drawn on Fig. 8.21 represents a least-squares fit of the data from 0 to 2 hours, inclusive; the 22-hour data were excluded since preliminary inspection indicated that they would fall well below this line. The best-fit equation is

$$-\ln(P/P_0) = 0.1315 + 0.04196 t \quad \text{Eq. (8.22)}$$

where

P = the volume porosity at time t, hours

P₀ = P at t = 0, i.e., immediately after pretreatment.

Figure 8.21. Densification of Thoria during Sintering. (Smid, 1976.)

Equation (8.22) and Fig. 8.21 may be characterized as follows:

1. Approximately 13 percent of the porosity initially present in these pellets disappeared very shortly after the start of sintering at 2023 K in wet hydrogen.
2. Thereafter, porosity present was eliminated at the rate 4.2 percent per hour as sintering continued.
3. This rate was relatively constant over the first 12 hours of sintering for a considerable range of initial densities (86 to 92.5 percent of theoretical).
4. At the end of 12 hours, according to Eq. (8.22), the porosity had decreased to 53 percent of the amount originally present.
5. Thereafter, little additional densification took place, to the longest sintering times examined (22 hours).

The final densities, attained after 12 hours of sintering, were, in the order of the caption of Fig. 8.21, 92.3, 94.3, 95.7, and 94.3 percent of

theoretical density. This material did not attain the density values in the vicinity of 97.5 percent of theoretical that were generally achieved in LWBR production runs.

In Chap. 7, Sect. 7.4.5, where ex-reactor hot pressing is discussed, and in Chap. 9, Sect. 9.3, where effects of in-reactor density changes in fully sintered fuel are discussed, the phenomenon of densification is considered as inward creep, as a result of the external pressure which supplies the driving force. It is demonstrated, for fully sintered oxide fuels, that such a mathematical treatment leads to predictions reasonably close to the densification actually observed. However, in the case of materials that are not fully sintered, the expressions for densification in those sections cannot be used. In such materials, densification proceeds at sintering temperatures without any large differential pressure acting as the driving force. This densification is the result of the decrease in the free energy of the system that takes place when grain boundaries and free surfaces are minimized.

Moorthy and Bahl (1967) attempted to study densification on a variety of incompletely sintered oxide materials, which were also subjected to hot pressing. The rates and progress of densification they observed were the result of a combination of the various phenomena taking place.

The final stage of sintering in thoria was studied by Jorgensen and Schmidt (1970). This investigation made use of CaO additions to permit densification to continue after the transition to the final stage, resulting in densities close to the theoretical. The $\text{ThO}_2\text{-CaO}$ binary system is discussed in Sect. 4.4.6 of Chap. 4. When the content of CaO exceeds 2.0 mole percent, precipitates of a CaO-rich second phase come out of solid solution and form at grain boundaries and grain boundary junctions.

Earlier, Johnson and Curtis (1954) and Curtis and Johnson (1957) had shown that ThO_2 can be sintered to high density by minor addition of CaO to the ThO_2 powder. These workers explained the improved sintering characteristics as a result of enhanced volume diffusion of the thorium ion brought about by the formation of oxygen ion vacancies as Ca^{+2} substituted for Th^{+4} .

Jorgensen and Schmidt (1970) characterized the final stage of sintering by stating that it may be regarded as a diffusion process, in which vacancies diffuse from the pores to the grain boundaries. The vacancies are eliminated at the grain boundaries, resulting in shrinkage and densification. Further densification depends on maintaining the vacancy flux from the pores to the grain boundaries at a high level. To maintain this high flux, the distance from the pores to the grain boundaries must be kept small, and grain growth must be retarded or halted. The CaO precipitates accomplish this by pinning the grain boundaries. A grain boundary migrating past such a precipitate

must provide additional grain boundary area equal to the cross section of the inclusion. The additional energy needed can be provided by shortening the grain boundary elsewhere; but this can no longer occur once the grain boundaries have reached a state in which they consist of straight segments, with precipitate grains at their junctions. In the absence of such a pinning mechanism, what Coble (1961) termed *discontinuous grain growth* occurs.

Jorgensen and Schmidt heated ThO_2 -2.0 mole percent CaO + 2273 K, removing samples after various times from 6 to 500 minutes to observe the grain size. The mean grain diameter increased from 3.5 μm at 6 minutes to 10 μm at 12 minutes. Thereafter, it remained virtually constant until the conclusion of the experiment; the curve showed a sharp discontinuity at 12 minutes as its slope decreased to zero. However, the porosity continued to decrease, and was virtually zero at the end of the experiment. An electron photomicrograph of the final material showed uniform, polygonal 10 μm grains, with precipitates of CaO , on the order of 0.1 μm in diameter, at grain boundary junctions. The CaO content of 2.0 mole percent, being just above the solubility limit, was found to be the optimum amount for the production of dense, optically clear thoria. The final grain size was found to be that predicted by the Zener relation, $D_f = 4d/3f$ (Eq. (8.21)).

Beyond the studies reported above, other factors have an influence on the final densities obtained. For example, Moorthy and Bahl (1967), Moorthy and Kulkarni (1963), and El-Fekey et al (1982) examined the effect of starting material, forming pressure, and calcining temperature on the density of the final product. In summary, thorium oxalate as the starting material led to higher ultimate densities, other things being equal, than thorium nitrate or tannate. Higher forming pressures and higher calcining temperatures led to higher green densities and to higher final densities.

Morgan and McCorkle (1972) and Morgan et al (1976) found that sintered ThO_2 sometimes becomes more porous, if held at high temperatures for a sufficient time. For example, Morgan et al (1976) reported that high density thoria and thoria-calcia (>99 percent theoretical) with very small grain size, sintered from sol-gel material at 1473 K, decreased from 99 to 89 percent of theoretical density after 15 hours in air at 2073 K, concurrently with grain growth from approximately 0.25 to 5 μm average diameter. The authors term this process *desintering*. The density loss was less marked if CaO additive were present. They suggested that the density decrease depends on factors that affect grain growth rather than on the elimination of gases that were trapped in pores.

Mohan and Moorthy (1971) observed densification in ThO_2 - UO_2 solid solutions. They found that the rate-controlling factor was macroscopic flow in the matrix. For their material, as well as for fuel fabri-

cated for LWBR, the sintering step is needed to complete the process of homogenization of the solid solution. A double sintering step, with intermediate regrinding, such that the solid solution fuels are largely homogeneous when they enter the final sintering, introduces additional complications. Accordingly, for a single sinter process, solid solution fuels are likely to consist of a matrix and inclusions, of different compositions, at the beginning of sintering. The sintering properties of such a mixture will, in general, be those of the matrix; and for fuels consisting predominantly of ThO_2 , the properties of ThO_2 can be used as reasonable approximation.

8.9.3 Grain Growth

There have been few studies of grain growth kinetics for ThO_2 or for $\text{ThO}_2\text{-UO}_2$. Laha and Das (1971) correlated their grain growth data with the simple expression $G = At$, but they found that the scatter was significant. The slopes of the plots for the various compositions and temperatures, instead of being constant, increased with both increasing temperature and CaO content.

Smid (1976) investigated the kinetics of grain growth in ThO_2 to determine the cause of a nonuniform grain structure encountered in the fabrication of fuel for LWBR (see Sect. 8.10). This condition, termed *picture framing*, consisted of the occurrence of a region, approximately 1 to 4 mm thick, immediately adjacent to the surface of the pellet, in which the grain size is considerably coarser than it is in the interior of the pellet. A reasonable threshold value, beyond which this phenomenon can be regarded as occurring, can be defined as an average grain diameter, in the surface region, of twice the value observed in the interior of the pellet. By this criterion, picture framing was observed in approximately 20 percent of a random sample of LWBR production pellets destructively examined.

Smid (1976) examined the phenomenon in detail and showed that it was characteristic of certain batches of material and was reproducible. The tendency for picture framing to occur in these particular batches was destroyed by an additional calcination of the raw powder. In a typical case in which the picture-frame phenomenon was observed in a pellet, the surface material had grain size comparable to normal material (20 to 60 μm diameter), but the interior showed virtually no grain growth from the powder stock used in the compaction. The material was not fully sintered and had a typical grain diameter of 3 to 10 μm . In some cases, the interior showed splotchy regions where there was some grain growth, but the grain size was still considerably less than that for the surface material. The boundary between the surface material and the interior was sharp and well

defined; it was sinuous, and clearly affected by occasional irregularities in the surface. At the bottom of the pellet, where it had rested against a support during sintering, the picture frame had less width.

It was postulated (Smid, 1976) that the failure of grain growth in the center of the ThO_2 pellet was due to an inhibitor, which was sufficiently volatile to be removed through the surface during the sintering process. It was established that the inhibitor, if present, was at very low concentrations; no difference could be found between the surface material and the interior by X-ray diffraction. Likewise, no component or composition differences could be detected by electron microprobe scans across the interface. The identity of the inhibiting material was not established.

8.10 LWBR EXPERIENCE WITH FABRICATION OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$ PELLETS

The results of pilot scale programs showed that existing fabrication processes did not consistently produce the high density, uniform grain structure, and structural integrity desired for meeting the LWBR design requirements. Powder preparations and manufacture of high-density, high-integrity ThO_2 and $\text{ThO}_2\text{-UO}_2$ fuel pellets involved modifications to the processes conventionally used for UO_2 fuel.

8.10.1 Powder Preparation Problems

Many variables have an effect on the quality of the final product. It was necessary to select appropriate values and limits for these variables in the light of the data previously discussed, and to maintain these specifications during production. Some of the problems encountered are discussed in the following sections.

(a) Thoria Powder Process

As a result of differences in the fuel compositions (ThO_2 , $\text{ThO}_2\text{-UO}_2$) and fuel pellet process differences (degree of powder comminution), the powder properties required of the source material to achieve high-density, high-integrity fuel pellets were different for various types of LWBR fuel. For example, fabrication of thoria fuel pellets required a more active thoria powder, i.e., one with a higher surface area, than did fabrication of $\text{ThO}_2\text{-UO}_2$ pellets because UO_2 helped promote densification and grain growth in $\text{ThO}_2\text{-UO}_2$. Thus, a lower surface area thoria powder could be used in the manufacture of the binary fuel. LWBR experience also confirmed that the thorium oxalate precipitation and calcination temperatures are the primary process variables for controlling the resulting thoria powder properties.

(b) Urania (²³³UO₂) Powder Process

The ²³³UO₂ powder for LWBR binary fuel production was fabricated by converting purified uranyl nitrate into the oxide through precipitation, calcination, and hydrogen reduction of ammonium uranate. The critical variable for controlling the urania powder properties was the hydrogen reduction temperature.

10.2 Powder Processing Problems*(a) Micronizing*

The LWBR process used a micronizer to comminute and thoroughly mix the ThO₂-UO₂ compositions. This micronizing resulted in high density ThO₂-UO₂ pellets with uniform uranium content. Micronizing is essentially self-comminution, and breaks up the powder agglomerates to produce a high-purity, uniform material.

Gas adsorption powder surface area measurements were used as controls to provide assurance of proper micronization. It was found that thoria powder surface areas had to be at least 6 m²/g to produce acceptable sintered densities. Very high surface area powders (>15 m²/g) had a detrimental effect on pellet fabrication. Such very fine powders promote rapid densification but, as a result, the diffusion of gases from decomposing organic binders at normal sintering heat-up rates is hindered. Gas is entrapped and causes pellet distortion.

(b) Agglomeration

The agglomeration process transforms the finely divided, micronized powder into a freely flowing, compactible, spherical material or press feed. This resolved two major problems associated with pressing a fine powder: nonuniform filling of the die and the formation of circumferential cracks in the green pellets. The spherical agglomerates flow more easily and uniformly into the die. Also, since they are higher in bulk density than the micronized powder, less entrapped air and fewer associated cracks result during compaction.

Agglomerates are formed by the addition of a wax binder in solution. Carbowax 6000, with a melting point of 335 K, was the binder used in the LWBR process. The solvent used was Oxylene M-6, a mixture of Freon and methylene chloride (trichlorofluoroethane). The boiling point of the mixture is about 309 K. Selection of these materials was based on their commercial availability, their ability to burn ash-free during heat treatment, and their suitability for mixing with fine powders. The optimum Carbowax content was found to be 1 to 1.25 weight percent of the powder charge. Less Carbowax resulted in poor granule and pellet integrity. Higher Carbowax levels

(2.0 weight percent) increased granule crush loads and produced granules so dense that they persisted even at very high compaction green densities. As a result, cracking occurred.

(c) *Granule Drying*

The agglomerated granules are dried to volatilize retained Oxylene and to provide a dry press feed suitable for compaction. The dry temperature was about 320 K, a level below the melting point of the wax but sufficiently high to evaporate the Oxylene effectively. If the drying temperature is increased to 340 K, the binder melts and densifies the granules by surface tension. This results in hard granules which do not deform during compaction, and thus they retain their individual identities in the sintered pellets.

(d) *Die Lubricant Addition*

A dry powder lubricant is added to the agglomerated fuel powders prior to pressing in order to decrease friction between particles, and between the fuel and the die wall. This minimizes pressing loads during pellet compaction, as well as the forces required to eject the pellet from the die cavity, thereby lowering internal pellet stresses which cause cracks.

Sterotex, a glyceryl ester of stearic acid, is the lubricant found to produce a high quality green compact for the LWBR process. This additive provides adequate lubrication during compaction and is removed at relatively low pretreatment temperatures with minimal carbonaceous residue. Sterotex levels used for compaction were 0.15 to 0.20 weight percent. Greater quantities increased the surface and internal porosity in the sintered pellets. Lesser amounts were insufficient for adequate lubrication during compaction and cracking resulted in the green pellets.

8.10.3 Pellet Pressing Problems

The purpose of the compacting operation is to form fuel pellets by cold pressing the feed powder. The forces of compaction establish the interparticle contacts in the powder which are necessary for pellet densification and microstructure development in the sintering operation. The compaction parameters determine the density level and density distribution within the pellet. These control dimensional uniformity and pellet shrinkage during sintering. Flaws or faults in the pressed pellet are seldom correctable in later pellet processing steps.

Double action compacting presses (i.e., those in which both an upper and lower ram are hydraulically activated) were used in the

LWBR process. Tungsten-carbide punches and dies were required to withstand the high compaction pressures and the abrasiveness of the ThO₂ and ThO₂-UO₂ fuel powders. Press feed variability and pellet geometry were evaluated by compacting pellets in the green density range of 58 to 64 percent of the theoretical density, sintering, and evaluating sintered density, pellet shrinkage, microstructure, and crack sensitivity.

Cracking is associated with both powder characteristics and compacting conditions. Pellets pressed from powders with high surface areas are especially prone to cracking. Factors which govern compacting conditions, such as die defects, die wear, improper taper design, overpressing, excessive speed in pressing, and large punch-to-die clearance, are related to cracking in the green pellets.

8.10.4 Pellet Pretreatment Problems

(a) Pretreatment of Thoria-Urania

Thoria-uranium pellets were placed in Inconel boats and pretreated using a CO₂ atmosphere in a continuous electric furnace. The green pellets were heated at the rate of 50 K per hour up to about 700 K and held at that temperature for 4 hours to decompose the additives and burn off the volatile products. The heatup was then resumed at 50 K per hour up to 1200 K and held at that temperature for three hours to complete the final carbon removal. These heatup rates were established to minimize thermal shock and subsequent pellet cracking. High flow rates provided some turbulence of the CO₂, improved the exposure of the pellets to the CO₂, and supplied sufficient CO₂ to oxidize the carbon in the pellets.

b) Pretreatment of Thoria

Pretreatment of thoria pellets was performed in molybdenum boats in a bell (batch-type) furnace with a CO₂ atmosphere at 700 K for 4 hours. The maximum heating rate was 50 K per hour. This relatively low-temperature treatment was established initially for the large LWBR ThO₂ reflector green pellets which, when pretreated at 200 K, severely cracked during the subsequent sintering operation. The 700 K pretreatment results in only partial removal of the organic additives by elimination of volatiles; the temperature is too low for carbon removal by CO₂ oxidation. Up to 5000 ppm carbon, i.e., approximately 50 percent of the carbon originally present, remained after this low-temperature pretreatment. The residual carbon was removed during subsequent sintering in a wet hydrogen atmosphere.

8.10.5 Pellet Sintering Problems

(a) General

The compacted and pretreated LWBR fuel pellets are sintered in hydrogen to obtain a high-density product meeting microstructural requirements. For the $\text{ThO}_2\text{-UO}_2$ compositions, additional solid solution and homogenization of the composition also takes place at this stage.

The LWBR sintering process consisted of heating the fuel pellets at a rate of 100 to 115 K per hour up to a sintering temperature of 2063 K and maintaining that temperature for a minimum of 12 hours. A wet hydrogen atmosphere (dew point around 300 K) was used.

The heating rate controls not only the rate of densification but also the rate and efficiency of removal of the residual carbon in the ThO_2 pellets by the wet hydrogen. The cooldown cycle of the sintering furnaces is equally important in the prevention of pellet damage by cracking resulting from thermal stresses. It was found that the cooldown rate should not exceed the heating rate of the pellets coming to temperature.

The time at sintering temperature controls both densification and grain growth. At the relatively high temperature used for sintering the LWBR fuel pellets, high densities were achieved quite rapidly, in two to three hours, and additional time did not cause appreciable increase in density. Grain growth, however, required longer sintering times, and a minimum time of 12 hours was established to achieve the desired grain sizes. If the grain size (or density) requirements were not met after the initial sintering cycle, an additional 12-hour resinter cycle was performed.

(b) Grain Size

Grain growth in the LWBR fuel pellets was related to their size; it was more difficult to grow grains in the larger pellets. The $\text{ThO}_2\text{-UO}_2$ fuel pellet structure displayed the picture frame effect seen in cross section in Fig. 8.22(a). The darker border seen in Fig. 8.22(b) consists of coarse grains with a transition to finer grains inside, seen in Fig. 8.22(c). Electron microscopy examination showed that the fine grain pellet centers contained high quantities of microporosity. Less porosity but larger pores were detected in the coarse grain edges. To determine the cause of the grain growth retardation, thermal studies of pellets were performed using sintering temperatures as high as 2075 K. The higher sintering temperature resulted in a significantly increased grain size. Use of the additive CaO and the increasing of the

(a) Picture Frame (Pellet Density
98.4% TD) (5X)

b) Edge Grain Size (ASTM 5)
250X; reduction factor 1/3

(c) Center Grain Size (ASTM 9)
250X; reduction factor 1/3

Figure 8.22. As-Polished and Etched Metallographic Cross Sections of a Typical $\text{ThO}_2\text{-UO}_2$ Pellet.

oxidation potential of the sintering atmosphere, i.e., raising the hydrogen dew point, were also investigated. Increase in the hydrogen

dew point coupled with a higher sintering temperature proved to be a far more effective process than minor additions of CaO. The combination of a higher sintering temperature (2063 K) with moist hydrogen (about 300 K dew point for $\text{ThO}_2\text{-UO}_2$ and 315 K dew point for ThO_2) was adequate to provide acceptable grain sizes for blanket pellets with a single sintering. The sintering time was increased from 12 to 15 hours for production of the ThO_2 pellets.

(c) *Coring of Thoria Pellets*

Pellet coring is characterized by low density in the geometric center of the pellet and is associated with large pores, high pore frequency, and lack of grain growth. Pellet coring results from a high rate of temperature rise combined with a high residual carbon content in the pellet. Under these conditions pellet surfaces densify before the carbonaceous products within the central region can diffuse to the pellet surface and react with the hydrogen atmosphere. This sintering at the surface traps the carbonaceous products inside the pellets, prevents their escape, and allows excessive internal pressure buildup which can lead to swelling, or fracture, and to lack of densification in that region.

Coring was initially observed in the larger thoria pellets (reflector and blanket) during LWBR production startup. Corrective actions taken were: (1) use of wet hydrogen to remove residual carbon; (2) loading of fuel pellets in an open array for pretreatment and sintering; and (3) use of lower pellet heatup rate (less than 150 K/hr) in sintering.

8.10.6 Pellet Post-Sintering Problems

(a) *Cleaning of Pellets*

After the post-sintering grinding operation, the fuel pellets were cleaned to remove any adhering particulate matter. To ensure the cleaning process itself left no residue, deionized water was used as the cleaning fluid. The as-ground pellets were placed in baskets and rinsed for one minute in a tank of still water, then moved to a second water-filled tank where they were ultrasonically cleaned for a minimum of 10 minutes. A second 10-minute ultrasonic cleaning in a third tank, followed by a one-minute still water rinse in a fourth tank, completed the cleaning process.

Pellet cleanliness is a major concern because uncleaned pellets can result in gas release in fuel rods if the contamination is not sufficiently removed by the subsequent degassing operation. The cleanliness problem resulted from several different sources. Among these

were machine oil contamination from the grinder that was not removed by ultrasonic cleaning in water, and grinding sludge that dries on the pellets prior to ultrasonic cleaning. These problems were resolved by more frequent changes in the grinder coolant, by the installation of traps to collect machine oil, by ensuring that ground pellets remained wet prior to the cleaning operation, and by more frequent changes in the ultrasonic cleaning water.

(b) *Degassing of Pellets*

Inspection of fuel pellets to ensure compliance with technical requirements was accomplished by nondestructive visual examination of all pellets and by dimensional, ceramographic, and chemical evaluation of random sample pellets taken from each blend. After being inspected, but before being loaded into fuel rods, the LWBR fuel pellets were subjected to a high-temperature vacuum degassing operation to remove any adsorbed moisture, surface contaminants, and residual gases within the fuel. These gases, which consisted predominantly of CO and H_2 with minor amounts of CO_2 and various hydrocarbons, are formed during the pretreatment and sintering steps in fuel manufacture as a result of the decomposition of the binder and lubricant additives and of subsequent chemical reactions of the decomposition products with the pretreatment and sintering atmosphere gases (CO_2 , H_2). Tests showed that the bulk of this gas can be removed by vacuum degassing at 1273 K (Smid, 1971).

The degassing cycle consisted of a controlled heatup which resulted in a 3-to-4-hour soak at a temperature of 1243 K to 1313 K at a pressure of 1.3 pascals or less. The degassed pellets were then loaded into Zircaloy-4 tubes, which were welded shut in a helium atmosphere. Air exposure was limited, since ThO_2 and $\text{ThO}_2\text{-UO}_2$, even in the form of a dense pellet, can adsorb moisture from the air. The amount of water adsorption by the pellet was found to be a function of time, temperature, and the partial pressure of water vapor in the ambient air. Charts were constructed to limit and control exposure time under various temperature-relative humidity conditions. Limiting the air exposure time and controlling the humidity during that exposure resulted in fuel pellets low enough in adsorbed surface moisture to avoid in-pile hydride failure of Zircaloy-4 cladding (Clayton, 1979).

11 SUMMARY

Two methods have been developed for the fabrication of thorium and thorium-uranium fuels on a production scale. The first of these is here termed the LWBR Reference Process; reference to its product as

oxalate-derived fuel is not as precise a term because thorium oxalate has been used as a starting material in other processes as well. It was used for the fuel of LWBR; earlier, less-refined versions were used for the fuel of the Elk River and Indian Point No. 1 reactors. The second method is termed the Sol-Gel Process; it has been employed to produce the microspheres of fuel for HTGR and for the shards that underwent vibratory packing in the Kilorod experiment at ORNL.

The LWBR Reference Process was developed from the pre-existing procedures used for fabricating UO_2 and UO_2 -base fuels. It was used in producing ThO_2 fuel, and ThO_2 - UO_2 solid solution fuels with less than 10 mole percent UO_2 , for LWBR. The starting material consists of aqueous solutions of thorium nitrate, from which the insoluble compound, thorium oxalate, is precipitated through the addition of oxalic acid. The precipitate is filtered off and calcined to the oxide; for ThO_2 - UO_2 solid solutions, uranium oxide powder is added at this stage. Carbowax 6M in Oxylene M-6 solution, which serves, after evaporation of the solvent, as an agglomerant and binder, is added, as is also a small amount of Sterotex, which functions as a die lubricant.

The mixture is swirled in a sieve to form a free-flowing die feed, with spherical agglomerates in the sub-millimeter range. It is then pressed into the desired shape and subjected to a series of heat treatments. The first of these, at 700 K in CO_2 in the case of ThO_2 and at 1200 K in CO_2 in the case of ThO_2 - UO_2 , removes the additives. Sintering then takes place at 2063 K for 11 hours in moist hydrogen.

The pellets are produced slightly oversized, and are reduced to final dimensions by centerless grinding. A degassing operation then takes place; and finally, storage times and conditions must be controlled to minimize adsorption of water vapor from the atmosphere while the pellets await loading and sealing into fuel rods.

The LWBR Reference Process proved capable of fabricating fuel pellets of complex geometries, to high densities and close dimensional tolerances, with satisfactory yield. In the case of thorium-uranium solid solutions, it was necessary to work remotely, due to the high activity of the fuel.

In the Sol-Gel process, oxide particles with diameters on the order of nanometers are dispersed in water. The resulting hydrosol is converted to a gel by drying. In some procedures, this is done by permitting droplets to fall through a countercurrent column of a long-chain alcohol, resulting in spheres of fuel with diameters in the sub-millimeter range. In other methods, the sol is dried in shallow trays, and breaks up into polygonal shards. In either case, the product is further dried, calcined, and sintered. In another variant of the pro-

cess, a thorium nitrate solution is freeze-dried by spraying into liquid nitrogen or a similar cold bath. Water is then removed from the frozen particles by sublimation. This results, after calcining, in a very low density product.

The products of the Sol-Gel Process have extremely small crystallite sizes, on the order of tens of nanometers. For the LWBR Reference Process, pellet grain diameters are typically tens of micrometers.

For the LWBR Reference Process and also for the variants of the Sol-Gel process, almost every variable that could possibly be controlled at every stage must be held to close tolerances. Temperatures, times, heating and cooling rates, feed and flow rates, concentrations, particle and crystallite sizes, moisture contents of gas and product, and even the conditions of storage of the finished product, all may have a significant effect on the resulting fuel.

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Chapter 9

IRRADIATION BEHAVIOR OF ThO_2 AND $\text{ThO}_2\text{-UO}_2$

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9.1 INTRODUCTION

The available information on thorium-base fuels, including results from irradiation tests undertaken for design purposes and from post-shutdown examinations of fuel rods, is presented in this chapter. Where there is a lack of data due to the lesser irradiation experience with thorium-base fuels than with uranium-base fuels, some analogies with the latter are explored as a guide to the understanding of the former.

A convenient measure of burnup, or fission density, consistent with SI units is the quantity 10^{26} fissions/ m^3 of 100 percent dense fuel. In this book, this quantity is termed the fission unit. One fission unit = 10^{26} fissions/ m^3 = 10^{20} fissions/ cm^3 = 0.438 percent burnup (in pure ThO_2 fuel) = 4072 MWD/MTM (megawatt days per metric ton of heavy metal content) assuming that each fission produces 200 MeV that eventually appears as thermal energy.

When identifying thorium-base fuels it is sometimes necessary to distinguish between $\text{ThO}_2\text{-}^{233}\text{UO}_2$ and $\text{ThO}_2\text{-}^{235}\text{UO}_2$. The former fuel was used in the LWBR reactor. This is typical of the equilibrium cycle light water breeder, i.e., a reactor that starts with predominantly ^{233}U loading and, at end of life, has a higher ^{233}U inventory than at beginning of life. The gains from conversion of ^{232}Th to ^{233}U exceed the losses of ^{233}U due to fissioning. However, since ^{233}U does not occur naturally, an initial cycle, designated a prebreeder, uses $\text{ThO}_2\text{-}^{235}\text{UO}_2$ as an initial loading, and the inventory of $^{235}\text{UO}_2$ and $^{233}\text{UO}_2$ at end of life could be used to fuel a new reactor. This is a so-called "mixed isotope" system, as described by Vogel (1982). After many such cycles the original ^{235}U is reduced to very small proportions and the equilibrium breeder cycle operates.

Since the physical and mechanical properties of $\text{ThO}_2\text{-}^{233}\text{UO}_2$ and $\text{ThO}_2\text{-}^{235}\text{UO}_2$ are indistinguishable, separate discussions of these two systems are unnecessary (the small amounts of other uranium isotopes, e.g., ^{234}U and ^{236}U , have negligible effects on properties). However, the fission yield, notably the fraction of iodine and noble gases, is different. Therefore,

when making a comparison between $^{233}\text{UO}_2$ and $^{235}\text{UO}_2$ systems with respect to fission products, it is necessary to distinguish between all three systems, namely $^{238}\text{UO}_2$ - $^{235}\text{UO}_2$ compared to both ThO_2 - $^{233}\text{UO}_2$ and ThO_2 - $^{235}\text{UO}_2$. Although about 10 percent more noble fission gas is generated per fission of ^{233}U than is the case for ^{235}U , the gaseous contribution to the swelling characteristics of ThO_2 - $^{233}\text{UO}_2$ at a given fissioning rate would be expected to be the same as that of ThO_2 - $^{235}\text{UO}_2$ at the same temperature and at a fission rate which is 10 percent higher. Similar reasoning has been used to infer properties of one isotopic mix when data are available only for the other isotope.

An extensive set of fuel rod irradiation tests, using predominantly ThO_2 - UO_2 fuels, was conducted in connection with the Light Water Breeder Reactor (LWBR) and Advanced Water Breeder Applications (AWBA) programs at the Bettis Atomic Power Laboratory. The backgrounds of these two programs have been provided by Connors et al (1979) and by Vogel (1982). The fuels used were not only the binary ThO_2 - UO_2 solid solutions but also the mixed isotopes of UO_2 ($^{235}\text{UO}_2$ - $^{238}\text{UO}_2$), the ZrO_2 - UO_2 binary and the ZrO_2 - UO_2 - CaO ternary. Some of the fuel rods were tested in the Engineering Test Reactor (ETR) or the Advanced Test Reactor (ATR) at the Idaho National Engineering Laboratory (INEL) in Idaho and some at the NRX Test Facility operated by Atomic Energy of Canada Ltd. (AECL) at Chalk River, Ontario. The rods tested at the former site were either short rods, approximately 12 inches long, the fuel stack being about 8 inches, or comparatively long rods, about 90 inches long, the active fuel length being about 66 inches. The rods tested at Chalk River were usually about 120 inches long. The LWBR test rods used solid pellets of ThO_2 - UO_2 , but in the AWBA test program many of the rods contained so called "duplex" fuel. This form of fuel arrangement consisted of an outer annulus containing fissile material (any of the above-mentioned fuel materials) and a center pellet of ThO_2 . The prime purpose of this arrangement was to convert the thorium in the center pellet into ^{233}U by neutron capture from fissioning of ^{235}U in the annulus. This provided the essential feature of the so-called prebreeder mentioned above, that is, a reactor that used ^{235}U to produce ^{233}U rather than a breeder proper that used ^{233}U to produce more ^{233}U . A bundle of rods containing ThO_2 - $^{235}\text{UO}_2$ irradiated side by side with UO_2 was also tested at high power ($\sim 52.5 \text{ kW/m}$) to compare the two different fuels. The specifics of the Bettis Atomic Power Laboratory tests on thoria-base and other oxide fuels are provided in the cited references of this chapter.

The results of observations of fuel rod behavior can be broadly categorized as:

1. Dimensional changes in the rods and resulting inferences on fuel swelling and densification
2. Fission product release

3. Integrity of the fuel based on visual observations of metallographic samples
4. Behavior of the fuel when a cladding defect permits entry of the coolant.

Since fuel rod performance behavior results from combined effects (for instance, cladding dimensional change is affected by fuel swelling, fuel densification, fuel plastic deformation, and cladding creep) the description of irradiation effects on specific properties is usually subject to some degree of interpretation. Computer programs, such as the CYGRO series, have been developed to study the integrated fuel rod test results and to interpret them in terms of these separate effects. CYGRO5, as developed by Newman and Kovscek (1982) for interpretation of long rods containing duplex fuel, is the most recent example. The use of this program to provide inferences on fuel property descriptions, and, in particular, on fuel volume swelling, is described by Duncombe et al (1982).

9.2 RADIATION DAMAGE IN FLUORITE-TYPE LATTICES

From the discussions in Chaps. 3, 4, and 5 on stability, it would be expected that the crystal structure of thoria would also prove exceptionally stable when subjected to the effects of irradiation. Experimental studies of irradiation damage to thoria have been limited mostly to observations on irradiated fuel rods. However, two types of information can be used to supplement the studies that are available. One of these consists of observations on comparable materials. The other consists of negative information—the absence of gross changes in fuel rod geometry that certainly would have been observed had they occurred.

9.2.1 Effect of Alpha Particles

Clinard et al (1971) implanted sintered plates of polycrystalline ThO₂ with 5-MeV alpha particles, using an accelerator. They observed spalling of the lattice parameter changes, as well as changes in the appearance of the material on examination by electron microscopy. The material was bombarded to various dosages between 9×10^{16} and 6×10^{17} particles/cm². Spalling was observed immediately only at the highest exposure levels; material irradiated to lower levels either did not spall or did so only after postirradiation annealing.

At the highest exposure level, a crack formed parallel to the surface, at a depth of 15 μ m. This represented the depth of penetration in thoria for alpha particles of this energy, and therefore the depth at which neutralized, spent helium atoms would lodge. The spalled material, between the surface and the maximum penetration depth, was found to have expanded; its lattice parameter had increased by approximately 0.6 percent, i.e.,

from 0.55975 to 0.5631 nm. On annealing, the lattice parameter returned to its original value; the recovery began at about 600 K and was complete by the time a temperature of 1100 K was reached. Transmission electron microscopy showed a multiplication of defects in the flake. Scanning electron microscopy showed a duplex structure of the surface underlying the flake; some grains had roughened surfaces, as would be appropriate if very small helium bubbles had formed at the grain boundary. In another publication (Clinard et al, 1970) the release of helium gas was reported from the spalled material.

Matzke and Routbort (1983) also used an accelerator to implant alpha particles into the surface of sintered, polycrystalline ThO_2 . The dosage they used (2.5×10^{15} particles/cm² maximum) was somewhat lower than in the work of Clinard et al (1971), but their energies were much higher (77 MeV, maximum). They observed an increase in fracture toughness of 25 percent, from 1.07 MPa·m^{1/2} for unirradiated material (see Chap. 7) to 1.34 MPa·m^{1/2} at the highest exposure reached. The 77-MeV alpha particles could penetrate their material to a depth of 1 mm. These experiments were conducted at room temperature.

9.2.2 In-Reactor Effects

Akabori and Shiba (1981) irradiated $\text{Th}_{0.937}\text{U}_{0.063}\text{O}_2$ to a maximum of 0.0044 fission units (as defined in Sect. 9.1). They observed the changes in lattice parameter shown in Fig. 9.1(a). The effects were analogous to those reported by Clinard et al (1971) for alpha particles. Both experiments took place at or near room temperature. The lattice parameter increased asymptotically to a maximum observed change of 0.094 percent; this value is essentially attained at exposures greater than 0.001 fission units (10^{17} fissions/cm³). For alpha particles, Clinard et al (1971) reported a larger change (0.6 percent) but the exposures were comparable: 10^{17} alpha particles/cm². It appears that an alpha particle and a fission fragment cause roughly comparable amounts of damage to the lattice, in the form of vacancies and interstitials created. The mass of the alpha particle is much smaller, but its range is larger. The material may retain more of this damage at saturation in the case of the alpha particles. The damage, both from alpha particles and from fission fragments, can be completely removed by annealing, after which the material is found to have returned to its initial lattice dimensions. Clinard et al (1971) reported that this occurred, for alpha particle-induced damage, at temperatures between 600 and 1100 K. For fission fragment damage, Akabori and Shiba (1981) show (Fig. 9.1(b)) that the annealing takes place largely between 650 and 1350 K. More highly irradiated samples are somewhat more resistant to annealing, and show some signs, in the irregularity of the recovery curves (Fig. 9.1(c)) as a function of time, that the recovery is a multistage

(a) FISSION DOSE DEPENDENCE OF LATTICE PARAMETER CHANGES FOR $\text{Th}_{0.937}\text{U}_{0.063}\text{O}_2$ PARTICLES AND POWDERED SAMPLES

(b) ISOCHRONAL ANNEALING CURVES OF LATTICE PARAMETER CHANGES FOR THE PARTICLES

(c) FRACTIONAL RECOVERY CURVES OF LATTICE PARAMETER CHANGES FOR THE PARTICLES

Figure 9.1. Changes in Lattice Parameter with Irradiation of $\text{ThO}_2\text{-UO}_2$ and Subsequent Recovery of the Material on Annealing (Akabori and Shiba, 1981).

process. Bradbury and Frost (1967) report that Wait made similar observations on thoria-urania solid solutions with 0.77 and 10.2 mole percent urania, irradiated to 0.1 fission unit.

Nakae et al (1978) irradiated UO_2 in an experiment essentially similar to that of Akabori and Shiba (1981). For samples irradiated to the vicinity of 0.001 fission units, results were very similar to those for ThO_2 . However, the UO_2 irradiations were continued to 0.0292 fission units. For these more highly irradiated samples, an additional stage of lattice damage was observed; maximum linear lattice expansion was 0.12 percent. This additional lattice damage could not be removed by annealing.

Berman et al (1960) examined UO_2 irradiated to 8 fission units and found that it retained its crystallinity, giving diffractograms comparable to those at the highest exposures reached by Nakae et al (1978). X-ray diffraction data have not been obtained from thoria-base fuels irradiated to such high exposures.

Thoria and urania, being cubic, are not subject to the anisotropic effects that cause uranium metal, as a typical example, to undergo substantial changes in exterior dimensions when irradiated. Likewise, urania and thoria appear not to be subject to phase changes in-pile such as those for $\text{ZrO}_2\text{-UO}_2$ fuels. Such phase changes are apparently confined to materials with crystal symmetries lower than the cubic. In cases in which a crystalline phase changes to a glassy one, the transition is associated with a volume change of several percent; no such change has been observed with thoria or urania.

9.3 STRUCTURE AND PROPERTY CHANGES

9.3.1 Microstructural Changes

(a) Lattice Parameter Changes

A review of the available irradiation studies of lattice damage in urania and thoria as a result of irradiation (Sect. 9.2) indicates that this damage is largely confined to the formation of vacancies and interstitials. As a result, the lattice is dilated to the extent that the lattice parameter increases a maximum of about 0.09-0.12 percent. However, this damage is largely annealed out in the temperature range from 500 to 1200 K, and would therefore not accumulate over most of the volume of an operating fuel element in a pressurized water reactor or a boiling water reactor. It would be, at most, a minor contributor to any macroscopic, externally observable dimensional changes.

(b) *Effects of Thermal Gradients*

In-reactor exposure of rod-type oxide fuel elements leads to considerable microstructural changes in the oxide as a direct result of the thermal gradients and temperatures imposed on the oxide. At sufficiently high temperatures and gradients, fission product inclusions and pores move, columnar grains are formed in the wake of moving pores, and equiaxed grains grow. These phenomena have been observed in both UO_2 and ThO_2 .

A comprehensive study of pore movement by Nichols (1967) leads to the conclusion that, although the effects are the same for ThO_2 as they are for UO_2 , they occur at higher temperatures for ThO_2 .

Cohen (1973) conducted some experiments designed to simulate conditions in-reactor using ThO_2 and ThO_2 -10 weight percent UO_2 to quantify these microstructural changes. In these experiments internal heating of annular pellets was accomplished by inserting a tungsten susceptor rod in the annulus and subjecting the rod to radio-frequency induction heating. Temperatures at the inner and outer radii (0.229 and 0.500 cm, respectively) were measured pyrometrically; a sight hole was provided for the interior measurement. Appropriate emissivity and window corrections were applied. Typical interior temperatures were 3000 K; exterior temperatures were 1800 K. The exterior surface was cooled by infrared and visible radiation to the environment. A positive pressure (approximately 1.5 atmospheres, absolute) of argon was maintained around the assembly during the experiments, which were run for 2, 4, and 8 hours.

The temperature profile in the radial direction of the pellets in these simulations can be characterized as a slightly modified straight line, whereas that of pellets in-reactor is a somewhat modified parabola, due to internal heat generation in the fuel. Nevertheless, over a considerable portion of the radii, the thermal gradients in the simulation were comparable to those generated in-reactor.

Photomicrographs of the annular oxide pellets (Fig. 9.2) after the simulation experiment showed marked densification and grain growth, increasing toward the higher-temperature region. There was also evidence of migration of pores up the thermal gradient, due to the evaporation of material on the hot side of a pore and its redeposition on the cold side. The pores that appear to have migrated are secant-shaped, with the arc on the high-temperature side and a planar surface on the low-temperature side. This planar surface was typically at the end of a single, long grain of dense material, outlined on its edges by small pores.

Migration of pores up the thermal gradient, as described above, is accepted as the most likely mechanism for the formation of in-reactor

Figure 9.2. Lenticular Pores Generating Columnar Grains together with Other Porosity Effects in a Temperature Gradient; Reduction Factor, 1/2 of Original (Cohen, 1973).

columnar grains. The columnar grains produced by the simulation experiments of Cohen (1973) have a rectangular cross section, whereas those observed in irradiated rods are elliptical; however, the experiment does demonstrate that the proposed mechanism operates as postulated. Differences from in-reactor conditions can be ascribed to the fact that a parabolic temperature profile was not developed, and also that the simulation could not be maintained for a sufficiently long time to develop steady-state configurations.

Cohen (1973) found that pore movement was pronounced only in the case of low density (89–91 percent theoretical) bodies containing large deliberately introduced pores. For high density (94–99 percent theoretical) oxide containing predominantly small pores the major effect observed was equiaxed grain growth. Quantitative estimates of the velocity of pore migration from photomicrographs were shown by Cohen to be in good agreement with values calculated using the model of Nichols (1967), in which it was assumed that the movement of gas-filled pores along a

thermal gradient is controlled by vapor transport, i.e., diffusion through the gas phase. In a reexamination of this subject, Nichols (1979) showed that a reasonable interpretation of Cohen's pore velocity data for $\text{ThO}_2\text{-UO}_2$ is obtained if the equilibrium vapor pressure of pure ThO_2 is used in the calculation. Use of the total vapor pressure, primarily UO_2 , results in predicted velocities well in excess of those measured. Although UO_2 is much more volatile and evaporates preferentially from $\text{ThO}_2\text{-UO}_2$ solid solutions (see Chap. 5), ThO_2 must evaporate and diffuse in order to move a pore. Thus the pore velocity is controlled by the vapor phase diffusion of the less volatile of the two chemical species, at least for compositions consisting primarily of ThO_2 .

Leigh and McCartney (1977) also examined the effects of a high thermal gradient on the microstructure of ThO_2 . In this work, simulation of irradiated oxide fuel was accomplished by adding simulated fission products to ThO_2 during pellet fabrication (see Sect. 9.4.2(c)).

A thermal gradient was generated in a stack of sintered pellets by direct electrical resistance heating after the samples had been externally heated sufficiently to lower their electrical resistance. Leigh and McCartney (1977) stated that the gradient was similar to that found in a nuclear reactor, and that the maximum temperature was such that a central void was formed. The authors did not give the length of time these conditions were maintained. After the heating run, a photomicrographic examination of the pellets was undertaken. Equiaxed grains were noted, but nothing comparable to columnar grains was observed. The difference between these results and those of Cohen (1973) may be due to shorter times, lower temperatures, smaller gradients, or the suppression of columnar grain growth by the simulated fission product additive in the Leigh-McCartney experiment. The amount of porosity initially present may also have been different from that in Cohen's experiment. However, the formation of a central void indicates that porosity migration took place. Leigh and McCartney (1977) suggest that the presence of a volatile species such as UO_3 may be responsible for the occurrence of columnar grains in UO_2 , but not in ThO_2 . This can, at best, be only partially true, columnar grains have been extensively observed in thorium fuels, both subjected to in-reactor and to simulated environments.

3.2 Dimensional Stability

Changes in fuel volume during irradiation arise (1) from the reduction in fabricated pore size (called densification) associated with sintering (surface tension effects), destruction of pores by fission spikes, and hot pressing; and (2) from the increase in bulk oxide volume arising from the generation of fission products and the nucleation of fission gas bubbles. The phenomena of small pore closure, larger pore closure, fission product

generation, and fission gas bubble formation occur simultaneously in a fuel element. Although these effects are discussed separately, they can be observed in isolation only by special tests where the other three effects are not significant or can be factored out.

(a) *Mechanistic Models for Densification*

A theoretical approach to the phenomenon of in-reactor densification was undertaken by Stehle and Assmann (1974). They assumed that a fission spike contains a high concentration of vacancies and, therefore, occupies a larger volume than the crystalline material from which it is derived. The expansion is on the order of the change observed in passing from the solid to the liquid state. If the spike is entirely surrounded by crystalline material and if the crystal structure is highly stable (as is the case with fluorite-type oxides), the spike is quickly recrystallized, and the vacancies diffuse to a grain boundary. Grain boundaries serve essentially as sinks; on reaching them, the vacancies experience a very much augmented diffusion rate and are quickly conducted to a free surface, i.e., a pore wall or the outer surface of the fuel. When the spike is entirely surrounded by crystalline material the change in volume is quickly rectified; strains in the crystalline lattice surrounding the spike are relieved, and the material returns to its former condition except for the presence of the fission fragments themselves at the ends of their tracks.

If, however, a portion of the fission spike borders on a pore, then the affected material bulges into the pore. The resulting lost pore volume is not fully recovered as the spike is recrystallized. As the spike's internal vacancies diffuse away, only a portion reaches the pore (from which, essentially, they all came). The remainder reaches other surfaces, including the exterior surface of the fuel. The net result is a reduction in pore size and an overall reduction in the exterior dimensions of the fuel.

Therefore, the rate of filling of pores depends on the frequency with which fission spikes intersect pores; this in turn depends on fission rate, porosity, and the length of the fission track. Another basic factor is the volume increment to be expected from each intersection. However, if the fission and vacancy diffusion rates are such that a second fission spike reworks material from which not all the vacancies have dissipated, then the full potential of the volume change will not be realized. The intragranular vacancy diffusion rate, in Stehle and Assmann's view, can serve as a rate-limiting step on the in-pile densification, and densification is accordingly a function of grain size. It is retarded below a theoretical maximum rate by the presence of large grains.

Stehle and Assmann (1974) give the following equation for densification:

$$\ln(r_0/r) = \frac{3(r_0 - r)}{WLFC} - \left\{ 1 + \frac{WLFG}{3D_v} \left[1 - \frac{G}{r_0 - r} \ln \frac{G + r_0}{G + r} \right] \right\} \quad \text{Eq. (9.1)}$$

where

t_0 = the time (sec) at which pores with an initial radius r_0 (cm) contract to a radius r . (In the sample evaluations shown in Figs. 9.3 and 9.4, r_0 is taken as 5×10^{-4} cm.)

W = the increment of volume (cm^3) due to one fission spike intersecting a pore. (Stehle and Assmann use the value $W = 5 \times 10^{-19} \text{ cm}^3$.)

L = the length of a fission track (cm). (The bimodal distribution of fission products (see Fig. 9.14 in Sect. 9.4.1) is such that a typical fragment representative of the heavy-fragment maximum is ^{139}Xe with an energy of 58 MeV; a typical light fragment is ^{95}Sr with 92 MeV. According to equations given by Mukherji and Srivastava (1974), the range of the heavy fission fragment in fully dense thorium-base fuel would be 6.2×10^{-4} cm; that of the light fragment would be 9.4×10^{-4} cm. A mean value of 7.8×10^{-4} cm is therefore used in the sample evaluations.)

F = the volumetric fission rate. (In this example we use the LWBR design value for F in high-zone seed fuel of 8.2×10^{12} fissions/ cm^3 sec.)

G = the radius of the grains. (A typical value (ASTM #6) is 2.3×10^{-3} cm.)

C = the concentration of vacancies in the spike. (Assmann and Stehle, in a later paper (1977), use the value $C = 0.002$, i.e., one vacancy per 500 locations.)

D_v = the diffusion coefficient for vacancies. (A satisfactory independent determination of this quantity is not available for thorium or uranium. For Figs. 9.3 and 9.4, D_v is taken as $1 \times 10^{-14} \text{ cm}^2/\text{sec}$, and the graphs therefore apply to the temperature (in the general vicinity of 2000 K) at which that

Figure 9.3. Densification of a 1- μm Pore under Reference Conditions Described in Sect. 9.3.2(a). According to the Stehle-Assmann Model; Solid Curve is Calculated from Eq. (9.1).

vacancy diffusion coefficient is appropriate. This value for D_v is consistent with a densification comparable to that actually observed.)

Figure 9.3 shows calculated values of the diameter of a pore with an initial value of 1 micrometer, at various times after the start of irradiation. In these calculations (the solid line in Fig. 9.3) the assumed values for the terms in Eq. (9.1) were used. The dashed line shows the curve that is generated on the assumption that a given increment of radiation would densify the material by destroying a fixed fraction of the porosity present. The result is an exponential curve. In contrast to the Stehle-Assmann model such a curve would never reach 100 percent theoretical density. Figure 9.4 shows the effect of varying grain size on the time that such a pore reaches half its initial diameter.

Dollins and Nichols (1978) developed this model further, presenting analytical equations for various components of C , the vacancy concentration. Using a model in which cascades of vacancies are created by fission

Figure 9.4. Effect of Grain Size on Densification of a $1\text{-}\mu\text{m}$ Pore to Half that Diameter under Reference Conditions Described in Sect. 9.3.2(a), According to the Stehle-Assmann Model. Dashed line shows typical evaluations using the Pfennigwerth-Matthews-Spahr Model.

nents, they derive equations representing the net losses and loss rates of interstitial-vacancy pairs from these cascades to dislocations and grain boundaries. Calculated densification curves are presented which are comparable, in general characteristics, to the solid line of Fig. 9.3.

In later work, Assmann and Stehle (1977) applied their model to the dimensional changes observed in a 95 percent dense UO_2 fuel rod irradiated to 4 fission units. It was necessary to elaborate their model further by distinguishing four temperature regions, with boundaries placed at 23, 1023, and 1673 K. In each of these regions, there was a different interaction between the athermal densification mechanism, i.e., the interactor densification described above, and the thermal densification mechanism, i.e., ordinary sintering. The thermal densification mechanism is

dominant in the region above 1673 K; the athermal mechanism in the region below 723 K; and a separate calculation was performed for each region.

Assmann and Stehle (1977) were able to show a good match between their observations and calculations. A similar, though simpler, model is discussed in Sect. 9.3.2(b) below. Assmann and Stehle (1977) recognized that the path taken by the densification curve is quite sensitive to pore size distribution, and could be expected to pass through a minimum if the predominant pore size is below $2\text{ }\mu\text{m}$ in diameter. As a first approximation, they advocate ignoring pores larger than this, as having no significant effect on the densification process. They subdivide pores with smaller diameters into two groups: large pores, above $0.1\text{ }\mu\text{m}$ in diameter and small pores, below this limit. They apply an exponential law to the small pores. The large pores are divided into size classes, to which the model of Eq. (9.1) is individually applied.

(b) Densification and Swelling Data at Low Temperature

An increase of volume must be expected when fragments are formed during fission of actinide atoms in oxide fuel. A simple linear law for swelling versus depletion is considered appropriate at temperatures for which the fission gases are held in the lattice and play a role similar to solid fission products. At higher temperatures fission bubbles nucleate and move towards grain boundaries. Swelling and gas release due to these phenomena are discussed in Sect. 9.4.3. For oxide fuel elements at center temperatures $\leq 2000\text{ K}$, the low temperature value of swelling amounting to about 0.7 percent per fission unit was first given by Bleiberg et al. (1963) for UO_2 and $\text{ZrO}_2\text{-UO}_2$ fuels. Pfennigwerth and Matthews, in work done at the Bettis Atomic Power Laboratory, and Giovengo (1970), found that it is a satisfactory approximation for thorium-base fuels as well.

Stress-free swelling may be expected to be isotropic. However, in reactor design there are physical constraints and thermal gradients that may direct the swelling in various directions. These alterations and departure from isotropy are significant in fuel element evaluations, as is discussed below.

As noted in Sect. 9.1, and as is discussed later in detail (see, for instance, Table 9.3) the fission gas yield (Xe plus Kr) is about 10 percent higher for ^{233}U than for ^{235}U . Consequently, all data affected by fission gas yield, taken from $\text{ThO}_2\text{-}^{235}\text{UO}_2$ fuels, must be reinterpreted to be valid for $\text{ThO}_2\text{-}^{233}\text{UO}_2$ fuels. In practice the data scatter completely masks such refined adjustments. However, since the data are taken almost entirely for $\text{ThO}_2\text{-}^{235}\text{UO}_2$ fuel these adjustments are theoretically necessary. Thus, the same fission gas contribution to swelling would be expected to occur about a 10 percent lower fissioning rate for $\text{ThO}_2\text{-}^{233}\text{UO}_2$ than for $\text{ThO}_2\text{-}^{235}\text{UO}_2$.

Giovenco (1970) reported changes in Zircaloy cladding length and diameter measured at room temperature for test rods irradiated to burnups ranging up to 3.4 fission units. Fuel compositions ranged from 2 to 30 mole percent $^{235}\text{UO}_2$ in ThO_2 ; however, this variable appeared to have no significant effect on the results. In the cases showing the greatest axial growth (those in which center temperatures reached values above 1650 K, and which had flat-end pellets) increases in cladding length reached 0.5–0.7 percent very shortly after the start of irradiation, at about 0.5 fission units. Thereafter, the rate of axial growth decreased considerably; a growth of 1 percent over the original length was reached at about 2.5 fission units. For conditions other than the most extreme cases (i.e., lower temperatures, or dished-end pellets) axial growth was one-half to one-fourth the worst-case values. Giovenco (1970) also gives data on cladding diametral measurements. Briefly stated, fuel swelling of about 0.7 percent per fission unit that was not accommodated in the axial direction, or in the dishes, was accommodated in the radial direction.

In work done at Bettis Atomic Power Laboratory, Pfenningwerth and Matthews examined measurements on the length change of a fuel stack of cylindrical pellets clad in Zircaloy-4. Their experiment also consisted of tests on a number of fuel rods, portions of which were loaded with pellets of one of the LWBR binary compositions (1–6 mole percent UO_2 in ThO_2), and the remainder of which (the part extending outside the high-flux region during irradiation) contained ThO_2 pellets. For the binary fuels, initial densities varied from 93 to 98.8 percent of theoretical, and grain diameters varied from 4 to 90 μm . Dished pellets were used in some rods; as a result, the total fuel element internal void volume ranged up to 8.6 percent in the binary pellet region of the stack.

The rods were subjected to irradiation in the ETR (Idaho) and the NRX (Chalk River, Ontario) test reactors to various depletions ranging up to 13.2 fission units. The lengths of the fuel stacks of the rods were measured at room temperature after discharge from the reactor. Changes from pre-irradiation values varied from –0.48 percent to +0.46 percent. Stack length reduction occurred primarily in low burnup rods containing relatively fine-grain fuel. Length increases were generally at the higher burnup levels.

The above behavior is the result of two separate processes. The first of these is a swelling process consisting of (1) transmutation-induced swelling resulting from the change in volume caused by the generation of solid fission products or gaseous products held as single atoms in the lattice; and (2) swelling from bubbles caused by gaseous fission products. These processes are discussed in Sects. 9.4.2 and 9.4.3, respectively.

The second process for irradiation-induced volume change is densification, caused mostly by the closure of small pores in the as-fabricated material. Bleiberg et al (1963) demonstrated, in a series of photographic cross-sections of plate-type $\text{ZrO}_2\text{-UO}_2$ fuel elements, that the porosity

initially present is not maintained under irradiation conditions. During the earliest stages of the irradiation—typically, before a depletion of 2 fission units is reached in the case of $\text{ZrO}_2\text{-UO}_2$ fuels—the initial porosity associated with small pores collapses, with a consequent decrease of the volume of the fuel. After this stage is completed, the fuel proceeds to swell at a rate of approximately 0.7 percent per fission unit, which is consonant with the accumulation of fission products to be described in Sect. 9.4. In work done at Bettis Atomic Power Laboratory, Pfennigwerth and Matthe found this value to apply to thoria-base fuels as well, at least for rods with free-standing cladding and large fuel-cladding gaps, in which fuel swells isotropically. (Cladding restraint effects are of slight significance in such rods when operated at moderate power.) The volume of an initially porous fuel, therefore, first decreases, until the small porosity has been essentially eliminated, and some of the larger porosity also reduced. The volume then increases as fission products accumulate. The amount of decrease is limited by the initial volume of pores susceptible to densification. Qualitatively, the curve followed by the total volume reflects these two counter-vailing tendencies, one of which is largely complete before depletion is far advanced, and the other of which continues to operate throughout irradiation. Quantitatively, the actual volume change with time depends on the size distribution of the pores.

In work done at Bettis Atomic Power Laboratory by Pfennigwerth and Matthews, this concept was applied to an empirical description of observed fuel stack length changes. Although it was generally recognized that densification affects pores of all sizes and is a function of pore size, it was convenient to make an empirical simplification. It was assumed that a rapid process occurs exclusively, and uniformly, in the pores with an initial diameter less than $2.3\ \mu\text{m}$. (This diameter happened to correspond to one of the digital settings of a quantitative television microscope used to determine pore size distribution.) The volume of these small pores, as a percentage of the total sample, was designated P_0 , and the observed percentage fuel stack length changes, $100(\Delta L/L)$, were fitted to equations of the form

$$100(\Delta L/L) = -AP_0[1 - \exp(-BF)] + CF \quad \text{Eq. (9.2)}$$

where F is the rod average fuel depletion, in fission units, and A , B , and C are fitted coefficients. Values of $+0.622$, $+1.27$, and $+0.154$ were obtained for them, respectively, from the data for large-diameter rods, i.e., those with cladding internal diameters greater than $1.27\ \text{cm}$. For smaller-diameter rods operated at high power, interaction with the cladding introduced complications that could not be fully evaluated.

The final term of the equation, $+0.154 F$, represents the low temperature swelling component associated with fission product generation (solids and gas in atomic form). The negative term of Eq. (9.2) represents the densification component and indicates an exponential decrease of the as-fabricated porosity associated with small pores. At start of life, the rate of volume change associated with densification in Eq. (9.2) is $ABP_0 dF/dt$, where dF/dt is the fission rate. This is appropriate if it is assumed that the al temperature is near or below the sintering temperature so that pore closure is caused primarily by the interaction of fission spikes with the pores.

Spahr (1978) carried out a comparable evaluation of fuel pellet diametral change, percent $\Delta D/D$, using the same mathematical model. In this study the fitted values for the coefficients A, B, and C, respectively, were $+0.5$, $+2.0$, and $+0.233$. A unit cube of fuel with no initial porosity will expand, after one fission unit, to dimensions of 1.00154 in the axial direction and 1.00233 in the two radial directions. The resulting volume, 1.0062, approximates the value of 0.7 percent volume swelling per fission unit discussed previously.

Pfennigwerth and Matthews recognized that measurements of P_0 are often not available, and accordingly provided a relationship between P_0 and the ASTM grain size #Z. (Although this relationship should be considered valid only for the particular manufacturing process used, it is believed that a similar relationship exists for other processes that do not use pore formers.)

$$P_0 = 0.130 (Z - 4.47) \text{ [for axial changes]}$$

$$P_0 = 0.636 (Z - 6.2) \text{ [for diametral changes]}$$

where $Z = 16.644 - 6.644 \log U$, and U = mean grain boundary intercept, μm . (The mean grain diameter is the intercept U multiplied by $2/\sqrt{\pi} = 1.12838$.) This implies that densification due to sintering will not place if the grain size is coarser than ASTM #4.47 (diameter $7 \mu\text{m}$) for axial changes or ASTM #6.2 (diameter $= 42 \mu\text{m}$) for diametral changes. However, the relationship applies only for the general range of manufacturing conditions and grain sizes treated in this experiment, and excludes hot pressing of the larger size pores which is treated separately.

The phenomenon of densification was examined by Ocken (1975) and by Meyer (1976) in response to observations in 1972, on the refueling of some reactors with unpressurized rods, such as the Ginna reactor, that axial contraction of the fuel had permitted unsupported cladding to collapse.

The fuel of the Ginna reactor was UO_2 with a density of approximately 92 percent of the theoretical value; it was, by present standards, insufficiently sintered during manufacture. Various empirical models were reviewed; these generally predicted an approximately linear approach to 96.5 percent of theoretical density at 0.5–1.5 fission units. Ocken proposed that the susceptibility of fuel to densification should be tested by subjecting a sample to resintering and examining it for further dimensional change. The supposition here is that a pore size distribution which is susceptible to rapid closure at normal sintering temperatures would also be susceptible to rapid closure by fissioning action. Typical current fabrication practices, such as the LWBR reference process described in Chap. 8, produce high-density materials that are dimensionally stable when subjected to resintering.

When the densification models of Pfennigwerth, Matthews, and Spahr (PMS), the later Assmann-Stehle model (AS77), and the contributions of Dollins and Nichols (DN) are reduced to specific applications in high-density oxide fuels, the differences among them become of secondary importance. All agree that, at temperatures below about 2000 K, aside from the densification of initial porosity, volume increases linearly with burnup. The PMS value of 0.7 percent per fission unit appears to be an appropriate consensus as a lower limit. All agree that, as a reasonable simplification, it may be assumed that porosity above a certain threshold diameter does not participate in the densification; PMS gives this value as $2.3 \mu\text{m}$, compared to the value of $2 \mu\text{m}$ proposed by AS77, which is not significantly different. All agree, also, that the volume in the smallest size fraction of the pores decreases exponentially with burnup. The remaining discrepancy between the analytical (AS77 and DN) and empirical (PMS) approaches lies in the treatment of pores with initial diameters in the size range from 0.2 to $2 \mu\text{m}$. The analytical approaches require detailed information on pore size distribution that is not readily obtained but, fortunately, yield results not greatly different from the empirical approach.

Any practical evaluation of volume change in-pile will clearly require the introduction of some empirical elements. Accordingly, there appears to be justification in using a slight modification of Eq. (9.2) which was proposed as part of the empirical PMS model. This modification may be written:

$$100 (\Delta V/V) = -P' [1 - \exp(-BF)] + CF \quad \text{Eq. (9.3)}$$

where F is the rod average fuel depletion, in fission units, P' is the percentage of susceptible porosity ($<2 \mu\text{m}$ diameter) in the total volume, C is assumed to be 0.7, and B is the reciprocal of the value of F at which $1/e = 0.368$ of the initial susceptible porosity remains. In high-density fuel, the value of B is not particularly critical at moderate to high burnups; the value of +1.27, given in the PMS model, is acceptable for initial estimates.

The volume of large porosity ($\geq 2 \mu\text{m}$) can be determined from measurements of photomicrographs of comparable material, the total amount of porosity can be determined gravimetrically, and the value of P' , the porosity subject to densification, can then be determined by difference.

Equation (9.3) may be applied to rod-type fuel elements, within the range of values of F represented by observation, i.e., <15 fission units. There is the further restriction that center temperatures must not exceed 2000 K. More elaborate treatments, such as those of the CYGRO series of computer programs, are based on the PMS model of densification for small ($\leq 2.3 \mu\text{m}$ diameter) pores and hot pressing mechanisms (Sects. 9.3.2(c) and 7.4.5) for larger pores. Like Eq. (9.3), these analyses represent empirical simplifications.

AWBA data (reported by Giovengo et al, 1982) indicate a rapid increase in fission gas release at about 20 fission units and, presumably, a reduction in swelling rate.

(c) Duplex Fuel Rod Dimensional Changes

The dimensional changes of long duplex fuel rods were reported by Hoffman et al (1982) and by Waldman et al (1982); those of short rods were reported by Sphar et al (1981). In these cases a model for fuel swelling was examined which was consistent with observed diameter and length changes. The swelling model was associated with the use of the CYGRO5 computer program, details of which have been published by Newman and Kovscek (1982) in the calculation of overall rod performance. The model for swelling, as described by Duncombe et al (1982), is made up of a temperature-dependent term for volatile products, and a temperature-independent term for nonvolatile products,

$$\frac{\Delta V}{V} = t_d C_d f_1(F) \times f_2(P,T) + kF \quad \text{Eq. (9.4)}$$

where

$\Delta V/V$ = the fractional volume change

t_d = a number for volatile atoms per fission and is 1.0 for ThO₂-²³⁵UO₂ fuel and 1.1 for ThO₂-²³³UO₂ fuel

C_d = a multiplier used for adjustment to data

$f_1(F)$ = a fission-dependent function, which is approximately a straight line

$f_2(P,T)$ = a multiplier, which is a function of the local pressure and temperature inside the fuel

k = the linear dependency of nonvolatile fission product volume on F

F = the fission density.

At 1505 K and atmospheric pressure, $\Delta V/V$ has an average value of 7×10^{-3} per fission unit in the range of zero to 10 fission units. However, this value becomes 3.2×10^{-3} at 533 K and 2.8×10^{-2} at 2200 K. This swelling formulation provided agreement with the rod dimensional measurements of Hoffman et al (1982) and of Sphar et al (1981). However, it appeared from the data of Waldman et al (1982) that, whereas the axial center of the annulus followed the above fuel swelling values, the ends of the pellet followed values about half this amount. This may be a spurious effect associated with the smaller as-manufactured diametral gap between the annulus and center pellet that existed in the center of the pellet compared with the gap at the pellet ends.

Similar variations in fuel rod diameters have been examined for rods with solid pellets by J. J. Brennan and J. Dunyak of the Bettis Atomic Power Laboratory. It was concluded that a single axially uniform representation of fuel swelling is probably not correct, but that the swelling is greater in regions further removed from the fuel surface. This is consistent with the assumption that the escape of bubbles along grain edges is governed by some type of diffusion mechanism in addition to the migration to the grain boundaries from nucleation sites inside the grains.

It was also found by Duncombe et al (1982) that, over the temperature ranges at which those fuels operated (<1500 K), no differences in the swelling of ThO_2 and UO_2 fuels could be identified. However, it is reasonable to expect that, at some higher temperature, ThO_2 would retain more fission gas and therefore swell more. This would occur at about 2100 K, which is above the threshold for pore migration in UO_2 but below the threshold for ThO_2 .

(d) Defected Fuel Rods

Ex-reactor tests of the action of high-temperature water on ThO_2 , $\text{ThO}_2\text{-UO}_2$, $\text{ZrO}_2\text{-CaO-UO}_2$, $\text{ZrO}_2\text{-UO}_2$, and UO_2 have shown a stability rating in that order, with ThO_2 being the most stable. These results were reported by Markowitz and Clayton (1970) and are discussed in Chap. 5. It is, therefore, to be expected that $\text{ThO}_2\text{-UO}_2$ fuels would be more stable than UO_2 fuels under conditions where the rod is defected.

A direct comparison between the behavior of $\text{ThO}_2\text{-UO}_2$ and UO_2 fuels has been provided by Sphar et al (1981). Two fuel rods containing duplex pellets were intentionally defected by drilling a hole in the cladding and were tested together. One fuel rod contained UO_2 for the annulus, and the other contained ThO_2 -34 weight percent UO_2 . In the former case, the power started at 42.6 kW/m and reached 29.5 kW/m at about 14 fission units. In the latter case, the power went from 49.2 kW/m to about 32.8 kW/m at a depletion of 18 fission units. The fission rates in the fuels were very high ($\sim 10^{14}$ fissions/cm³ • sec) because of the small size of the

fuel rod (~ 0.3 inch overall diameter) and the concentration of power in the annulus. Therefore, any relative effects of fission rate would be apparent.

The condition of the fuel as seen from neutron radiographs of defected rods is shown in Figs. 9.5, 9.6, and 9.7. In these radiographs the lighter pellets at each end of the stack, and the light band along the axes of the other pellets are thorium; the dark annuli are uranium. The dished-end configuration of the pellets can be seen.

Figure 9.5 shows radiographs of the UO_2 annulus in the intentionally defected rod 97-13D. Gamma scanning after 29.5 effective fuel power days of irradiation indicated the existence of an abnormality of the fuel stack. In Fig. 9.5, (a) is the neutron radiograph taken after 29.5 effective full power days of irradiation and shows a fractured duplex pellet just above the location of the defect hole. In the same figure, (b) shows the same fuel after a total of 222.0 effective full power days of irradiation. No significant worsening of the condition is noted.

The neutron radiographs of rod 97-48D, which had a $\text{ThO}_2\text{-UO}_2$ annulus, taken after 255 effective full power days of irradiation to a peak depletion of 18 fission units, are shown in Figs. 9.6 and 9.7. Figure 9.6 reveals the fuel condition, and Fig. 9.7 was overexposed to bring out cladding features. Figure 9.7 is an enlargement of a portion of Fig. 9.6(b). The fuel is seen to be intact, the only notable feature being several transverse cracks in the central thorium pellets. The overexposed print shows darkened areas in the cladding immediately adjacent to the 50-mil thick thorium spacers. These were shown by metallographic examination of the cladding to be accumulations of hydrogen, resulting from corrosion of the cladding internal surface, which migrated to the colder cladding regions associated with the lower power generation in the thorium spacers. It is concluded that, as expected, thorium-base fuel is, if anything, more resistant than UO_2 to corrosion effects of high-temperature water during defect operation even at high fission density.

In work done by L. A. Waldman, of Bettis Atomic Power Laboratory, other tests on defected rods, using UO_2 and $\text{ThO}_2\text{-UO}_2$ fuels and solid pellets rather than duplex pellets, were run in the NRX Test Facility at Chalk River, Canada. These tests showed that less activity release occurred for $\text{ThO}_2\text{-UO}_2$ even though the fuel temperature was higher. These data are consistent with the other tests on duplex fuel at lower temperature and the out-of-pile corrosion tests of Markowitz and Clayton (1970).

(e) Metallographic Comparison of Fuels

A comparison of the performance of thorium-base fuels at high depletion with other fuels can be obtained from metallographic observations at

Figure 9.5. Neutron Radiographs of Defected Duplex Fuel Rod 97-13D Having a UO_2 Annulus.

Fig. 9.6. Neutron Radiographs of Defected Duplex Fuel Rod 97-48D Having a $\text{ThO}_2\text{-UO}_2$ Fuel Core.

Figure 9.7. Enlargement of Neutron Radiograph (Fig. 9.6(b)) of Defected Duplex Fuel Rod 97-48D Having a ThO₂-UO₂ Annulus.

varying depletions of the annuli of duplex fuels. These data were obtained by Sphar et al (1981). Figures 9.8 (a), (b), (c), and (d), 9.9 (a), (b), and (c), and 9.10 (a), (b), (c), and (d) show the appearance of three fuel compositions, UO_2 , $\text{ZrO}_2\text{-CaO-UO}_2$, and $\text{ThO}_2\text{-UO}_2$, at different stages of depletion. The latter rod operated at a power that was about 30 percent higher than the power for the other two rods because all rods were designed to operate at about the same homologous temperature, i.e., fraction of the melting point on the absolute scale. (The maximum annulus fuel temperature was about 1644 K.) Detailed pore counts were made to determine fuel porosity at various places and at various times. The resultant calculated porosity is summarized in Table 9.1. The data indicate that the porosity at first decreased as a result of the closure of small pores, but subsequently increased as a result of the formation of fission-gas pores. These results are qualitative to the extent that the porosity readings do not include the irregular dark spaces, for instance on Fig. 9.8, which are attributed to pull-out of grains during surface preparation.

Metallography of surfaces of fuel from companion rods at still higher depletions (about 22–24 fission units) became available subsequent to the report of Sphar et al (1981). These are shown as Figs. 9.8(d) for UO_2 and 9.10(d) for $\text{ThO}_2\text{-UO}_2$ supplied from unpublished work by C. D. Sphar of

Figure 9.8. Microstructure of UO_2 Annulus as a Function of Irradiation (As Polished); (a) Pre-Irradiation; (b) After Approximately 2.6 Fission Units (Rod 97-23).

Figure 9.8. Microstructure of UO₂ Annulus as a Function of Irradiation (As Polished): (c) After Approximately 11.6 Fission Units (Rod 97-24); (d) After Approximately 24 Fission Units (Rod 97-1).

Bettis Atomic Power Laboratory. The same trend, i.e., an increase of porosity with depletion, is shown for both fuels. Note also that the pores are larger at the inside surface of the annulus, leading to higher porosity in this region. Moreover, the appearance of the pores in ThO₂-UO₂, Fig. 9.10(d), indicates somewhat less porosity increase than in the case for UO₂, Fig. 9.8(d), despite the higher power reported by Sphar et al. It can be concluded that swelling correlations such as that given by Eq. (9.4) should be adjusted so that the temperature-sensitive term $f_2(P,T)$ provides for a lower value of swelling for ThO₂-UO₂ than for UO₂ in the temperature range over which these tests were conducted. As noted before, this trend would be expected to be reversed at still higher temperatures.

9.3.3 Property Changes

(a) Melting Point

No direct measurements have been made of the effects of irradiation on the melting points of ThO₂ or of any ThO₂-UO₂ solid solution, but there are some data on UO₂. Christensen et al (1964) reported measurements of the melting points of "nearly" stoichiometric UO₂ samples that had been

ID (a)

OD

(b)

0.01 INCH

(c)

Figure 9.9. Microstructure of $\text{ZrO}_2\text{-CaO-UO}_2$ Annulus as a Function of Irradiation (As Polished): (a) Pre-Irradiation; (b) After Approximately 2 Fission Units (Rod 97-37); (c) After Approximately 12 Fission Units (Rod 97-39).

Figure 9.10. Microstructure of $\text{ThO}_2\text{-UO}_2$ Annulus as a Function of Irradiation (As Polished); (a) Pre-Irradiation; (b) After Approximately 2.8 Fission Units (Rod 97-5).

irradiated to various burnup levels from about 0.5 to 13 fission units. Measurements were made relative to unirradiated UO_2 , which was assumed to have a melting point of 3073 K. Their data indicated a nearly linear decrease of melting point with irradiation exposure at a rate of 9 kelvins per fission unit. In earlier work, Christensen (1962) reported an increase in the melting point of about 100 K to a burnup of 0.2 fission units followed by a decrease at higher irradiation levels of about 130 K below the melting point after 23 fission units. It is not known to what extent these observations were influenced by variations in oxygen content. Bates (1970) did not find any change of the melting point with irradiation at lower temperatures and lower irradiation levels.

Of irradiation effects, only the incorporation of transmuted elements into the solid and liquid phases would be expected to change the melting point significantly. Other irradiation effects, such as structural damage, should, for the most part, be annealed out as the melting temperature is approached. Because of the high melting points of urania and thoria, it

Figure 9.10. Microstructure of $\text{ThO}_2\text{-UO}_2$ Annulus as a Function of Irradiation (As Polished): (c) After Approximately 18.6 Fission Units (Rod 97-17); (d) After Approximately 22 Fission Units (Rod 97-33).

would normally be expected that the introduction of other oxides would cause a decrease in the melting point. This decrease would be expressed as a downward slope of the solidus as it left the thoria or urania side of binary phase diagrams such as those shown in Chap. 4. In the composition range normally attainable as a result of irradiation (<10 mole percent solute), the solidus is approximately linear with composition. Those results that report a linear decrease in the melting point of urania with irradiation exposure are therefore in accord with expectations.

If it is assumed that the only significant effect of irradiation on the melting point of thoria is the decrease in the solidus caused by the incorporation of transmuted elements, an estimate can be made of the change to be expected. Tables 9.3 and 9.4, which are discussed in Sect. 9.4, provide calculations of the expected fission product and actinide concentrations in typical thoria-base fuel. The binary diagrams of Chap. 4 provide a means of estimating the slope of the solidus at low concentrations.

TABLE 9.1—SUMMARY OF DUPLEX PELLET ANNULUS POROSITY ANALYSIS

Fuel Material	Fuel Depletion (fissions units)	Volume Percent Porosity	
		Total	With Diameter $<3\mu\text{m}$
UO ₂	0	5.3	4.6
	2.6	2.9	2.8
	11.6	1.4	1.3
ZrO ₂ -UO ₂ -CaO	0	10.5	3.3
	2	3.4*	†
	12	7.1	4.6
ThO ₂ -UO ₂	0	2.3	1.8
	2.8	1.6	1.0
	18.6	~5.0‡	~4.0‡

*Uneven distribution of very large pores results in increased uncertainty

†Pores with diameter $<3\mu\text{m}$ not numerous enough for analysis

‡Translucency of sample necessitates qualitative correction

On the basis of Tables 9.3 and 9.4, it can be calculated that one fission unit in a typical thorium-uranium fuel will result in the incorporation of 0.21 mole percent of lanthanides and 0.06 mole percent of zirconium among the total metal atoms of the fluorite phase. In addition, the amount of uranium will be augmented by 0.05 mole percent. It can be estimated, on the basis of the binary phase diagrams of Chap. 4, that the melting point of thorium would be depressed 5 kelvins per mole percent of uranium, 10 kelvins per mole percent of zirconia, and 20 kelvins per mole percent of lanthanide-series oxides. An irradiation of one fission unit should therefore depress the melting point of thorium-uranium fuel by about 5 K.

The value of melting point depression given above for a comparable irradiation of uranium is 9 kelvins per fission unit. The difference may be ascribed to variations in oxygen content, or to the accumulation of about 0.3 mole percent of plutonium in the uranium fuel. The effect of the plutonium on the melting point would be in addition to those of the lanthanides and zirconia, which would be present in concentrations comparable to those in the thorium-uranium fuel. Binary phase diagrams permitting estimates of the slope of the solidus in the uranium-plutonium system are not available, but it may be assumed to be of the same general magnitude as the values quoted above. (The diagrams of the plutonium-uranium system in Chap. 4 represent

stigations that terminated well below the melting point.) For urania, before, a decrease of 9 K in the melting point per fission unit would be expected and within the range that can satisfactorily be explained by the effect of transmuted elements on the solidus. On this basis a value of 9 K per fission unit would be expected for thorium and thorium-uranium of high thorium content.

Thermal Conductivity

oxide fuel materials exposed to reactor irradiation are subject to a number of effects, each of which can affect the thermal conductivity of the material in a different manner. Those microstructural changes in the oxide that develop from irradiation-induced high temperatures and thermal stresses affect thermal conductivity in the same manner as do similar microstructural features developed under ex-reactor conditions. In addition, however, there are effects unique to irradiation, i.e., lattice damage and fission depletion effects. And finally, there is the concomitant effect of thermal cracking.

As discussed by Belle et al (1967) and by Berman et al (1972), the thermal resistivity ($R = 1/\lambda$) of nuclear oxide fuels can be corrected as an approximation for the effects of irradiation by adding two terms to the resistivity of unirradiated material (R_0) as follows:

$$R_{irr} = R_0 + \frac{C}{T} + \frac{DF}{T}, \quad \text{Eq. (9.5)}$$

where C and D are constants equal to 32.4 and 11.1, respectively, R and R_0 are in (m · K)/W, F is in fission units, and T is in kelvins. The term C/T was included to account for increases in thermal resistivity during the early stages of irradiation due to concentration of lattice defects caused by thermal and fission damage. The term DF/T was included to account for increases in thermal resistivity, due to the accumulation of transmuted elements, to the concentrations discussed in Sect. 9.3.3(a). These fission products

become more mobile with increasing temperature and tend to agglomerate and precipitate. This effect as well as that due to concentration of lattice defects was assumed to decrease with increasing temperature. It is assumed also that the user, in making an estimate of R and the effect of irradiation on R, will take into account the porosity of the material at the time (and irradiation exposure) of interest. The effects of irradiation on porosity changes due to fission gas bubble formation are discussed in Sect. 9.4.3. Relationships between thermal conductivity and porosity are described in Chap. 6.

The evidence from the considerable amount of work on the effects of irradiation on the thermal conductivity of UO₂ is summarized by many authors; see, for example, the critical review by Brandt et al (1976). In

brief, the thermal conductivity of UO_2 after irradiation below 773 K is reduced as a result of induced lattice defects. Between 773 K and the melting point of UO_2 (3120 K) no substantial change in the thermal conductivity is observed. This is true for irradiations up to 1 fission unit. No conclusions can be made concerning changes at higher burnups for UO_2 since such data are not available.

A small amount of information is available on lattice damage and fission depletion effects for ThO_2 and $\text{ThO}_2\text{-UO}_2$; some of this work is summarized by Berman et al (1972). MacEwan and Stoute (1969) measured the thermal conductivity of ThO_2 -1.3 mole percent UO_2 at 333 K before and after irradiation and found that irradiation at low temperatures (below 429 K) decreased the thermal conductivity. Irradiation exposures were varied from 3.1×10^{-6} to 4.7×10^{-3} fission units, and saturation of damage apparently occurred at around 10^{-3} fission units. Increasing the irradiation temperature into the range 600–692 K reduced the extent of decrease in thermal conductivity, indicating annealing of damage during irradiation.

Jacobs (1969 and 1970) measured the thermal conductivities of ThO_2 and some $\text{ThO}_2\text{-UO}_2$ compositions during reactor irradiation. He observed no statistically significant difference between in-reactor and unirradiated values (Springer and Lagedrost, 1968) for ThO_2 and ThO_2 -9.8 mole percent UO_2 below 1273 K and between postirradiated (Matolich and Storhok, 1970) and in-reactor values for ThO_2 -3 mole percent UO_2 below 1473 K. However, Jacobs (1970) points out that the low temperature (<673 K) in-reactor data points were obtained only subsequent to irradiation at higher temperatures, and thus any irradiation effects on thermal conductivity at the lower temperatures may have been annealed out at the higher temperature.

Matolich and Storhok (1970) determined postirradiation thermal conductivities from thermal diffusivity measurements using the laser flash technique on three irradiated $\text{ThO}_2\text{-UO}_2$ compositions: ThO_2 -3 mole percent UO_2 , ThO_2 -9.8 mole percent UO_2 , and ThO_2 -14.8 mole percent UO_2 . No significant difference between unirradiated and irradiated measurements was observed for the ThO_2 -3 mole percent UO_2 composition. Matolich and Storhok concluded that the result was due to annealing of the lattice damage at the high irradiation temperature (~ 1173 K).

The result for the ThO_2 -9.8 mole percent UO_2 composition was anomalous, i.e., the postirradiated thermal conductivity was higher. The specimen on which the diffusivity measurements were made was cut out of the columnar grain growth region of the sample which operated at a maximum in-reactor temperature of about 1993 K. Higher measured thermal conductivity could therefore be anticipated. However, these results are uncertain since an accurate geometric density could not be obtained.

Still a third effect was found for the postirradiation conductivity of ThO_2 -14.8 mole percent UO_2 . The measured postirradiation conductivity was lower. After thermal cycling between 573 and 1473 K, irradiated thermal conductivities were approximately 55 percent below unirradiated values. Matolich and Storhok attributed the lack of an annealing effect to the high burnup (4 fission units) of this specimen. The material also undoubtedly contained internal cracks. Thus, it appears from these post-radiation experimental observations that no quantitative conclusions can be made regarding the lattice damage and fission depletion effects on the thermal conductivity of ThO_2 and $\text{ThO}_2\text{-UO}_2$.

(c) Irradiation Creep

Irradiation-induced or irradiation-enhanced creep is of importance because it leads to deformation of fuel elements under the influence of applied stresses. It has been investigated theoretically and experimentally by Wisnyi et al (1966) and by Germann (1967) for urania, zirconia-uranium, and thorium-uranium; by Mueller-Lyda (1980) for mixed uranium-plutonium oxides and carbides; and by Clough (1977) and Kirihara et al (1980) for uranium dioxide.

Wisnyi et al (1966) expressed the observed creep in terms of apparent viscosity (shear force divided by shear rate), as a function of applied force, although the creep rate appeared not to be proportional to the applied stress. (The case can be made that viscosity is a material property, whereas creep rate is not.) He examined thorium with 2 and 10 weight percent uranium added in solid solution. Results are given in Table 9.2. A convenient SI unit for viscosity in these materials is the terapascal second, $\text{TPa} \cdot \text{s}$; $1 \text{ TPa} \cdot \text{s} = 40290 \text{ psi} \cdot \text{hr}$. To calculate the strain rate $\dot{\epsilon}$ in hr^{-1} , given the viscosity V in these units and the applied stress σ in MPa, the relationship $\dot{\epsilon} = 3.6 \sigma/V$ can be used.

Equation (7.9) in Chap. 7 can be evaluated for the rate of steady-state creep to be expected in the absence of irradiation. The coefficients appropriate to fine-grained thorium ($<100 \mu\text{m}$ grain size) are used, and the applied stress and temperature are taken as the highest values in Table 9.2: 87.6 MPa and 858 K. The equation is based on measurements obtained at temperatures no lower than 1703 K, and an evaluation at 858 K represents a questionable extrapolation. The unirradiated creep rate calculated under these conditions is $4.9 \times 10^{-16} \text{ hr}^{-1}$. The viscosity of 5000 $\text{TPa} \cdot \text{s}$ shown for irradiated material in Table 9.2 is equivalent, for a stress of 87.6 MPa, to a creep rate of 0.631 hr^{-1} , or 15 orders of magnitude greater. It is evident that the creep observed in the experiments of Wisnyi et al (1966) is entirely radiation induced.

TABLE 9.2—IN-REACTOR VISCOSITY OF ThO₂-UO₂
SOLID SOLUTIONS* AND UO₂†

Weight Percent Urania	2	10	100
Temperature, K	768	858	858
Fissions/cm ³ · sec. × 10 ⁻¹³	4.0	5.8	5.8
Applied Stress, σ (MPa)	Bulk Viscosity, V (TPa · s)		
34.5	23000	30000	7200†
69.0	12400	17000	668†
87.6	ND**	5000	290†

*Wisnyi et al (1966)

†Hagrman (1981)

‡Calculated from FCREEP subroutines of Hagrman (1981), using 96.5 percent theoretical density, 10⁶ seconds after start of irradiation; grain diameter = 10 μ m.

**Not Determined.

Irradiation-induced creep may be expected to be largely athermal, since it actually occurs, for the most part, at the extremely high temperature of the thermal fission spike, regardless of the overall temperature of the fuel. The fission-induced creep may be expected to be related to the size and character of the fission spike and the applicable diffusion rates of point defects in its neighborhood.

The in-pile creep of UO₂ has been studied by a number of workers including Clough (1977), Solomon and Gebner (1972), Solomon et al (1971), Sykes and Sawbridge (1969), Brucklacher and Dienst (1972), and Perrin and Wilson (1971). This body of in-pile-creep work is not reviewed in detail here to avoid repeating what was done by Hagrman et al (1981) in the course of developing a series of standard computer subroutines and functions, collectively called MATPRO, for the material properties of uranium and uranium-plutonium. Hagrman's consensus, for the available creep data, was incorporated into a computer function called FCREEP, which can be used to determine strain rates and viscosities, given values for temperature, applied stress, plutonium and oxygen content, initial density, fluence, and time since the start of irradiation.

Function FCREEP was used in evaluating the final column under "Bulk Viscosity" of Table 9.2, for stoichiometric UO₂ of 96.5 percent theoretical density and average grain size of 10 μ m, 10⁶ seconds after the start of

liation. Except for the composition, the specified variables were comparable to those for experimental determinations by Wisnyi et al (1966) ThO_2 -10 mole percent UO_2 . Viscosities are about an order of magnitude higher for UO_2 .

Since the information available for thorium-base solid solutions is much more complete than that for uranium, a series of graphs (Figs. 9.11 through 9.13) is presented, showing evaluations of FCREEP for stoichiometric ThO_2 under various specified irradiation conditions. It may be useful to note that thorium-uranium fuels would vary in a comparable manner, except that the viscosity would be approximately one order of magnitude lower.

9.11. Variation in Viscosity of $\text{ThO}_2\text{-UO}_2$ and UO_2 with Applied Stress under Irradiation.

Figure 9.12. Variation in Viscosity of UO_2 with Fluence for Various Grain Sizes.

These evaluations are for urania undergoing reactor irradiation. As is the case for thorium, the viscosity of ex-reactor urania is many orders of magnitude higher, to the extent that calculation is not meaningful at low temperatures. The ex-reactor viscosity cannot be deduced by extrapolation of the curves of Fig. 9.12 or 9.13 to zero fluence or burnup.

(d) *Comparison of Fission-Induced Creep Mechanisms for ThO_2 and UO_2*

During irradiation, there are two principal mechanisms by which the properties of an oxide ceramic fuel are altered: (1) the formation of fission spikes and (2) the accumulation of fission products. The fission spike is a volume containing approximately 10^6 atoms in the vicinity of the track of a

Figure 9.13. Variation in Viscosity of UO_2 with Burnup.

fission fragment. These atoms are displaced, and the crystal structure within the volume is disrupted. Approximately 10^4 of these atoms are displaced as a result of direct collision with the fission fragment; each of these primary collisions gives rise to approximately 100 secondary displacements before its energy is finally dissipated. The fission spike can be envisioned simply as the volume embraced by atoms which have, on the average, an energy higher than that required to break the bonding, i.e., to cause melting.

On the time scale of microseconds after the fission, the fluorite crystal structure reforms within the fission spike. Some hundreds of vacancies and other imperfections remain in the recrystallized material; these, however, diffuse away, or combine and cancel each other out, on the time scale of milliseconds. During the lifetime of the fission spike, the material within

it has essentially no resistance to deformation. Creep, coalescence of fission bubbles, and densification can take place. As the material recrystallizes, foreign fission products, such as gases and noble metals that have been dispersed throughout the affected volume, can be excluded from the newly formed crystal structure and deposited as separate phases.

Differences in behavior between thoria and urania with regard to these properties depend on the characteristics of the fission spikes in the two materials. These characteristics include the volume of the fission spike, its lifetime, the concentration of defects within it, and the diffusion rate of these defects. The penetration of fission fragments through the two materials is comparable, and so are the number of primary collisions between the fragment and the atoms of the material. However, the number of secondary displacements per primary collision might well be less in thoria than in urania. The secondary displacements are analogous to melting, and because of the higher melting point of thoria, the energy of the secondary collisions would drop sooner below the threshold at which unbonded atoms could exist. The volume of the fission spike would therefore be expected to be less in thoria.

The higher thermal conductivity of thoria can cause the energy of the fission spike, once it is formed, to be conducted away faster. This is over and above any effect on lifetime that could arise from the smaller volume of the spike. It may therefore be assumed that the lifetime of the fission spike is shorter in thoria. The effects, such as creep and densification, which depend on the fission spikes, should therefore occur to a greater extent in urania than in thoria, other things being equal. As presented in the previous section, the fission-induced viscosity of urania does appear to be lower than that of thoria-uranium, although the considerable data scatter does not permit a complete resolution of this issue.

The fission spike mechanism is very prominent in causing radiation damage in materials such as zircon (zirconium silicate), which cannot readily recrystallize during the very rapid quenching of the fission spike. Such materials are converted to glasses, usually with very considerable changes in volume. The crystal structures of fluorite-type oxides, however, show no tendency to form glasses, and essentially heal themselves after a fission spike. A more significant class of radiation effects in the materials is associated with the fission products—not with the millions of atoms that are temporarily disturbed, but with the two atoms that remain permanently changed, for these accumulate throughout the irradiation. These atoms, and the chemical and physical effects they cause, are discussed in the following section.

9.4 FISSION PRODUCT RELEASE AND CONTAINMENT

9.4.1 Fission Yields of ^{233}U and ^{235}U

Computer programs are needed for detailed calculations of the accumulation and decay of fission products; see, for example, CINDER-7, which was described by England et al (1975). The fission yield depends on power history, which determines the interaction rates of the various isotopes with neutrons.

Figure 9.14 shows the fission yield of the product nuclides by atomic mass number, according to values incorporated into this program. ^{233}U ,

Figure 9.14. Fission Yields of ^{235}U and ^{233}U by Mass Number.

like ^{235}U , fissions asymmetrically into a large and a small fragment; both fragments are, on the average, one atomic mass smaller for ^{233}U fission than in the case of ^{235}U fission. (The sum of the masses of the two fragments are constrained to be two mass units less, i.e., 233 rather than 235.)

However, the accumulation, and eventual concentration, of these fission fragments is controlled not only by the initial yield, as shown in Fig. 9.14, but also by the configuration of the decay chains and the half-lives of each of the steps. It is therefore a function of the rate of irradiation. The CINDER program was used to make the appropriate calculation for total inventory of isotopes, by atomic number and atomic mass, for two specific cases. The first of these consisted of the initial composition, neutron energy spectrum, and expected energy variation history of the LWBR high-zone standard blanket. It was specified that the initial composition of the fuel consist of 97.7 mole percent fertile material (thoria) and 2.3 mole percent of the fissile isotope (as $^{233}\text{UO}_2$). The simulated irradiation continued for 30,000 hours, to the point at which 1.65 percent of the original actinide atoms present had fissioned. It was also specified that the fuel would be permitted to stand and cool for 5000 hours (208 days) after removal from the reactor. Such a time span is reasonably typical of postirradiation laboratory studies or reprocessing. While the specified neutron energy spectrum and history were characteristic of the design of one particular reactor, it was not particularly critical to the calculation; most fissions were the result of thermal neutrons, and those due to more energetic neutrons had no great effect on the relative concentrations of the nuclides present after the irradiation. Conditions for the second case were similar to the above, except that the 97.7 mole percent of fertile material consisted of $^{238}\text{UO}_2$, and the fissile material was $^{235}\text{UO}_2$. The difference in the overall fission cross section of the two fuels was compensated by reducing the neutron flux in the urania-base fuel to 91 percent of its level in the thoria-base fuel.

The resulting concentration of fission product atoms in the thoria-base (ThO_2 - $^{233}\text{UO}_2$) and urania-base ($^{238}\text{UO}_2$ - $^{235}\text{UO}_2$) fuels may be compared in Table 9.3, where fission yields per 100 fissions are listed. Although the calculation is made for a specific time, the relative concentrations of products may be considered as steady-state values that would have prevailed, at least to an approximate extent, at a comparable time after a shutdown through much of the irradiation history. The concentration of fission gases at various times throughout the irradiation history was specifically calculated, and the steady-state condition was found to be a valid assumption. The results of one such calculation, at 1 percent burnup, are shown in the brackets in Tables 9.3 and 9.4.

The other values in Table 9.3 show the concentrations of nuclides after 30,000 EFPH and 5000 hours cooling time. Of the fission fragments

TABLE 9.3—FISSION YIELDS (%) AT 1.65 % BURNUP
30,000 EFPH, 5000-HOUR COOLING

ThO ₂ - ²³³ UO ₂	²³⁸ UO ₂ - ²³⁵ UO ₂	
0.0191	0.0036	
0.0080	0.0011	
1.0519	0.4572	
0.3084	0.1821	
6.2006	2.8019	[6.27, 3.03]*
5.9243	2.6387	
11.9127	6.5614	
6.3276	3.4780	
32.9646	25.7937	
0.0279	0.0271	
21.0351	23.8053	
4.3935	5.6108	
7.1308	15.6457	
1.2035	3.7787	
1.3309	8.5885	
0.0341	0.5162	
0.0962	0.4197	
0.0058	0.0123	
0.3566	0.2690	
0.0992	0.0853	
3.3080	2.4312	
2.1604	1.2314	
23.7855	24.5790	[24.12, 24.75]*
15.4580	16.6165	
6.9090	7.2090	
6.3655	5.9431	
13.7109	12.1660	
6.5652	5.5595	
17.9951	18.7891	
0.5287	0.7121	
2.3567	3.3628	
0.3475	0.6774	
0.0775	0.0466	
Concentration of Actinides (in same units)		
5889.314	0.000	
0.008	0.000	
150.161	5985.948	
0.000	1.619	
0.000	71.711	

Values in brackets represent a separate calculation of steady-state concentrations of inert gases at a typical time during the irradiation: 18,000 hours, 1 percent burnup, no cooling.

TABLE 9.4—OXYGEN BALANCE (100 FISSIONS)

	ThO ₂ - ²³³ UO ₂	²³⁸ UO ₂ - ²³⁵ UO ₂
Case I. Nb Included in Metallic Ingots		
Inert gases	29.986 [30.36]*	27.381 [27.78]*
Molecules Cs (Br.I)	2.469	1.413
Excess as (Cs,Rb) ₂ O	9.457	8.921
Molecules (Ba,Sr)ZrO ₃	18.822	13.770
Metallic ingots	35.156	57.972
Zr in Fluorite Phase	14.143	12.023
CdO, In ₂ O ₃ , Sb ₂ O ₃ , GeO ₂	0.585	0.791
Total fluorite-type cations	6107.902	6122.036
Oxygen otherwise uncommitted	12235.933	12285.711
O/M ratio in fluorite phase	2.003	2.007
Case II. Nb as Dioxide		
Inert gases	29.986	27.381
Molecules Cs (Br.I)	2.469	1.413
Excess as (Cs,Rb) ₂ O	9.457	8.921
Molecules (Ba,Sr)ZrO ₃	18.822	13.770
Metallic ingots	35.128	57.945
Zr in fluorite phase	14.143	12.023
Niobium as dioxide	0.028	0.027
CdO, In ₂ O ₃ , Sb ₂ O ₃ , GeO ₂	0.585	0.791
Total fluorite-type cations	6107.902	6122.036
Oxygen otherwise uncommitted	12235.877	12285.657
O/M ratio in fluorite phase	2.003	2.007

*Values in brackets represent a separate calculation of steady-state concentrations of inert gases at a typical time during the irradiation: 18,000 hours, 1 percent burnup, no cooling time.

having a yield greater than 1 percent, the most notable differences between the ²³³U and ²³⁵U yields are those involving Kr through Zr, which are substantially more prevalent for ²³³U fission, and the noble metals Ru, Rh and Pd, which are more prevalent for ²³⁵U fission. All these elements are associated with the small-fragment maximum, i.e., that appearing on the left side of Fig. 9.14. The elements occurring in the larger-mass maximum have similar concentrations for both isotopes.

The occurrence of more than twice as much Kr in ²³³U-bearing fuels (Table 9.3) results in a total of approximately 10 percent more fission gas (Xe plus Kr) in those fuels, other things being equal (Table 9.4). Since the fission gases are primarily responsible for volume changes of oxide fuel during irradiation, this would be more disadvantageous for ²³³U than ²³⁵U fuels except that, due to higher thermal conductivity, ThO₂-base fuel

swells less than UO₂ at the same rod power. Strontium and zirconium are accommodated, together with barium, in the zirconate phase, which is approximately 37 percent more prevalent in ²³³U fuels. The noble metals occur as metallic ingots. Their concentration depends on the extent that they include the available molybdenum; however, as the two alternate calculations in Table 9.5 show, they can in any case be expected to occupy a larger volume in ²³⁵U fuels than in ²³³U fuels, other things, once again, being equal.

9.4.2 Behavior of Solid Fission Products

(a) Physical State of Fission Products

The distribution and nature of fission products in UO₂ nuclear fuels after irradiation, and the state of their chemical combination, have been studied by Morgan et al (1961), Kamogawa et al (1964), Bates (1965), Oi and Tanabe (1968), Oi and Takagi (1965, 1974), Brown and Faircloth (1976), and Hastings et al (1976), among others. This work has been extended to "mixed oxide" fuels, i.e., urania-plutonia solid solutions in which plutonia is incorporated at the time of manufacture (in addition to being generated in-pile). Results are described by Anselin (1969), O'Boyle and Meyer (1974), Davies and Ewart (1970), Johnson et al (1971), Meyer et al (1972), Bahl and Freshley (1972), Mouchnino (1972), Smailos and Geithoff (1972), Trotabas et al (1972), and Sari et al (1979), among others. Techniques included autoradiography, gamma scanning, electron probe studies, radiochemical studies of microdrilled samples, simulations

TABLE 9.5—VOLUME (cm³) OF SOLID FUEL PRODUCTS
IN 1000 INITIAL MOLES OF FUEL

	ThO ₂ - ²³³ UO ₂		²³⁸ UO ₂ - ²³⁵ UO ₂	
	Density (g/cm ³)	Volume (cm ³)	Density (g/cm ³)	Volume (cm ³)
Initial fuel	10.015	25932.378	10.958	24237.459
Uranate phase	8.770	26188.881	9.620	24474.105
(Ba,Sr)ZrO ₃	5.843	130.110	5.966	95.902
Metallic ingots	10.908	51.921	11.276	84.020
Barium as dioxide	5.999	0.096	5.999	0.093
(Br,I)	4.593	22.556	4.593	12.864
Caesium as (Cs,Rb) ₂ O	4.247	94.015	4.279	92.289
Total after irradiation		26487.580		24759.273
Volume change		2.141		2.153

in unirradiated material, and thermodynamic calculations. Much of this work was summarized by Camozzo (1971). A consensus of this literature indicates that an irradiated UO_2 or $(\text{U,Pu})\text{O}_{2\pm x}$ fuel can contain phases of the following types:

1. A matrix, consisting of a mixture of actinide and lanthanide oxides, having the fluorite lattice;
2. Gas bubbles, containing xenon and krypton;
3. Metallic inclusions, containing ruthenium, rhodium, technetium, and palladium, at least some of the molybdenum, and perhaps uranium;
4. Nonmetallic inclusions, consisting of BaZrO_3 and SrZrO_3 in mutual solid solution;
5. Volatile CsI and CsBr , condensed in the cooler parts of the fuel; tellurium may also be associated with this fraction.

(b) *Chemical State of Fission Products*

Assuming that the irradiated fuel is thermodynamically stable, each of the fission products (and actinide transmutation products) will lodge in one or more of the phases described above in such a manner that the free energy of the entire fuel will be at a minimum, i.e., as negative as possible. Among the questions that arise is whether one or another of the elements would lodge in a phase in which the oxidation state is zero, such as the metallic inclusions, or in one of the oxidized phases, such as the fluorite or zirconate phase.

As a thorium or uranium atom in the oxide fuel is destroyed by fission, the two oxygen atoms with which it was formerly associated become available. These may be accommodated either by oxidation of the fission products, or of the remaining fuel, or of the Zircaloy cladding. The eventual disposition of the oxygen will depend on which of the available reactions will cause the greatest decrease of free energy. Whether the fission product is stable as an element or an oxide in the presence of irradiated fuel depends on the difference between the free energy of formation of the fission product oxide and the oxygen potential of the fuel. This is a function of the temperature, the initial stoichiometry, and also of the fuel element atmosphere. A defected rod will not necessarily behave in a manner comparable to undefected rods.

The oxygen potential ($\Delta G_{\text{O}_2} = RT \ln P_{\text{O}_2}$) and the decrease of free energy associated with oxidation of the fuel were discussed in Chap. 5. The use of the Ellingham plot (Fig. 5.23) to determine the oxygen state of the various fission products was also discussed in Chap. 5. And finally, it was shown in Chap. 5 (Figs. 5.19–5.21) that $(\text{Th,U})\text{O}_{2\pm x}$ is not an ideal solution. However, for compositions that are relatively dilute in uranium, the oxygen potential for stoichiometric or slightly hyperstoichiometric

thoria-uranium solid solutions can be approximated satisfactorily by assuming that the uranium has a mean valence appropriate to the amount of excess oxygen present, and is distributed uniformly in an inert thoria matrix. Accordingly, the oxygen potentials for the solid solutions can be estimated by consulting data, such as contained in Fig. 5.23, which were determined on stoichiometric and hyperstoichiometric uranium.

Table 9.6 lists the Gibbs free energies of formation per mole of oxygen for the more abundant fission products as well as of those for thoria and

TABLE 9.6—GIBBS FREE ENERGIES OF FORMATION PER MOLE OF OXYGEN OF FISSION PRODUCT AND ACTINIDE OXIDES

Oxide	ΔG_f° (kJ/mol O ₂)	Temperature Range (kelvin)	Reference
UO	-1181 + 0.1918T	298—1041	Blackburn and Johnson (1982)
U ₂ O ₃	-1265 + 0.1878T	298—1799	Blackburn and Johnson (1982)
UO ₂	-1092 + 0.1844T	298—2183	Blackburn and Johnson (1982)
ThO ₂	-576.8 + 0.1656T	298—1300	Blackburn and Johnson (1982)
PaO ₂	-423.9 + 0.1640T	298—1200	Blackburn and Johnson (1982)
NpO ₂	-294.1 + 0.1547T	298—1300	Blackburn and Johnson (1982)
PrO	-246.9 + 0.094	298—1123	Blackburn and Johnson (1982)
LaO	-985.0 + 0.1397	298—983	Blackburn and Johnson (1982)
U ₂ ZrO ₃	-1186 + 0.2081T	—	Blackburn and Johnson (1982)
U ₂ O ₃	-1193 + 0.1880T	298—2593	Blackburn and Johnson (1982)
	-1208 + 0.1849T	298—1960	Blackburn and Johnson (1982)
U ₂ O ₃	-1203 + 0.1849T	298—2545	Blackburn and Johnson (1982)
U ₂ O ₃	-1222 + 0.1952T	—	Blackburn and Johnson (1982)
O ₂	-1217.6 + 0.1785T	293—3000	Table 5.12, Chap. 5
O _{1.955}	-1174 + 0.1672T	2400—2655	Table 5.16, Chap. 5
U ₂	-1081.7 + 0.1707T	298—3120	Ackermann et al (1980)
U _{1.96}	-1057 + 0.1644T	2080—2700	Tetenbaum and Hunt (1968)
U _{1.90}	-1021 + 1569T	2080—2705	Tetenbaum and Hunt (1968)

urania. These data were taken, for the most part, from the compilation by Blackburn and Johnson (1982). A comparison is given in Table 9.7 of the oxygen potentials calculated at 1500 K for these fission product oxides with those of ThO_2 , UO_2 , and $\text{ThO}_2\text{-UO}_2$.

It is shown below that urania and thoria-urania fuels are approximately stoichiometric throughout life if they are stoichiometric as manufactured, and, hence, the oxygen potential from Fig. 5.23 of Chap. 5 is approximately -280 to -500 kJ/mole of oxygen gas over the temperature range interest. Therefore, when excess oxygen is made available, the fuel cannot compete successfully for it with the elements shown at the lower part of Fig. 5.23 such as Ba, Zr, Nd, and Y. The free energy of the system can be decreased by 1000 kJ/mole or more by the oxidation of these fission products. Accordingly, these fission products occur as oxides in the fuel. On the other hand, the fuel competes successfully for oxygen with Ru and Pd, and these fission products therefore occur in the elemental form, as components of the metallic ingots.

TABLE 9.7—OXYGEN POTENTIALS AT 1500 K FOR THORIA, URANIA, THORIA-URANIA SOLID SOLUTIONS, AND FISSION PRODUCT OXIDES

Oxide	$-\Delta G_{\text{O}_2}^0$ (1500 K) (kJ/mol O_2)	Reference
Y_2O_3	983	†
Ce_2O_3	931	†
Sm_2O_3	929	†
Nd_2O_3	919	†
La_2O_3	911	†
SrO	893	†
BaZrO_3	874	†
ZrO_2	815	†
BaO	775	†
MoO_2	328	†
TcO_2	178	†
PdO	99	†

†Calculated from equations given in Table 9.6

TABLE 9.7—OXYGEN POTENTIALS AT 1500 K FOR THORIA, URANIA, THORIA-URANIA SOLID SOLUTIONS, AND FISSION PRODUCT OXIDES (Continued)

Oxide	$-\Delta G_{O_2}^0$ (1500 K) (kJ/mol O ₂)	Reference
RuO ₂	62	†
O ₂	950	†
MO ₂	826	†
UO ₂	536	Blackburn and Johnson (1982)
UO ₂	328	Perron (1968)
MO _{1.96}	810	Tetenbaum and Hunt (1968)
MO _{1.90}	786	Tetenbaum and Hunt (1968)
MO _{2.01}	240	Perron (1968)
MO _{2.0101}	253*	Ugajin (1983)
MO _{2.05}	201	Perron (1968)
MO _{2.0386}	210*	Ugajin (1983)
h _{0.8} U _{0.2} O _{2.0105}	166*	Ugajin (1982)
h _{0.9} U _{0.1} O _{2.0107}	113*	Ugajin (1982)
h _{0.95} U _{0.050} O _{2.0035}	113*	Ugajin (1982)

Data are for 1473 K

*Calculated from equations given in Table 9.6

At full power, the coolest parts of the fuel, adjacent to the cladding, could have temperatures in the vicinity of 750 K. At this temperature, the formation of a mole of molybdenum dioxide from the metal and oxygen as is associated with a decrease of about 500 kJ in the free energy of the system. Such a value may be compatible with the existence of molybdenum dioxide in equilibrium with the coolest parts of the fuel. Over most of the temperature range of interest, however, the stable form of molybdenum in equilibrium with the fuel is the metal. In the calculations to be discussed subsequently, it is first assumed that the available molybdenum occurs entirely in the metallic form, and then the consequences of the possible occurrences of some molybdenum dioxide are discussed. It may

well be that Mo and possibly Nb occur both as metals and as oxides in different parts of typical fuel elements; the partition of these materials between the metal and oxide phases would be functions of temperature, burnup, and cooling time, and would change during the irradiation history.

Bramman et al (1968) reported uranium metal in the metallic inclusions of urania-base fuel operating at very high temperatures. The metal may have precipitated from hypostoichiometric fuel on cooling, as a temperature was reached at which a given degree of oxygen deficiency was longer stable in the fluorite phase.

The oxidation state of the fission fragments depends on the state of stoichiometry of the surrounding fuel. In mixed-oxide plutonia-urania fuels, hypostoichiometric material can occur, particularly at the high temperature region in the interior of the fuel element. Camozzo (1971) has reported that the metallic inclusions in this region contain elemental molybdenum; in the outer portion of the fuel element, where the oxidation state is higher, only the noble metals are observed in the metallic ingots.

Bramman et al (1968) reported nonmetallic inclusions in irradiated oxide fuels, and showed that they were characterized by barium. Anselin (1969) studied the fuel-fission product system from the standpoint of oxygen potential and free energy considerations, and came to the conclusion that virtually all the barium and strontium present should form zirconates, with some excess zirconium going into solid solution in the fluorite phase. However, Sari et al (1979) disagree; on the basis of electron probe studies of mixed-oxide fuel, they conclude that about 1.6 weight percent of barium is soluble in $(U,Pu)O_{2-x}$, and that a separate barium zirconate phase can form only after this solubility is exceeded.

Leigh and McCartney (1977) simulated irradiated thoria-base fuels by incorporating materials representing fission products in thoria powders which were then fabricated as sintered pellets and equilibrated under various conditions representing reactor service (but not irradiated). Electron microprobe images of the resulting samples indicated the presence of a separate phase of which Nd and Zr were major constituents. The authors proposed that this material consisted of the perovskite-type phase $Nd_2Zr_2O_7$, which, they stated, might be stable under the reducing conditions produced in their material by elemental molybdenum and other metallic constituents of the mixture of simulated fission products. However, Ugajin et al (1979) established that $Nd_2Zr_2O_7$ is converted to barium zirconate (plus Nd in solid solution in the fluorite phase) in the presence of BaO, and does not occur in irradiated thoria-base fuel. This finding was supported by thermodynamic calculations, indicating that the barium zirconate would be more stable than the perovskite-type neodymium compound. The neodymium is lodged in the fluorite-type phase, together with

the other lanthanides and yttrium. Further evidence that these elements are in the fluorite-type phase was observed by Berman (1976) in electron fluorescence photographs of irradiated fuel. Fluorescence images of elements that had segregated into separate phases showed small, irregular regions with sharp boundaries, containing high concentrations. The elements distributed in the fluorite-phase matrix, although they showed nonuniform distributions on the scale of the entire fuel element cross section, did not show these clearly defined segregations. The evidence for molybdenum was equivocal; some appeared to be in segregations, while the remainder was distributed in the matrix.

For purposes of calculation, it may be assumed that the barium and strontium are accommodated as zirconates, with three oxygen atoms per molecule, and the excess zirconium is lodged in the fluorite phase. It may also be assumed that all the available halides are combined with cesium, and the excess cesium occurs at Cs_2O . On the basis that the fluorite phase is combined with the remaining available supply of oxygen, it is possible to calculate the amount of each of these phases that would be present at a given burnup—10 percent of the original fuel atoms, for example—and what the oxidation state of the fluorite-type phase would be. This calculation was carried out for urania fuels by Davies and Ewart (1971) and by Findlay (1974). They calculated that the fluorite-type phase should be slightly hyperstoichiometric, with a subscript less than 2.01. Table 9.4 shows the result of a repetition of their calculation, using the data of Table 9.3 and the burnup associated with the LWBR design.

The metallic ions of the fluorite phase, at the end of the irradiations simulated in the CINDER calculations described above, consist, to the extent of approximately 93 percent, of the initial or transmuted actinides, with an additional 5 percent divided, approximately equally, between Ce, Nd, and Zr. The calculations were carried out first with the assumption that Nb is in the metallic phase, and then with the assumption that it occurs as the dioxide. In both cases, as is shown in Table 9.4, the calculated subscript of the fluorite phase was 2.007 in the case of urania-base fuels, 2.003 in the case of thorium-base fuels, in good agreement with the

results of Davies and Ewart (1971), who predicted very slightly hyperstoichiometric compositions for urania. The effect of the oxidation of some molybdenum would be to bring the composition of the fuel even closer to stoichiometry. Molybdenum is not a sufficiently strong reducing agent to bring the composition of the fuel below stoichiometry, especially in the low-temperature region in which molybdenum dioxide might form.

Davies and Ewart (1971) also examined plutonia and plutonia-uranium fuels. In these, as a result of greater yield of chemical species of lower valence, the amount of excess oxygen made available through fission is 6

to 7 atoms per 100 fissions. As a result, the fuel becomes more oxidized as irradiation proceeds. In addition, the oxygen is redistributed, such that the cooler portions of the fuel element are more oxidized than the hotter regions in the center of the rods, particularly if there is formation of columnar grains.

The noble metals ruthenium, rhodium, technetium, and palladium form metallic inclusions in the hotter portions of oxide fuel elements. These inclusions also contain a greater or lesser amount of the molybdenum present, depending on the local oxidation potential.

It is evident that the stable assemblage of oxidation states and phases in a fuel after irradiation is not fully determined. These assemblages undoubtedly change as irradiation proceeds, and then as cooling proceeds, with the decay of isotopes after removal from the reactor. Also, the achievement of complete thermodynamic equilibrium at near-room temperature during this post-irradiation phase is unlikely. However, the calculations indicate that the behavior of a thorium-cycle reactor should not be greatly different from a urania-cycle reactor in this regard.

(c) Fuel Swelling due to Solid Fission Products

The fluorite, alkaline earth oxide, and zirconate phases are cubic. The method in Chap. 4, based on Vegard's law, can be used to calculate a theoretical density for them, and therefore the volume of these phases in the two fuels postulated in Table 9.4 can be calculated. The metallic ingots are essentially ruthenium-base alloys and probably hexagonal; however, their volumes can be estimated on the assumption that they are ideal solutions, with no volume change on mixing. The resulting volumes of each of these phases, as they would occur in 100 percent dense fuel under the conditions described by the calculations of Table 9.4, are shown in Table 9.5, together with the value of the density of each phase, as it was used in the calculation.

Table 9.5 also shows a calculation indicating the initial volume of the fuel, at 100 percent density; it is slightly smaller than the irradiated volume, for both fuel types. The difference represents the so-called volume swelling. However, both of these nearly identical numbers were calculated from many pieces of data, each of which incorporated some uncertainty. It appears that, in both ^{233}U and ^{235}U fuels, after 10 percent of the initial metal atoms have fissioned (24 fission units for $\text{ThO}_2\text{-}^{233}\text{UO}_2$, 22.8 fission units for $^{238}\text{UO}_2\text{-}^{235}\text{UO}_2$), the solid products occupy a volume about 2.1 percent greater than they did initially. The value usually quoted for total swelling is 0.7 percent per fission unit. It therefore appears that the solid swelling contribution of 0.088 percent per fission unit (2.1 percent per 24 fission units) is about 13 percent of the total swelling, the remainder being due to volatile materials such as free Cs, I, and Br, and gas atoms Xe and Kr, which are not included in Table 9.5.

(d) Fission Product Migration

Bates (1965) demonstrated that autoradiographs of cross sections of irradiated fuel rods were not uniformly dark; that the activity was concentrated at the outer margin of columnar grains and, apparently, selectively removed from the columnar grains themselves. In his discussion of mixed-oxide fuels, Camozzo (1971) pointed out that plutonium, whether produced initially or generated in-pile, is redistributed in much the same manner, and by the same mechanisms, as the trivalent and quadrivalent fission products of chemical species that are normally incorporated into the fluorite-type lattice of urania solid solutions. These elements are distributed within the fluorite-type phase, although the distribution is not necessarily or even generally uniform, particularly in samples that have attained a high temperature during irradiation. Work by Berman (1976) and others showed that fission products were depleted from the region of columnar grains in urania- and thoria-base fuels, and accumulated at the outer margin, due to the vapor transport mechanism that formed the columnar grains.

Padden et al (1967) examined a radial section of a pellet of ThO_2 -5.3 weight percent UO_2 which had been irradiated to 1.6 fission units. Because of the low initial density of the pellet (86.4 percent of theoretical), high temperatures were reached at the center; a central void was formed, and there was extensive development of columnar grains. These were shown by autoradiography to be depleted in high-activity nuclides, in comparison to the remainder of the sample. At the edge of the central void, however, there was a thin, well-defined crust that was very high in alpha activity. Examination of the photographs accompanying the reference indicate that this material probably melted; it intrudes, apparently by capillary action, along cracks that intersect it. The crust of high-activity material probably consists of urania and thoria approximately at the eutectic ratio, into which a high concentration of fission products has been dissolved. Clearly, if the temperature is permitted to rise to the melting point, other mechanisms for concentration of fission products may become important.

4.3 Behavior of Volatile Fission Products*a) Introduction*

For those fission products that are gases at the higher fuel operating temperatures (krypton and xenon, the halogens bromine and iodine, and also cesium), bubbles can nucleate and become mobile. The gases then migrate up the temperature gradient leaving a path of recrystallized fuel or possibly columnar grains in their wake. Such effects would be in addition to the formation of columnar grains resulting from the movement of voids present in the fuel as originally manufactured porosity.

It has already been noted (Sect. 9.4.1) that the fission gas generated per fission is about 10 percent higher for ^{233}U than for ^{235}U (Table 9.3). Thus, any conclusions on fission gas swelling, fission gas release, or iodine release will be different for $\text{ThO}_2\text{-}^{233}\text{UO}_2$ than for $\text{ThO}_2\text{-}^{235}\text{UO}_2$. However, the measurements and analyses for $\text{ThO}_2\text{-}^{235}\text{UO}_2$ can be applied to $\text{ThO}_2\text{-}^{233}\text{UO}_2$ if expressed in terms of swelling or fission product release per unit of fission gas or iodine generated. This generation is not, of course, that of the immediate products after fission but that in terms of all the isotop produced after the equilibration of all the decay chains.

It is customary to express fission product release as a fraction R of the fission products generated and thus ensure an automatic normalization between $\text{ThO}_2\text{-}^{235}\text{UO}_2$ and $\text{ThO}_2\text{-}^{233}\text{UO}_2$. However, in the case of volume swelling, it is usual to express swelling as fractional volume change per fission. In this case, the data and predictions for $\text{ThO}_2\text{-}^{235}\text{UO}_2$ must be corrected by a multiplication factor of 1.1 for application to $\text{ThO}_2\text{-}^{233}\text{UO}_2$.

Johnson and Crouthamel (1970) irradiated (U,Pu) O_2 fuel in type 316 stainless steel cladding, and their examination included electron probe images of the cladding and the fuel immediately adjacent. Considerable concentrations of cesium, in approximately the same locations as concentrations of iodine, were observed in both fuel and cladding. They also showed that some of this cesium was ^{134}Cs , which was found only in these concentrations, while ^{137}Cs was found throughout the fuel pin. This segregation was ascribed to the difference in half life of the iodine precursors, I^{133} and I^{137} , of the cesium isotopes. The half life of ^{137}I is only 24 seconds, and there is little opportunity for migration before it transmutes to cesium. However, ^{133}I has a half life of 21 hours, which is apparently sufficient for migration toward the cladding.

Studies of the distribution of the fission fragments in thorium-base fuels have been much more limited. Berman (1976) examined radial electron probe profiles of thorium and thorium-21 mole percent uranium fuel rods, irradiated up to 14.5 fission units. He found concentration gradients, metallic nodules, and (Ba,Sr) zirconate inclusions comparable to those observed for uranium- and plutonium-uranium base fuel. Clayton (1979) showed that some of the fission product iodine in thorium- and uranium-base fuels could be extracted by organic solvents and, therefore, apparently existed in the elemental form.

(b) Fission Gas Swelling

At fuel temperatures above 2000 K the major source of dimensional instability in rod-type oxide fuel is the accumulation of fission gases. The volume of these fission gases is a function of burnup, temperature, pressure, and the distribution of bubble size. In evaluating the pressure inside the bubbles, it is necessary to consider the contribution of surface tension. In small bubbles, this contribution can exert a major effect. The volume

occupied by the fission gases is in addition to the contribution to swelling that is attributable to a change in the volume of the solids as shown in Table 9.5. This solid volume swelling is calculated to be about 0.21 percent per percent burnup (0.09 percent per fission unit), and is about equal in thorium- and uranium-cycle reactors.

The integrated fission yield of volatile species during irradiation, rather than after shutdown, provides the source of gaseous swelling. To explore whether this value differed greatly from the postshutdown values, a number of exploratory CINDER runs were made for interim irradiation times and zero cooling time. It was found that the fission yields of the gases converged on a steady-state value early in the irradiation, and thereafter changed little. The values in brackets in Tables 9.3 and 9.4 are typical; they represent fission yields of Kr and Xe at 18,000 hours, with 1 percent burnup, with zero cooling time specified.

An approximation to the amount of volume swelling can be derived as follows. For each fission unit, 3×10^{19} atoms, or 5×10^{-5} moles, of fission gas will be generated. To estimate the average temperature of this gas in a typical rod-type oxide fuel element during normal full-power operation, it is assumed that typical values for fuel surface and center temperatures are 700 and 1700 K, respectively. In a solid cylinder with uniform thermal conductivity and heat generation, the temperature profile along a radius would be parabolic, and the volume average temperature would be the mean of the surface and center temperatures, or 1200 K. Thermal conductivities are, in fact, lower in the interior than on the exterior of the rod, and the high-temperature region is therefore more extensive than the parabolic model would indicate. However, gas is also not uniformly distributed in the rod; it is more concentrated toward the exterior depending on the amount of self-shielding. As a first approximation, these two effects offset each other. The mean temperature of gas in the rod is herefore taken as 1200 K.

It is assumed, for purposes of this calculation, that the hydrostatic pressure in the fuel outside the fission gas bubble amounts to 150 atmospheres. However, there is an additional pressure imposed by surface tension. It is therefore also assumed that the gas atoms are lodged in a bubble with a typical radius of $1 \mu\text{m}$. As discussed in Chap. 5, a value for the surface energy S of 1.25 J/m^2 at 1200 K was estimated by Inoue and Matzke (1981) from their fracture surface energy measurements on zirconia between room temperature and 673 K (Matzke, 1980 and Inoue and Matzke, 1981). The pressure increment to balance surface tension forces can be calculated as follows:

$$P = 4S/r = 4(1.25)/10^{-6} = 5 \times 10^6 \text{ Pa} \quad \text{Eq. (9.6)}$$

$$= 50 \text{ atmospheres}$$

For a bubble size of $0.1 \mu\text{m}$, P would be equal to 500 atmospheres. The pressure inside a $1 \mu\text{m}$ radius bubble is therefore not 150, but 200 atmospheres.

It can be further assumed that the gas departs from ideality in a manner comparable to pure xenon. Appropriate empirical coefficients for the Van der Waals equation,

$$(P + a/V^2)(V - b) = RT, \quad \text{Eq. (9.7)}$$

are, for pure xenon,

$$a = 4.194,$$

$$b = 0.05105,$$

in units for which $R = 0.08206$ liter-atm/mole $\cdot$ K.

At $P = 200$ atm and $T = 1200$ K, it can be calculated that the volume V for pure xenon is 2.8 percent greater than it would be for a comparable molar quantity of an ideal gas. The quantity of fission gas generated per fission unit (10^{20} fissions per cubic centimeter) will therefore occupy

$$(5 \times 10^{-5}) (22400) (1200/273.15) (1/200) (1.028) = 0.0253 \text{ cm}^3.$$

This volume would represent 2.53 percent volume swelling if the 10^{20} fissions occurred in 1 cm^3 of fuel. This is approximately 3.5 times the amount actually observed (0.7 percent per fission unit). This would be consistent with an average bubble size of about $0.3 \mu\text{m}$ or with approximately 70 percent of the gas still distributed throughout the fuel and not collected into bubbles.

Various models have been developed to calculate the nucleation, growth, and migration of fission gas bubbles in the case of UO_2 , and these are also applicable to fuels containing ThO_2 . At a sufficiently low temperature, the volatile species are expected to behave in the same manner as the solid fission products. Although gases such as xenon are not solids, their mobility at low temperatures is so low that they will not coalesce into pores. On the other hand, at sufficiently high temperatures, bubbles will form and migrate out of the fuel. The volume swelling due to fission gas bubbles is again small. Hence, there exists an intermediate temperature at which bubbles form but migrate sufficiently slowly to give rise to an inventory of porosity in the fuel. Models such as that of Dollins and

Nichols (1977) and Dollins (1981a, 1981b) provide the mechanistic basis for calculations designed to follow these trends. It has already been noted that the higher melting point of ThO₂ would lead to the expectation that the temperature for maximum swelling would be displaced to a higher value than that for UO₂, but the value at low temperatures would be about the same.

1) Fission Gas Release

As mentioned previously, Dollins and Nichols (1977), and also Dollins (1981a, 1981b) provided a model for swelling and fission gas release, in which the gas atoms coalesce to form bubbles, then migrate to grain boundaries, edges, and corners. At the corner sites, the bubbles coalesce further and, at approximately at the point when gas bubble swelling at edges and corners reaches 5 percent, tunnels are formed, and the gas can then be released to the exterior in the fuel. The grain boundary migration rates are many orders of magnitude higher than those prevailing in the grain interior, and the migration rates in the grain interior therefore represent the rate-controlling step. A simplifying assumption may be made that all gas reaching the grain boundaries is conducted to the surface and released. A feature of this model is that, as gas bubbles coalesce, their radii increase, and the increment of pressure supplied by surface tension decreases. The quantity of gas in the coalesced bubble is then greater than the equilibrium value at the reduced pressure, and the bubble increases in size. Dollins (1981a, 1981b) makes provision for a mechanism whereby the excess gas is also resorbed into the fuel as a result of fissioning action. It is necessary to recognize that, during transients, the walls of the pore are sufficiently strong to temporarily contain the excess, or a small amount of local cracking takes place to supply the needed extra volume.

Warner (1969) proposed a model for fission gas swelling and release whereby the inventory of gas bubbles is associated with their capture on other dislocations (small size bubbles) or grain boundaries (larger size bubbles). On the basis of this model, Goldberg et al (1978, 1979) fitted fission gas release data from ThO₂ and ThO₂-UO₂ fuel rods to an equation which combines low temperature release by recoil and knockout with high temperature release from grain boundaries and dislocations. The equation is as follows:

$$R = (100/\rho)^{10.25} (0.05F) + A \left(\frac{T_c - T_{gb}}{T_c - T_s} \right) + B \left(\frac{T_{gb} - T_d}{T_c - T_s} \right) \quad \text{Eq. (9.8)}$$

where

R = fission gas release (percent)

ρ = initial fuel density (percent of theoretical)

F = fission density, fission units

T_c = fuel center temperature (K)

T_{gb} = grain boundary release temperature (K)

T_s = fuel surface temperature (K)

T_d = dislocation release temperature (K)

and A and B are fitted coefficients. Recommended values are $A = 90$ and $B = 5$. Equation (9.8) applies for temperature conditions in which $T_c > T_{gb} > T_d$. The three terms (separated by + signs) on the right side of Eq. (9.8) represent, respectively, (1) direct and immediate fission gas release, by such processes as recoil and knockout, (2) fission gas release from grain boundaries, and (3) fission gas release from dislocation networks.

Equation (9.8) expresses the condition that A percent of the fission gas is released from regions of fuel where the temperature is greater than T_{gb} and B percent is released from regions where the temperature is between T_{gb} and T_d . The first term of the equation, namely, that associated with recoil and knock-out, $(100/\rho)^{10.25} (0.05F)$, applies to all fuel regions and is not temperature-dependent.

The temperature for the release of gas from grain boundaries (T_{gb}) and the temperature for the release of gas from dislocations (T_d) are functions of burnup, according to the model developed by Warner (1969). A graph showing their variation with time at power is given by Goldberg *et al.* (1978). For burnups less than approximately 2.4 fission units and for fuel elements operating in the normal temperature range, the amount of gas generated is small, and the amount of gas released is even smaller. For higher burnups, which represent the condition of primary interest, the transition temperatures T_{gb} and T_d are nearly constant. T_d is approximately 1450 K for urania and 1750 K for thoria, and T_{gb} is approximately 420 K higher for both fuels: 1870 K for UO_2 and 2170 K for ThO_2 . Thoria-urania solid solutions consisting principally of ThO_2 have temperatures T_{gb} and T_d comparable to those of ThO_2 . The higher threshold values for release of

bubbles from dislocations and from grain boundaries are the result of the more stable structure of ThO_2 as evidenced by its higher melting temperature.

To illustrate the evaluation of Eq. (9.8), it is assumed that the density ρ is 97 percent of theoretical, the center temperature T_c is 2000 K, and the surface temperature T_s is 750 K. These were typical operating values for LWBR. The fission depletion term F is taken as 3.77 fission units, the value that was assumed in calculating the fission yields shown in Tables 9.3 and 9.4 (other than those in brackets). Under these conditions, the contribution to fission gas release represented by the first term of Eq. (9.8) is, for all temperatures and all fuel compositions,

$$\left(\frac{100}{97}\right)^{10.25} (0.05 \times 3.77) = 0.258 \text{ percent of the total fission gas generated.}$$

On inserting the values for T_c , T_{gb} , and T_s for UO_2 in Eq. (9.8), the additional contribution to the percent of fission gas released in the case of UO_2 becomes 11.04 percent, leading to a total fission gas release of $11.04 + 0.26 = 11.3$ percent of the fission gas generated. For ThO_2 and $\text{ThO}_2\text{-UO}_2$ solid solutions of low UO_2 content, T_c is less than T_{gb} and is intermediate between T_{gb} and T_d .

There is no contribution to the gas release from grain boundaries and a reduced contribution from dislocation networks. Equation (9.8) may still be used provided that no value higher than T_c is used for T_{gb} or T_d . Thus, the calculation becomes:

$$90 \left(\frac{2000 - 2000}{2000 - 750} \right) + 5 \left(\frac{2000 - 1750}{2000 - 750} \right) = 1 \text{ percent,}$$

and the sum of $1.00 + 0.26 = 1.26$ percent of the total fission gas generated.

The difference shown by this illustrative example, namely 1.26 percent fission gas release for ThO_2 and ThO_2 -base solid solutions and 11.3 percent

UO_2 under comparable and representative operating conditions, far outweighs the somewhat higher fission yield of the noble gases in the case of ThO_2 . The calculation also shows that, for reasonably representative operating conditions, the fission gas release attributable to the mechanisms represented by the first term of Eq. (9.8) is small. At burnups below about 20 fission units, significant amounts of gas release are not obtained unless temperatures are reached at which dislocation and grain boundary mechanisms become significant. This is supported by the experimental data reported by Goldberg et al (1978, 1979).

(d) *Fuel Element Test Data*

Lindemer (1977) irradiated HTGR-type thorium fuel spheres coated with pyrolytic carbon to burnups as high as 17 percent at very high neutron fluxes (up to 4×10^{15} n/cm²·s). The irradiated spheres were equilibrated at temperatures as high as 2270 K and crushed. Particularly for those spheres equilibrated at the highest temperatures, the amounts of krypton and xenon released approached the theoretical fission yield. Also released was carbon monoxide, apparently generated from the pyrolytic carbon coating. If the quantity of carbon monoxide is taken as a measure of oxygen released from the fuel, then this quantity is found to vary linearly with burnup.

Goldberg et al (1978, 1979) reported fission gas release data from LWBR test rods containing ThO₂ and ThO₂-UO₂ fuel that had been irradiated to various burnup levels to about 13.7 fission units. They found no relationship between gas release and fuel composition in the range from zero to 30 mole percent UO₂; the materials included specimens with ²³³U as well as ²³⁵U. Several rods that operated with very high center temperatures (>2000 K) showed fractional gas release much greater than those rods that represented more typical operating conditions, i.e., about 15 percent as contrasted with a range of 0.1 to 5.2 percent. On the basis of data from 54 irradiated fuel rods, it was shown that the fission gas release from ThO₂-UO₂ fuel, as a percentage of the amount formed, is a function of temperature, initial porosity, and burnup. It was not a function, within the range studied, of uranium content or rod diameter.

The effect of high burnup and low temperature on fission gas release from ThO₂ and ThO₂-UO₂ was reported by Giovengo et al (1982). In this work, fission gas release measurements were obtained for five fuel rods that had been irradiated at low fuel temperature (below about 1750 K) to burnups up to about 24 fission units. Four of these fuel rods contained ThO₂-33.6 weight percent UO₂, and the fifth rod contained ThO₂ pellets. These data, shown in Table 9.8, indicate that the low temperature component of fission gas release increases significantly at burnups exceeding about 20 fission units. Also shown in Table 9.8 are some older data: Rabin et al (1965) and Olsen et al (1966) on ThO₂-4.5 weight percent UO₂ to about 25 and 26 fission units, respectively. The new data reported by Giovengo et al (1982) as well as the earlier data reported by Goldberg et al (1978, 1979) were correlated by Giovengo et al (1982) by using a modified form of Eq. (9.8), which is discussed below and presented as Eq. (9.9). The measured gas release measurements are plotted against the amounts predicted by Eq. (9.8) and the modified Eq. (9.9) in Fig. 9.15. General agreement is indicated.

The AWBA fuel rod test program with duplex fuel pellets provided another means of determining fission gas release at very high depletions,

TABLE 9.8—FISSION GAS RELEASE FROM ThO₂-UO₂ FUEL RODS

Composition (weight %UO ₂ in ThO ₂)	Fuel Average Density (%T.D.)	Peak Fuel Burnup (fission units)	Peak Fuel Temperature (K)	Fission Gas Release Measured (%)	Reference
0	88.5	17.6	1465	1.8	Giovengo et al (1982)
33.6	97.3	3.0	1522	0.1	Giovengo et al (1982)
33.6	97.3	18.9	1655	1.8	Giovengo et al (1982)
33.6	96.4	24.1	2011*	7.9	Giovengo et al (1982)
33.6	97.3	23.3	1633	4.3	Giovengo et al (1982)
4.5	93	24.6	1683	14.0	Rabin et al (1965)
4.5	93	26.4	<1683	22.8	Olsen et al (1966)

*This temperature occurred for a short time following initial startup. For most of its irradiation history this rod operated below about 1750 K.

Figure 9.15. Fission Gas Release Observed from Irradiated Thoria and Thoria-Urania Fuel Rods Plotted against Amount Calculated (Giovengo et al, 1982).

since the annulus fuel volume was about half the total fuel volume and, therefore, the fission density was about twice the compartment value. As discussed above, Giovengo et al (1982) showed the fission gas fractional release for ThO_2 and $\text{ThO}_2\text{-UO}_2$ at depletions up to about 25 fission units; these data are shown in Fig. 9.16. This illustration also includes unpublished AWBA data on gas release from both short and long rods (~ 120 inches) having similar fuel design and operating with similar power histories. Note that, at a threshold value of depletion which is a 20 fission units (10 fission units based on compartment volume) the fuel became less able to contain the fission gas, although the maximum fuel temperature was well below the quoted temperature for release of gas from dislocations (1450 K for uranium and 1750 K for thorium).

Daniel et al (1962) reported that the microstructure of UO_2 changes at depletions greater than 20 fission units. Original grain boundaries cannot be resolved, and a much finer structure appears. This fine structure is apparently a result of the extensive damage caused by the loss of about 10 percent of the uranium atoms and replacement by fission products. The increase in fission gas release at very high depletions is apparently due to

the growth of new interconnecting paths that are similar in function to the initial grain boundaries. Giovengo et al (1982) correlated the upswing in gas release with depletion and not with temperature. As shown in Fig. 9.16 the upswing in gas release occurs for three different fuels in about the same way. Although thoria-base fuel (ThO₂ with about 20 weight percent urania) operated at about 15 percent higher power than the other two fuels, the gas release fraction was quite comparable. The relation for gas release modified from Eq. (9.8) becomes

$$R = (100/\rho)^{10.25} (0.05F) [1 + \exp \{0.3(F - 20)\}] + A \left(\frac{T_c - T_{gb}}{T_c - T_s} \right) + B \left(\frac{T_{gb} - T_d}{T_c - T_s} \right) \quad \text{Eq. (9.9)}$$

where the terms are as defined for Eq. (9.8). The gas release from these fuels would also be expected to increase, as shown by Eq. (9.9), when fuel temperatures exceed the values of T_d specified above.

At depletions below 20 fission units, the influence of the A and B (grain boundary and dislocation) terms on gas release is dominant. Since the

Figure 9.16. Measured Fission Gas Release as a Function of Fuel Burnup.

temperatures T_{gb} and T_d are composition dependent, fission gas release is strongly dependent on composition at a given temperature and strongly temperature dependent at a given composition, as shown by the illustrative example in the previous section. When depletions of 20 fission units are exceeded, however, the first term of Eq. (9.9) becomes dominant in determining the amount of gas release, and the percent of fission gas release is a function neither of composition nor of temperature. At high depletions, fractional gas release is primarily a function of initial density and of depletion, and since the total gas available increases with depletion, the total amount of fission gas released rises very sharply after a burnup of 20 fission units is reached. This upturn is believed to be possible at a much lower burnup for UO_2 according to an NRC correlation (Meyer et al, 1978) used for design purposes. The NRC correlation for UO_2 provides for an accelerated fission gas release at about 10 fission units, whereas the ThO_2 - UO_2 data indicate accelerated gas release at about 20 fission units.

(e) *Correlation of Gas Release with Grain Growth*

Fission gas release at high temperatures, corresponding to peak linear power outputs of 49.2 to 72.2 kW/m, was shown by Goldberg et al (1979) to be correlated with fuel grain growth for two compositions: ThO_2 -19.6 mole percent UO_2 and ThO_2 -29.5 mole percent UO_2 . Fission gas release was relatively high (up to 15 percent) for fuel rods that operated at high power in contrast to the relatively low fission gas release (0.1 to 5.2 percent) measured for rods that operated at lower power. Postirradiation ceramographic examination revealed extensive equiaxed grain growth in the oxide fuel in those rods that had high values of fission gas release.

Measured grain sizes were compared with values calculated from the cubic rate law grain growth relationship (see Chap. 8) of Nichols (1966):

$$D^3 - D_i^3 = kt \exp(-Q/RT) \quad \text{Eq. (9.10)}$$

where:

D = final grain diameter (cm)

D_i = initial grain diameter (cm)

t = time (hours)

Q = activation energy constant (kJ/mol) = 594.1

T = temperature (K)

R = gas constant

k = fitted coefficient (cm³/hr) = 800

The value of the fitted coefficient was obtained from the work of Nichols (1966), and the value of the activation energy constant was determined by adjusting the value for UO₂ used by Nichols (519 kJ/mol) by the ratio of the heats of sublimation of the ThO₂-UO₂ composition to that of UO₂. In making their estimates, Goldberg et al (1979) used heats of sublimation for UO₂ and ThO₂ reported, respectively, in Belle (1961) and Belle and Berman (1978). They estimated heats of sublimation for the ThO₂-UO₂ composition by interpolation, using ratios of melting temperatures. This procedure for estimating the appropriate value for the activation energy constant in Eq. (9.10) is similar to that used by McCauley (1969).

Results of the grain growth calculations are compared to the measured values in Fig. 9.17. It is seen that there is good agreement between the measured and calculated final grain diameters for two of the three rods (79-405, which contained ThO₂-19.6 mole percent UO₂, and 79-375, which contained ThO₂-29.5 mole percent UO₂). The disagreement observed for the third rod (79-349, which contained ThO₂-19.6 mole percent UO₂) is related to its power history, where grain growth associated with high power (and thus high temperature) was limited to a relatively short period of time early in life.

(f) Iodine and Cesium Release

Section 9.4.2(a) listed the phases likely to be present in irradiated oxide fuel, and the disposition of fission products among these phases. Among those listed are the volatile compounds CsI and CsBr. It was also noted that tellurium may be associated with this fraction. Tables 9.3 and 9.4 show that the amount of cesium present is considerably more than is needed to combine with the available halides; the remainder probably occurs, together with rubidium, in the oxide form. Also, Clayton (1979) showed, as previously stated, that some of the iodine could be removed by organic solvents, and was therefore in elemental form. Cesium halides are very soluble in water; cesium and iodine isotopes account for much of the activity released from crushed, irradiated oxide fuel by washing with distilled water at room temperature and atmospheric pressure. Cesium and iodine isotopes are also very prominent in the activity of water coolant that comes in contact with defected fuel elements.

- △ MEASURED VALUES-PEAK POWER 79-349
 □ MEASURED VALUES -90% POWER 79-405
 ○ MEASURED VALUES-PEAK POWER 79-405 AND 79-375

Figure 9.17. Measured Versus Calculated Grain Size.

Berman (1976) obtained an electron probe profile of relative iodine concentration along the radius of a fuel pellet, consisting initially of thorium, in which 1.1 mole percent of $^{233}\text{UO}_2$ had accumulated, and net depletion was 15 fission units. The irradiation had been conducted at a sufficiently high peak fuel temperature that a central void had developed by migration of fabricated porosity to the center of the fuel. The central void had a diameter of 0.19 cm, compared to the 0.54 cm of the fuel exterior. The size of this central void represented an isotherm of approximately 2000 K at full power; the exterior surface, under these conditions, was at about 700 K.

It was found that the iodine concentration increased approximately linearly with radius, from about 50 percent of the mean concentration, at the edge of the central void, to about 125 percent adjacent to the cladding. It was not possible, in the absence of comparable standards, to interpret the observed signal intensity in terms of absolute amount of iodine present. However, the less volatile element tellurium, which has a similar response in generating an X-ray fluorescence signal, was also observed. The mean intensity of the tellurium signal was 1.7 times that of iodine. Table 9.3 shows that the fission yield of tellurium in thorium-base fuels is about 1.6 times that of iodine. Since it is unlikely that both elements were lost at the same rate, it is concluded that little of either was lost, and that the major portion of iodine (and tellurium) formed in-reactor was still within the fuel, even under the rather severe conditions and long testing that this specimen underwent. The iodine was moved about within the fuel, but not, for the most part, driven out to recondense on the cooler parts of the cladding.

The above results are in agreement with the results of Clayton (1979), who found that as much as 1.5 grams of iodine could be adsorbed on the surface of a ground, unirradiated 20-gram thorium pellet at room temperature, and that this iodine was held extremely tenaciously; temperatures as high as 1200 K were needed to remove it.

The iodine that escapes from the fuel, however, represents a potentially serious problem. Elemental iodine on the surface of Zircaloy is known, from ex-reactor experiments, to promote stress corrosion cracking. It results in a characteristic dendritic, intergranular crack pattern. This same crack pattern has been observed in irradiated cladding failures. It cannot be stated whether the problem is less severe in thorium-base than in uranium-base fuels, because the adsorption of the iodine by thorium is offset by the increased iodine production of ^{233}U fissions. Among the measures taken to limit the amount of iodine release is the avoidance of high center temperatures, particularly as higher exposures are reached.

Ivak and Waldman (1979) irradiated Zircaloy-4 clad thorium and thorium-uranium fuel rods, then measured the fission gases released and also the amount of iodine deposited on the interior surface of the cladding. They

found that the fractional release of fission-generated iodine was approximately half the fractional release of krypton and xenon. This is in close agreement with work of Clayton (1979) showing that about half of the iodine in irradiated thorium fuel is in the combined form, and the remainder is in the free state. In Fig. 9.18, the measured amounts of fission iodine are plotted against the amounts calculated on this assumption. The experiments included burnups as high as 12.8 fission units, and releases of krypton and xenon as high as 2.8 percent of the amount generated.

9.5 SUMMARY OF FUEL BEHAVIOR

This chapter may be summarized by reviewing the characteristics and behavior of thorium-base fuel as observed in reactor service or experiments, or postulated from the differences in known properties of UO_2 and ThO_2 .

Figure 9.18. Comparison of Iodine Found in Cladding to Iodine Calculated on the Assumption that the Fractional Release is approximately Half that of Krypton and Xenon.

(1) Dimensional and density changes under irradiation conditions are comparable in thorium-base and uranium-base fuels. Steady-state fuel-cladding interaction is therefore also comparable. Fission products generated in $\text{ThO}_2\text{-}^{233}\text{UO}_2$ fuels, other things being equal, contain a larger amount of inert gas and a smaller amount of metallic ingots than those from $^{238}\text{U}\text{-}^{235}\text{UO}_2$ fuels. However, the amount of extra volume due to the additional gas is not as great as would be calculated from the ideal gas laws. Moreover, the gas is under greater pressure in the pores of thorium-base fuels than of uranium-base fuels. This is due to the greater surface energy and the higher melting temperature of thorium.

(2) At comparable temperatures and depletions, thermal conductivity is higher in thorium-base fuel than in uranium-base fuel, over most of the temperature range and compositions of interest, and center temperatures are lower at the same rod power. Since the melting point of ThO_2 is higher, center melting is very much harder to attain. A considerably higher heat flux is necessary in thorium for comparable development of columnar grains in the two fuels. This is due not only to the higher conductivity of thorium, but also to its lower vapor pressure and higher heat of sublimation.

(3) At temperatures leading to pore migration, (2) also leads to the conclusion that fission gas retention is higher in thorium-base than in uranium-base fuels under comparable conditions. This is due to the higher temperatures needed to release the gas atoms that accumulate at dislocations and grain boundaries. These mechanisms also operate to limit the release of iodine, although in this case, adsorption of the iodine on the thorium fuel also probably plays a role.

(4) The combination of lower release of fission products and lower thermal expansion than in the case of UO_2 is expected to decrease the susceptibility of the cladding to stress corrosion cracking, under constant conditions. Alternatively, this combination of more favorable thermal and mechanical characteristics has the potential of permitting ThO_2 -base fuel rods to operate at higher power.

(5) Thorium fuel is less subject than uranium to certain types of chemical degradation, such as oxidation. This contributes to the physical integrity of the fuel when a cladding defect occurs, and limits the amount of fission products released. In-reactor tests on thorium and thorium-uranium fuel have confirmed the thermal, mechanical, and chemical stability of the thorium fuel system, even in the presence of through-cladding defects. No significant evidence of erosion or corrosion of the ThO_2 -base fuel was apparent in defected fuel elements.

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Chapter 10

REPROCESSING OF ThO₂-UO₂ FUELS

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0.1 INTRODUCTION

Efficient utilization of the thorium fuel cycle depends on the recovery and recycling of the fissile and fertile materials by reprocessing the spent cores of both the prebreeder and breeder phases of the cycle. Figure 10.1 shows the central position of reprocessing in the thorium fuel cycle and both the prebreeder and breeder phases of the thorium fuel cycle and their interrelationship. The main objective of reprocessing the spent fuel of the thorium fuel cycle is to recover the ²³³U and ²³²Th free of neutron-poisoning fission products (FP) which could interfere with the breeding capability of the refabricated fuel.

0.1.1 Nuclear Reactions of the Thorium Fuel Cycle

The neutron-induced transmutation chains of thorium are discussed in Chap. 2. In summary, the fissile ²³³U is bred from the fertile ²³²Th by the following series of nuclear reactions:*

Recovery and further use of both the bred ²³³U and the unconsumed thorium are complicated by the presence in the spent fuel of ²³²U, which is formed from the thorium mainly as the result of the 37 MeV threshold (n,2n) reaction shown in Eq. (10.2).

* β^- decay, a high energy electron is emitted; this changes Z by +1 unit and leaves A unchanged.
 α decay, an alpha particle is emitted; this changes Z by -2 units and A by -4 units. a = years, d = days, h = hours, m = minutes, s = seconds, $\mu\text{s} = 10^{-6}$ second.

Figure 10.1. Thorium Fuel Cycle with Uranium-235 Driver Fuel in Prebreeder Cycle.

The complication due to the ^{232}U arises from the daughter products of its decay. The isotope ^{232}U decays by emitting an alpha particle to yield ^{228}Th . Through a long chain of additional alpha and beta particle emissions, this unstable ^{228}Th is converted into short-lived ^{208}Tl . This nuclide produces an intense radiation field, emitting a 2.6 MeV hard gamma photon as it undergoes beta decay to stable

²⁰⁸Pb. The series of nuclear reactions through which unstable ²³²U decays to stable ²⁰⁸Pb is:

10.1.2 Effect of ²³²U on Reprocessing Operations

In the thorium fuel cycle reprocessing operations, ²³²U cannot be chemically separated from the recovered ²³³U; also ²²⁸Th, which is the first decay daughter of ²³²U, cannot be chemically separated from the recovered thorium. Consequently, following the reprocessing operations, the chain of ²³²U decay daughters rebuilds in the recovered ²³³U, establishing a secular equilibrium, with an activity half life corresponding to that of ²³²U. Likewise, the chain of ²²⁸Th decay daughters rebuilds in the recovered thorium, establishing a transient equilibrium, with an activity half life corresponding to that of ²²⁸Th. As a result, due to the gamma-emitting ²⁰⁸Tl in the common decay chain of both these equilibria, both ²³³U and ²²⁸Th, which are recovered from reprocessing the spent thorium fuel cycle cores, develop high energy gamma radiation fields on standing.

Pittman (1962) suggested that the radiation problem associated with using the reprocessed thorium in fuel fabrication operations can be overcome by storing the recovered thorium for about 15 years to allow its ²²⁸Th content to decay. This is no solution, however, to the more severe radiation problem associated with the reprocessed ²³³U. Because of the long half life of the ²³²U, no reasonable storage period significantly reduce the high energy gamma radiation field associated with the recovered ²³³U.

In the recovered ²³³U, the decay of its ²³²U content rebuilds the high energy gamma radiation field, attenuated by removal of the ²³²U decay daughters during reprocessing, to the secular equilibrium value (practically steady-state value) over a 10-year period. Under conditions of equilibration with its decay daughters, 1 mg of ²³²U has a gamma radiation field of approximately 100 mrem per hour at a distance of 0.3 m. Calculations (Arnold, 1962) show that, in the ongoing thorium fuel cycle, the concentration of ²³²U in the recovered ²³³U will equilibrate at more than 2000 ppm. At this ²³²U concentration, the high level of the hard gamma radiation field from the reprocessed uranium fuel, which develops even after a short rebuild-up period, requires remote core refabrication and reprocessing operations.

Fuel reprocessing in the thorium fuel cycle does nevertheless result in some reduction in the gamma radiation field during subsequent fuel refabrication, especially if a purification separation is performed just prior to the fuel refabrication. Most important, fuel reprocessing in the thorium fuel cycle eliminates those fission product poisons of high neutron cross section. Table 10.1 lists the fission products, many of which are nonradioactive, that are significant in reactor poisoning, along with their half lives and thermal neutron cross sections. The significance of these fission product neutron poisons is applicable also to fast reactors, since a large proportion of the neutrons of a fast reactor is still in the range of 10 keV to 1 MeV, where serious fission product poisoning occurs.

10.2 HEAD-END PROCESSING OPERATIONS

Head-end processing operations, which precede separation procedures for recovery of the uranium and thorium, include mechanical

TABLE 10.1—SIGNIFICANT FISSION PRODUCT NEUTRON POISONS

Nuclide	Half Life	Thermal Neutron Capture Cross Section (barns)
⁸³ Kr	stable	205
⁸⁵ Kr	10.4 a	<15
¹³¹ Xe	stable	120
¹³³ Xe	5.3 d	200
¹³⁵ Xe	9.1 h	3.4×10^6
¹³³ Cs	stable	29
¹⁰⁹ Ag	stable	84
¹¹³ Cd	stable	2.5×10^4
¹³⁹ La	stable	8.4
¹⁴¹ Pr	stable	11.2
¹⁴³ Nd	stable	300
¹⁴⁵ Nd	stable	45
¹⁴⁶ Nd	stable	9
¹⁴⁷ Pm	2.6 a	60
¹⁴⁹ Sm	stable	6.6×10^4
¹⁵⁰ Sm	stable	85
¹⁵¹ Sm	73 a	1.2×10^4
¹⁵² Sm	stable	220
¹⁵³ Eu	stable	420
¹⁵⁴ Eu	16 a	1.5×10^3
¹⁵⁵ Eu	1.8 a	1.4×10^4
¹⁵⁷ Gd	stable	1.6×10^5
⁹⁵ Mo	stable	13
⁹⁹ Tc	2.1×10^5 a	100
¹⁰³ Rh	stable	150

decanning, mechanical or chemical decladding of the fuel, and aqueous reprocessing, dissolution of the fuel, and preliminary treatment of the solution prior to adjusting it for solvent extraction.

The mechanical arrangement and packaging of the reactor fuel largely determine the preliminary mechanical processing operations to which the spent fuel is subjected in preparation for fuel reprocessing. Various forms of ThO₂-UO₂ fuel have been considered for exploiting the thorium fuel cycle, some of which do not involve sheathing the fuel with a metal cladding. Two such forms are small spheres of ThO₂-UO₂ in a pebble-bed reactor (Bicevskis et al, 1968) and fine particles of ThO₂-UO₂ suspended as a slurry in the recirculating coolant. For application as fuel in commercial power reactors, however, ThO₂-UO₂ is conveniently used as sintered pellets or vibration-compacted powder (Kosiancic et al, 1968) in the form of metal-clad, rod-shaped fuel elements. Only this fuel type is discussed in head-end operations.

Zircaloy and stainless steel are used for the cladding and the structural containers in power reactor applications. Aluminum is a suitable cladding for thorium-uranium fuel in low temperature test reactors and production reactors (Boswell et al, 1968), but not for power reactor fuel. At power reactor operating temperatures, the normally protective oxide film on aluminum is not stable, and the aluminum undergoes excessive corrosion both in water and in alkali metal (sodium, sodium-potassium, and lithium) coolants (Kutateladze et al, 1959). As structural accessories, other corrosion-resistant metals, such as Inconel, Nichrome, and titanium alloys, find application in the fuel element assemblies. The very low neutron cross section of Zircaloy, its adequate strength, and its excellent corrosion resistance to high temperature water make Zircaloy the superior material for cladding and subassembly structural accessories for use in water-cooled reactors under high-temperature conditions. Further discussion of head-end decladding and decanning operations is restricted to Zircaloy.

For installation in the reactor core, a number of the fuel elements assembled into square or hexagonal canisters, with end-box fittings and adapters for support and for directing the coolant flow. The resulting subassembly or fuel-rod bundle may contain hundreds of fuel elements positioned in an appropriate array. The fuel elements of the array are separated from each other and from the inner surface of the enclosing canisters by grids located at intervals along the fuel-element length or by means of wire-wrap helices that spiral the length of the fuel elements.

The presence of cladding, canister, and accessory metal, designated as *inert* material or structurals, can hinder the reprocessing operations. If these materials undergo dissolution during the reprocessing,

they consume dissolvent and increase the volume of the liquid radioactive waste. Also, their existence in solution can interfere with the operations for separating out the fissile and fertile materials. Therefore, before reprocessing, the inert metal is largely or completely removed, exposing the $\text{ThO}_2\text{-UO}_2$ fuel to the reprocessing reagents.

10.2.1 Decanning

The inert canister material, including end-boxes, adapters, and accessories, is removed from the subassembly by remotely controlled mechanical cropping operations. In cropping the fuel element bundles, carried out dry (in caves or cells) or wet (under water in canals or pits), the end-plugs, fittings, and tangs are cut from the fuel elements. However, at this juncture the integrity of the fuel rods themselves is not breached. Hack saws, disk saws, abrasive wire cutters, and abrasive cut-off wheels can be used dry (normally with cutting fluid directed at the kerf) or under water. However, high-speed disk saws and cut-off wheels are not preferred for underwater use because of high friction losses. Electric-arc wheel cutting and electrical-discharge machining are applicable under water, but plasma-arc cutting is not applicable under water with Zircaloy. Laser cutting, which is conveniently amenable to remote application, can be used for dry cutting Zircaloy. The canister itself can be opened by milling or slitting and is removable by remotely operable hydraulic clamps and jacks. Sawing and machining operations on Zircaloy, even when carried out under water, require extreme precautions against the hazard of fire, due to the pyrophoricity of the Zircaloy sawdust, chips, and globules.

10.2.2 Decladding

Decladding or dejacketing of the $\text{ThO}_2\text{-UO}_2$ fuel can be carried out mechanically or chemically. Variations of mechanical technique used to remove fuel rods from a fuel subassembly have been evaluated for decladding the ceramic fuel of the individual fuel elements. Other mechanical techniques that have been evaluated include cutting the fuel rod into short lengths by means of a tube cutter, and rolling and swaging the fuel rods to crush the $\text{ThO}_2\text{-UO}_2$ fuel and split the cladding to release the comminuted fuel particles. However, none of these mechanical decladding techniques has found as widespread application as shearing (Watson et al, 1959; Kelly, 1960; Nicholson et al, 1968; Siemens et al, 1979). Of mechanical decladding, only the shearing technique is discussed.

(a) Mechanical Decladding by Shearing

In carrying out shearing, the fuel element or cluster of fuel elements is cantilevered over a support anvil and fed into the shear of a hydraulically operated blade. In the usual shear design, the shear blade has a wide face that strikes the clad fuel, shattering it into fine particles, while partly flattening the short length of cladding ring at it is sheared off. The shorter the cut relative to the fuel-rod diameter, the smaller the particle size of the comminuted fuel, and the more complete the dislodgment from the cladding.

Studies of impact shearing Zircaloy-clad fuel rods containing high-density $\text{ThO}_2\text{-UO}_2$ fuel pellets were carried out in support of the Light Water Breeder Reactor (LWBR) Proof-of-Breeding Program (Parks et al, 1978; Fagan et al, 1981). For fuel rods ranging in diameter from 0.777 cm to 2.113 cm and for cut lengths no greater than 60 percent of the fuel-rod diameter, the fuel is comminuted to a powder and is completely dislodged from the cladding. The disadvantage, however, is that the short lengths require a greater number of cuts, thus increasing the wear on the shear blade. Figure 10.2 illustrates the sequential steps in the mechanical decanning and shearing of a fuel subassembly.

Consideration has been given to subjecting short-cut sheared fuel elements to rotatory or vibratory sieving to separate the cladding hulls from the $\text{ThO}_2\text{-UO}_2$ fuel particles. In this case, the fuel-free cladding rings can be sent to radioactive solid waste disposal, while the comminuted fuel is sent on to reprocessing to recover uranium and thorium. The finely divided thorium-uranium fuel is in convenient form to react readily with the reprocessing reagents.

For aqueous processing, however, the fuel elements are usually sheared directly into a perforated basket of material resistant to attack by the aqueous dissolvent. The perforated basket is enclosed in thin aluminum or carbon steel to contain fuel fines during transit to the dissolver. In the dissolver the aluminum or carbon steel is quickly dissolved, allowing the solution to have access to the contents of the perforated basket.

The aqueous dissolvent for $\text{ThO}_2\text{-UO}_2$ not only dissolves the ceramic fuel from the Zircaloy cladding but also etches the surface of the cladding and takes some of the Zircaloy into solution along with the fuel. The undissolved, left-over cladding hulls are usually discarded as solid radioactive waste. However, it has been demonstrated (Levine and Nowak, 1977) that the sheared Zircaloy hulls can be readily converted into zirconate ion exchange material; this can be used to concentrate and stabilize for disposal the radioactivity from the high-level liquid waste generated in the aqueous reprocessing of

Figure 10.2. Pressurized Water Reactor Core Module Disassembly Sequence.

the $\text{ThO}_2\text{-UO}_2$. Shearing the fuel rods into short lengths for ease of handling can also be adapted for nonaqueous chemical processing of the fuel.

(b) Chemical Decladding

In the chemical decladding processes, metal-clad oxide fuel rods are exposed to aqueous reagents to remove the cladding from the fuel. However, processes using molten metal, gas volatilization, and fused salt to remove Zircaloy cladding from ThO₂-UO₂ fuel have also been studied.

(1) AQUEOUS DISSOLUTION OF ZIRCALOY CLADDING. The more practical aqueous chemical decladding processes for removing Zircaloy are all based on the use of fluoride ion as the decladding reagent. Boiling 9 M hydrofluoric acid was proposed early as the dissolvent for Zircaloy cladding (Culler and Blanco, 1958). The hydrofluoric acid dissolves the zirconium of the Zircaloy as the hexafluorozirconate ion, with evolution of hydrogen gas. However, tin, which makes up 1.5 percent of the Zircaloy, is left as an undissolved mud with the fuel. Later, during dissolution of ThO₂-UO₂ in a solution of high nitric acid concentration, the tin is converted into metastannic acid. This gelatinous product coats the fuel and interferes with its dissolution. The presence of the metastannic acid in the fuel solution can promote emulsification at the aqueous-organic interface and thus interfere with the subsequent extraction operation.

The Zirflex process for dissolving Zircaloy cladding has undergone extensive development (Swanson, 1958; Blanco et al, 1962) and is well established in fuel reprocessing. The Zircaloy-clad urania fuel of the PWR-1 blanket was declad by this process (Davis, 1966; Boldt and Ritter, 1969).

In using the Zirflex process, the Zircaloy-clad thorium-uranium fuel is subjected to a boiling aqueous solution of 6 M ammonium fluoride, 1 M ammonium nitrate. The Zircaloy is dissolved with essentially no hydrogen evolution, as indicated by the following equation:

The ammonium nitrate also oxidizes the tin, causing it to dissolve. Thus, the tin is eliminated with the decladding solution and is not present during the fuel dissolution and extraction steps. The ammonia evolved during dissolution of the Zircaloy cladding is not returned to the solution, to avoid raising its pH and precipitating a sludge of zirconium hydroxide.

In developmental studies of the decladding of Zircaloy-clad, low-density (83 percent of theoretical) ThO₂-UO₂ fuel pellets, uranium losses to the Zirflex solution ranged from 0.2 to 0.4 percent.

High-density pellets (>95 percent of theoretical, as in LWBR binary ThO₂-UO₂ pellets) can be expected to exhibit significantly less loss of uranium to the solution. A series of test runs made on decladding Zircaloy-clad PWR fuel rods containing UO₂ fuel of 96 percent of theoretical density, irradiated to 15,750 MWD/tonne (Goode and Baillie, 1962), showed that after 3 hours the boiling Zirflex dissolvent yielded uranium losses to the solution of only 0.04 percent.

(2) **NONAQUEOUS CHEMICAL DECLADDING.** Various nonaqueous processes for removing Zircaloy cladding from ThO₂-UO₂ fuel have been proposed and studied. These processes can be applied under less moderating conditions and can yield a smaller volume of radioactive waste than the aqueous processes. Because these nonaqueous processes are carried out at elevated temperature, reaction kinetics are enhanced, and thus a shorter operating time is required than is the case for aqueous decladding.

a) *Molten Zinc.* Zircaloy cladding can be dissolved with zinc (melting point, 692 K; boiling point, 1180 K) at temperatures of 773 K and above, with no reaction between zinc and ThO₂-UO₂. After drain-off or decantation of the zinc solution of the cladding, the zinc is recoverable by vacuum distillation, leaving a residue of the solid cladding for disposal as radioactive waste. Molten zinc decladding is conveniently used as a head-end operation in pyrochemical fuel reprocessing operations where equipment for processing the molten metal is an inherent part of the facility (Steunenberg et al, 1969).

b) *Gaseous Hydrochlorination.* By means of the Zircex process, in which the Zircaloy-clad thorium-uranium fuel is subjected to dry hydrogen chloride gas at 673 K to 923 K, the Zircaloy cladding can be removed by volatilization. The constituents of the Zircaloy cladding (Zr, Sn, Fe, Cr, Ni) are converted into chlorides (ZrCl₄, SnCl₂, FeCl₂, CrCl₃, NiCl₂) with the production of hydrogen gas, while the oxide fuel remains unreacted. The gaseous hydrochlorination of Zircaloy cladding constituents in the Zircex process is described by the following reactions:

Eq. (10.5)

Zirconium tetrachloride (ZrCl₄, sublimation temperature >604 K) sublimes at the temperature of the hydrochlorination, leaving SnCl₂, FeCl₂, NiCl₂, and CrCl₃ with the fuel. The exit gas stream, containing excess hydrogen chloride and also hydrogen gas produced in the hydrochlorination reaction, is passed through a desublimer where the zirconium tetrachloride is solidified for disposal.

Removal of Zircaloy cladding by volatilization with dry hydrogen chloride gas is normally a precursor to nonaqueous reprocessing of the fuel. This decladding process can be applied, however, to decladding ThO₂-UO₂ fuel for aqueous reprocessing. In this case, it is desirable to rinse the declad fuel with water or dilute nitric acid to dissolve the residue of cladding metal chlorides from the surface of the fuel. This avoids the presence in the fuel solution of dissolved chlorides which, at high enough concentration, can interfere with the solvent extraction of uranium and thorium from the solution.

c) *Salt Melt Hydrochlorination.* Zircaloy-clad thorium-uranium fuel can also be dejacketed by volatilizing the cladding. The Zircaloy cladding is removed by immersing the fuel element in a molten 1:1 molar mixture of anhydrous aluminum chloride (AlCl₃, sublimation temperature >451 K; melting point, 467 K) and ammonium chloride (NH₄Cl, sublimation temperature >793 K) and refluxing at 673 K. A stream of dry hydrogen chloride gas, bubbling through the molten salt mixture, converts the constituents of the Zircaloy cladding into the chloride salts, and also converts ThO₂-UO₂ fuel into nonvolatile thorium chloride (ThCl₄, melting point, 1043 K; boiling point, 1194 K) and nonvolatile uranium trichloride (UCl₃, melting point, 1151 K; boiling point, 1683 K). The conversion of the Zircaloy cladding constituents to the chlorides in the salt melt hydrochlorination process is described by Eq. (10.5). Hydrochlorination of ThO₂-UO₂ fuel proceeds as follows:

Zirconium tetrachloride and a small amount of stannous chloride (SnCl₂, melting point, 520 K; boiling point, 896 K) are vaporized and are swept out of the salt melt by the hydrogen chloride gas stream, along with the refluxing vapors of the salt melt and with the steam and chlorine gas produced by the hydrochlorination reaction. The thorium chloride and the uranium chloride are not volatilized, but remain in the salt melt. The volatilized zirconium chloride does not efflux, but passes to a special condenser where it is converted to a solid. The solid zirconium chloride is in a convenient form for disposal as solid radioactive waste.

At the end of the decladding, the temperature of the salt melt is raised and the aluminum chloride and the ammonium chloride constituents of the salt melt are sublimed without reflux and are recovered for reuse. The residue of stannous chloride in the salt melt is volatilized with the salt melt constituents. The nonvolatile thorium chloride and uranium chloride from the $\text{ThO}_2\text{-UO}_2$ fuel, with any residual unsublimed salt melt, are dissolved in nitric acid. This solution is boiled down repeatedly, with additions of concentrated nitric acid, to rid it of chloride. The concentration of the resulting chloride-free solution of thorium nitrate and uranyl nitrate is adjusted as required for solvent extraction of the thorium and uranium.

Like the Zircex process, the salt melt hydrochlorination process yields the Zircaloy cladding waste in the compact form of the solid zirconium chloride salt. The salt melt combines decladding and preparation of the solvent extraction feed into one process; however, it has the disadvantage that it is extremely corrosive on stainless steel reprocessing equipment.

10.2.3 Voloxidation

Prior to its dissolution, the declad thorium-uranium fuel can be subjected to an oxidizing burn, called voloxidation (Goode and Stacy, 1979). This burning in air at a temperature of 873 K or higher for an extended period of time drives off tritium (as T_2O and THO), carbon-14 (as $^{14}\text{CO}_2$ and ^{14}CO), the fission gases (e.g., ^{85}Kr), and significant amounts of radioactive iodine, cesium, and ruthenium. These expelled radioactive fission products are trapped for disposal. If, as in the case of some HTGR fuels, the ratio of uranium to thorium in the thorium-uranium fuel exceeds 3 to 2, the oxidation of the uranium to U_3O_8 causes the fuel matrix to spall, resulting in comminution of the fuel to a powder. Carbon-coated $\text{ThO}_2\text{-UO}_2$ HTGR fuels, along with crushed structural graphite, are subjected to fluidized bed oxidation at 973 K to 1023 K in air on an aluminum heat transfer medium (Steyer and Stelling, 1968; Nicholson et al, 1968). The carbon is burned away and volatile fission products are released from the fuel into the expelled gas. The hot, expelled gas is cooled and then treated by cycloning and filtering and by passing it over silica gel adsorbent. Depending upon its radioactivity content, the treated, expelled gas may be released to the atmosphere or held in pressurized storage.

Voloxidation studies (Pickett, 1980) were carried out on irradiated $\text{ThO}_2\text{-UO}_2$ fuel from the Elk River reactor to evaluate the effects of fuel comminution, temperature, and time on tritium removal. It was found that only moderate comminution, to a particle size less than 2 mm, was adequate for the voloxidation. However, temperature and

time requirements were stringent; the comminuted fuel had to be heated to a temperature of 1173 K for up to 12 hours to remove the tritium completely.

10.2.4 Fuel Dissolution for Aqueous Reprocessing

The thoria-urania fuel, declad by whatever method, is dissolved in fluoride-catalyzed nitric acid. If chemically declad, the fuel is given a prior water rinse to remove residual decladding chemicals that could interfere with the dissolution or subsequent reprocessing operations. Of all the aqueous dissolvents evaluated for $\text{ThO}_2\text{-UO}_2$, the one generally used is boiling Thorex. This dissolvent contains, as prepared, 13 M to 13.5 M nitric acid, with 0.01 M to 0.06 M fluoride ion catalyst in the form of sodium fluoride or hydrofluoric acid, and 0.06 M to 0.32 M aluminum nitrate inhibitor, used to prevent excessive corrosive attack on the dissolver equipment.

Dissolution of the $\text{ThO}_2\text{-UO}_2$ in the refluxing Thorex dissolvent, boiling at about 393 K under atmospheric pressure, proceeds with the buildup of thorium and uranyl ions in solution and with consumption of acid. At a residual acidity of 8 M nitric acid or less, the dissolution rate drops to an impractically low value. When this low acidity is reached, the solution is drained from the dissolver, leaving a heel of liquid and undissolved fuel. An additional charge of thoria-urania fuel and fresh dissolvent are added, and the dissolution is continued.

Detailed studies of the application of the Thorex dissolvent in dissolving $\text{ThO}_2\text{-UO}_2$ fuels have been made (Rathvon et al, 1968; Goode and Flanary, 1965; and Blanco et al, 1962). These studies show that the rate of dissolution of the thoria-urania fuel in the Thorex dissolvent depends on (1) fuel characteristics, (2) solution characteristics, and (3) temperature:

1. Increasing uranium content, especially at 10 percent or greater, increases the rate of dissolution of $\text{ThO}_2\text{-UO}_2$. Decreasing the fuel particle size increases the rate of dissolution, provided adequate agitation maintains the particles in suspension. Allowing the particles to settle out in the solvent without agitation can result in their cementing into a refractory mass. Fuel density has a major effect on the dissolution rate. In a comparative study, low-density $\text{ThO}_2\text{-UO}_2$ pellets (60 percent of theoretical) dissolved at a rate of 18 mg/min/cm², while high-density pellets (90 to 95 percent of theoretical) dissolved at a rate of 2 mg/min/cm².

2. At low acidity (8 M nitric acid or less) of the Thorex, the rate of dissolving $\text{ThO}_2\text{-UO}_2$ becomes impractically slow. The optimum concentration of fluoride catalyst in the range of 0.01 M to 0.06 M in the Thorex dissolvent increases with the concentration of aluminum

nitrate. A fluoride catalyst concentration in excess of the optimum deposits a film of insoluble thorium fluoride on the fuel surface and retards its dissolution.

3. Conventionally $\text{ThO}_2\text{-UO}_2$ is dissolved with agitation in the Thorex dissolvent boiling at approximately 393 K under atmospheric pressure with reflux. Studies by Levitz et al (1981) show that contacting $\text{ThO}_2\text{-UO}_2$ with the Thorex dissolvent, boiling with reflux at approximately 473 K under about 9 atmospheres of inert gas pressure drastically increases the rate of fuel dissolution. Under these high temperature, elevated-pressure conditions, the dissolution of sheared Zircaloy-clad $\text{ThO}_2\text{-UO}_2$ fuel proceeds rapidly even with the Zircaloy cladding hulls present in the Thorex solution. The fluoride complex of zirconium formed during the dissolution is dissociated at the elevated temperature to yield an adequate catalyzing concentration of fluoride ion.

10.2.5 Auxiliary Reprocessing Operations

The solution of the spent $\text{ThO}_2\text{-UO}_2$ fuel in the Thorex dissolvent is subjected to preliminary treatments to decontaminate the solution partially and to eliminate or to recover special constituents. Application of these preliminary operations increases the effectiveness of the subsequent solvent extraction in recovering the uranium and thorium values free of fission products and temporarily free of ^{232}U decay products.

(a) Sparging

Two studies (Holm, 1951; Foster, 1953) showed that sparging the Thorex fuel solution at 368 K to 373 K with air at the rate of $1.7 \text{ cm}^3/\text{min}$ per ml of solution removes about 95 percent of the iodine content of the solution in 3 hours. The same results were obtained on carrying out the sparging with oxygen or nitrogen, regardless of whether the iodine was added to the Thorex dissolvent as iodide iodate ion, or the element. The iodine volatilizes into the sparging air in the elemental form and is removed by passing the air through a column, the packing of which is wetted with aqueous silver nitrate. Alternatively, the air is scrubbed with an aqueous solution of sodium hydroxide and sodium nitrate to strip out the iodine.

Sparging the hot (368 K) Thorex fuel solution, containing 0.01 M cobalt nitrate as a catalyst, with approximately 5 volume percent of ozone in air volatilizes more than 95 percent of its ruthenium in the form of ruthenium tetroxide in 10 hours (Blanco and Watson, 1961). This preliminary sparge to remove ruthenium is necessary because it is difficult to obtain a clean separation of uranium and thorium from

ruthenium in solvent extraction. The volatilized ruthenium is scrubbed from the expelled gas with aqueous sodium hydroxide.

(b) *Scavenging*

Removing a solute from solution by adsorbing it on the surface of a finely divided suspenoid which is then separated from the solution is termed scavenging. Numerous scavenging agents have been evaluated and used, such as kieselguhr, activated carbon, bentonite clay (Superfiltrol), and silica gel. However, manganese dioxide has general use in scavenging Thorex fuel solutions. Manganese dioxide in the amount of 1.5 to 10 grams per liter of the solution is precipitated *in situ* by dissolving potassium permanganate in the Thorex fuel solution and reducing the permanganate with hydrogen peroxide or manganous nitrate or by decomposing the solution through heating. The permanganate destroys any organics in the solution, thus avoiding their interference with the solvent extraction operation. Manganese dioxide adsorbs more than 99 percent of the zirconium and niobium. Decomposing the permanganate by heating the solution also results in volatilizing or adsorbing more than 95 percent of the iodine and ruthenium. In addition, the manganese dioxide adsorbs the micelles of gelatinous silicic acid and metastannic acid which, if present in the solution during solvent extraction, promote the formation of emulsions that reduce extractive efficiency by interfering with the separation of the organic and aqueous phases. The manganese dioxide precipitate, with the materials adsorbed on it, is separated from the solution by filtration or centrifugation. As an alternative to manganese dioxide scavenging, the emulsifying characteristics of silicic acid and metastannic acid can be masked in the solution by adding 0.1 gram of gelatin per liter of the solution and boiling for 30 minutes.

(c) *Recovery of ^{233}Pa*

As shown in Eq. (10.1), ^{233}Pa is the immediate precursor whose beta decay yields ^{233}U . If the spent $\text{ThO}_2\text{-UO}_2$ fuel cooldown period prior to reprocessing is about 275 days (10 half lives of ^{233}Pa), the decay of ^{233}Pa to ^{233}U is complete for all practical purposes. However, for short cooldown times, a preliminary separation to recover the ^{233}Pa can be carried out. This separation can be made by percolating the Thorex fuel solution through 60-mesh to 200-mesh unfired Vycor glass particles. The Vycor glass-particle surfaces adsorb the ^{233}Pa almost quantitatively, without retaining uranium or thorium. The adsorbed ^{233}Pa is desorbed from the Vycor glass by a solution of 0.5 M oxalic acid. This recovered ^{233}Pa is allowed to decay to isotopically pure ^{233}U . Also, if the manganese dioxide scavenging is carried out on the

solution with ^{233}Pa present, the ^{233}Pa is adsorbed on the manganese dioxide and is removed from solution with it. After decay of the ^{233}Pa , the manganese dioxide is dissolved and reprecipitated, leaving the ^{233}U in solution, but scavenging the fission product contaminants. The ^{233}U is recovered isotopically pure from the filtered solution by solvent extraction or by ion exchange.

10.3 SEPARATION OPERATIONS

Following the head-end operations, the spent fuel is subjected to separation operations to recover the fissile and fertile materials free of fission products and temporarily free of the decay products of ^{232}U . The three types of separation processes whose present state of development makes them applicable to reprocessing $\text{ThO}_2\text{-UO}_2$ fuels are solvent extraction (with and without supporting ion exchange), halide volatility, and pyrochemical. In the discussion of these processes, it is assumed, in the case of the halide volatility and pyrochemical processes, that the spent fuel cooldown time is long enough for the ^{233}Pa to have decayed to ^{233}U . In the case of solvent extraction it is assumed that either the spent fuel cooldown time is long enough for decay of the ^{233}Pa to ^{233}U , or that appropriate disposition of the ^{233}Pa during the extraction operation prevents radiation damage to the organic extractant. Allowing the longer cooldown time is preferable because it permits the decay of ^{234}Th prior to solvent extraction. However, the decision on cooldown time would be based on the overall economics of fuel recycle. The high energy beta particles emitted by this nuclide cause severe radiation damage that degrades the extractant. The isotope ^{234}Th , formed by double neutron capture in the ^{232}Th during core irradiation, cannot be removed from the fuel solution by auxiliary reprocessing operations.

10.3.1 Solvent Extraction from Aqueous Solution

Solvent extraction is the main separation process for recovering the fuel in aqueous reprocessing. The three established solvent extraction processes applicable to reprocessing thorium-uranium fuel are the Thorex process, the Interim ^{233}U process, and the Hexone ^{233}U process. The overall uranium losses in these three processes are of the order of 0.25 percent or less.

(a) Solvent Extraction Feed Preparation

To prepare the feed stock for solvent extraction, the thorium-uranium fuel solution, which has undergone the auxiliary reprocessing operations and preferably is free of ^{233}Pa , is adjusted to 0.2 N acid defi-

ciency by evaporating the solution to concentrate it and then by steam stripping nitric acid from it at 408 K to 428 K. At this acid deficiency, the extractability of the fission products, especially zirconium and ruthenium, and of the ^{232}U decay products is greatly decreased. The acid-deficient solution is adjusted to a thorium nitrate concentration of 1 M to 1.5 M and made 0.1 M in sodium bisulfite and 0.1 M to 1 M in aluminum nitrate. It is then held at 323 K for several hours to allow the bisulfite to reduce Ce^{+4} to the less extractable Ce^{+3} and to reduce any ruthenium left in the solution following the auxiliary reprocessing operations to the nonextractable form. Aluminum nitrate is added to assure complexing of the fluoride ion, which otherwise interferes with the solvent extraction and also promotes corrosive attack on the extraction equipment. At the higher end of its concentration range, the aluminum nitrate serves as a salting-out agent. In the Thorex process, where both uranium and thorium are extracted, the salting-out capability of the aluminum nitrate comes into play when the concentration of thorium in the aqueous phase is reduced to a low value. In the Interim ^{233}U process and in the Hexone ^{233}U process, where only uranium is extracted, the concentration of the thorium remains high in the aqueous phase. In these two processes the thorium serves as the salting-out agent for uranium, and a high aluminum nitrate concentration is not required.

(b) Organic Extractants

Uranium and thorium are extracted by contacting the aqueous nitrate solution of the thorium-uranium fuel with an onium-ion-forming organic compound (usually a phosphonium or oxonium derivative) dissolved, if required, in kerosene as a diluent (Blake et al, 1958; Flagg, 1961; Haas, 1961; Siddall, 1961). The protonized onium ion combines with the nitrate complex of the metal ion undergoing extraction to form an ion-association adduct that is soluble in the organic phase. The organic-to-aqueous distribution coefficient $E_{o/a}$ of the ion-association adduct is comparatively small. Consequently it is generally necessary to salt out the ion-association adduct by adding to the feed solution a water-soluble salt of a polyvalent transition metal ion with a common anion, e.g., aluminum nitrate. The added salt reduces the solubility of the ion-association adduct in the aqueous phase and promotes its association in the organic phase.

Among the organic extractants applicable in actinide extraction, two are firmly established for solvent extraction in the thorium fuel cycle: hexone, methylisobutyl ketone (Flagg, 1961), and TBP, tri-n-butyl phosphate (Siddall, 1961). Of these two extractants, TBP finds by far the greater use.

(1) TRI-N-BUTYL PHOSPHATE (TBP). As an extractant, TBP forms strong adducts with the actinides, with the lanthanides, and with some of the transition metals. Consequently, TBP itself does not have high selectivity as an extractant. That TBP extraction does exhibit greater specificity for the actinides than for the fission products is due largely to the selectivity of the nitrate ion in forming nitrate complexes with the actinides rather than with the fission products. Nevertheless, in spite of the selectivity of the nitrate ion in complexation, TBP still can extract significant amounts of the fission products of higher valency: Zr^{+4} , Nb^{+5} , Ru^{+4} , and Ce^{+4} . Much of the developmental work on the extraction process with TBP in the thorium fuel cycle has been dictated by the requirement to prevent coextraction of these fission product species along with the actinides. To avoid extracting these fission products along with the uranium and thorium, it is necessary either to reduce drastically the concentration of the fission products or to stabilize them in solution by the head-end auxiliary reprocessing operations previously discussed.

TBP undergoes hydrolytic degradation under the influence of radiation to yield mono- and di-n-butyl phosphates, with splitting off of butanol. These impurities in the TBP extractant cause the formation of a gummy deposit that can interfere with the proper functioning of the extraction equipment. The di-n-butyl phosphate forms strong adducts with the fission products, as well as with uranium and thorium. The carryover of the extractable fission product adducts into the organic phase reduces the decontamination factor of the solvent extraction operation. The distribution coefficients of the actinide and fission product adducts of the di-n-butyl phosphate degradation products are comparatively large. In consequence, the presence of this degradation product hinders the stripping of uranium from the organic phase and, as a result, process losses of unstrippable uranium in the organic phase occur. To prevent these undesirable effects, the TBP extractant must be cleaned up at intervals by contacting it with adsorbents, e.g., manganese dioxide, and by subjecting it to alkaline and acidic washes.

TBP at high concentration in a hydrocarbon diluent (Amsco or Ultrasene) is used as the extractant in the Thorex solvent extraction process in which both ^{233}U and thorium are extracted from the aqueous feed. Selective stripping then allows partitioning of the ^{233}U and the thorium. By reducing the concentration of TBP in the extractant, the selectivity of the extraction is enhanced. Thus, in the interium ^{233}U process the TBP is used at very low concentration to recover ^{233}U from irradiated thorium, while leaving the thorium and protactinium unextracted.

(2) **HEXONE.** Used as the undiluted extractant at 100 percent concentration, hexone still forms comparatively weak ion association adducts. As a result, hexone exhibits specificity in its extraction of the actinides. At low acidity, i.e., under conditions of acid deficiency, hexone extracts uranium without extracting thorium. This specificity is the basis for the use of hexone in the hexone ²³³U process; ²³³U is recovered, while thorium, the fission products, and undecayed ²³³Pa are left unextracted. Acid-deficient extraction with hexone also results in higher decontamination factors for the uranium product. At normal acidity, hexone extraction of zirconium and ruthenium occurs readily. Under conditions of acid deficiency, however, hexone extraction of zirconium and ruthenium is drastically repressed.

Hexone, which was the first extractant used to recover the actinides on a large scale, is readily available commercially, since it is produced in large volumes as a lacquer solvent. The commercial hexone contains mesityl oxide and methylisobutyl carbinol as impurities. The methylisobutyl carbinol interferes with the separation of cerium, zirconium, and niobium. Before it is used as an extractant, the commercial hexone is purified by washing the fresh solvent first with an aqueous solution of 1 M sodium dichromate in 1 M nitric acid, then with dilute aqueous caustic soda, and finally with water as a rinse.

In its use as an extractant, hexone exhibits high resistance to radiation damage. However, the hexone is consumed by reaction with nitrous acid, formed from the nitric acid of the extraction medium, to yield dinitrosomethylisobutyl ketone. This product hydrolyzes to methylisopropyl diketone and dinitroisobutane, or it decomposes to yield more nitrous acid, thus resulting in autocatalytic degradation. The degradation products interfere with the recovery of uranium in the stripping column by retaining the uranium in the organic phase. At intervals the stripped hexone extractant is purified to remove the accumulated impurities. The unstripped uranium is recovered from the hexone by washing the hexone with 2 percent aqueous sodium carbonate. Then, the uranium-free extractant is rewashed with an aqueous solution of 5 to 10 percent aqueous sodium hydroxide, from which the hexone is steam distilled to yield the purified extractant for reuse.

c) Solvent Extraction Processes

(1) **THOREX PROCESS.** The Thorex process is applicable for recovering and partitioning ²³³U and thorium from the dissolved spent ThO₂-UO₂ fuel of the thorium fuel cycle by extraction with TBP. Several versions of the Thorex process have been developed. In some

versions, ^{233}U and thorium are partitioned by selective extraction by using one or more organic extractants in addition to TBP or by using different concentrations of the TBP extractant. Thus, in a version of the Thorex process, the uranium is extracted alone with 5 percent TBP in n-dodecane. Then, the aqueous raffinate is reextracted with 40 percent TBP in n-dodecane in order to recover the thorium, which was not extracted by the more dilute, and thus more selective, TBP extractant.

Other variations of the Thorex process permit recovering the ^{233}Pa present in short cooldown-time fuels. In one such variation this is done by means of the head-end protactinium recovery operation previously described, in which the fuel solution is percolated through unfired Vycor glass to adsorb the protactinium. In other versions the protactinium is coextracted into the organic phase and is partitioned from it by selective stripping conditions. Because of the high specific activity of ^{233}Pa , variations of the Thorex process that involve extracting protactinium into the organic phase expose the extractant to excessive radiation damage, with concomitant operational problems.

In another version of the Thorex process, applicable to fuel with a long cooldown time, the thorium and ^{233}U are recovered together by coextraction from an acid deficient feed into a concentrated TBP solution in hydrocarbon diluent. Unlike the dilute 5 percent TBP solution used in one version of the Thorex process, the concentrated TBP solution exhibits no selectivity among the actinides, and extracts both thorium and uranium. The acid deficiency of the feed solution and also of the aluminum nitrate salting-out scrub solution represses the extraction of the fission products and the ^{232}U decay products. The thorium is selectively partitioned from the uranium by stripping the thorium out of the organic phase with dilute nitric acid, which serves as a salting-out agent for the uranium, to hold it in the organic phase. Then the uranium is stripped from the organic phase with water.

A simplified schematic of the Thorex process, indicating both head-end and tail-end processing, is shown in Fig. 10.3. The design of the thorium-uranium fuel may or may not be subjected to a voloxidation process. The schematic also accommodates HTGR thorium-uranium carbide fuel, which may be subjected to head-end fluidized bed oxidation, as indicated in the schematic, or may be treated by the grind-leach procedure. In preparation for Thorex extraction, the dissolved spent fuel is adjusted to a 0.2 N acid-deficient feed solution containing 1.5 M thorium nitrate and 0.65 M aluminum nitrate, with approximately 0.06 M fluoride ion and from 0.3 g/l to 1.2 g/l uranium as uranyl nitrate. In this application of the Thorex process, the cooldown time of the spent fuel is long enough that all of the ^{233}Pa can be considered to be converted into ^{233}U .

Figure 10.3. Thorex Process Schematic.

By means of a 43.5 percent solution of TBP in Amsco (a proprietary *n*-dodecane diluent) and an acid-deficient 0.5 M aluminum nitrate scrubbing solution, both thorium and uranium are extracted from the acid-deficient feed, leaving the fission products and the ²³²U decay products, except ²²⁸Th, in the aqueous phase. This aqueous raffinate is evaporated to recover the nitric acid, and the concentrate of fission products and decay products is sent to waste. At high concentration of thorium in the TBP solution in Amsco, a third liquid phase forms which interferes with the coextraction. This problem can be overcome by replacing the *n*-dodecane Amsco diluent with decahydronaphthalene (decalin) as the solvent for the TBP.

The organic phase, containing both the thorium and uranium, is subjected to selective stripping. First the thorium is stripped from the organic phase with 0.25 M aqueous nitric acid. Then the uranium is stripped from the thorium-free organic phase with water. In the schematic of Fig. 10.3, the recovered uranium is subjected to tail-end purification by percolation through silica gel to remove residual ⁹⁵Zr, ⁹³Nb, and ¹⁰⁶Ru. In addition, the uranium solution may undergo ion exchange with Dowex 50 resin to remove residual traces of thorium including ²²⁸Th which is in the decay chain of ²³²U along with trace amounts of fission products and other ²³²U decay products. The

partitioned solutions of thorium and ^{233}U are concentrated for storage by evaporation and the recovered nitric acid is recycled to the process.

Removal by ion exchange of ^{228}Th , the first decay product of ^{232}U , allows any subsequent members of the ^{232}U decay products which are not retained on the resin to decay out without rapid regrowth. This results in a temporary increase in the decontamination factor of the ^{233}U product. In the special case of ^{233}U produced by short-time irradiation of ^{232}U of low ionium (^{230}Th) content with thermal neutrons a production reactor, the ^{232}U content may be held below 10 ppm. At this low ^{232}U concentration, the ion exchange elimination of ^{228}Th and its subsequent ^{232}U decay products from the ^{233}U product solution reduces the gamma activity level of the ^{233}U to a very low value, and it also results in a comparatively slow regrowth of the ^{233}U gamma radiation field. Under these circumstances the ^{233}U product can be handled for up to a month without gamma shielding for fuel fabrication (Lloyd, 1980).

In both the prebreeder and full-fledged thorium fuel cycle, there is a high concentration of ^{232}U in the ^{233}U product. As a result, the gamma-radiation field of the ^{233}U is not eliminated by the ion exchange cleanup, necessitating heavy gamma shielding and remote handling throughout core refabrication. Although tail-end purification in the Thorex process reduces the gamma-radiation field of the ^{233}U product, the gamma-field reduction in the case of the ongoing thorium fuel cycle is of short duration due to rapid regrowth of the ^{232}U decay products. Solvent extraction satisfies the main objective of the fuel reprocessing, which is the elimination of the fission product neutron poisons from the spent fuel. In view of these factors, the value of tail-end purification in thorium fuel cycle reprocessing is questionable.

(2) INTERIM ^{233}U PROCESS. The interim ^{233}U process was developed to recover ^{233}U from short cooldown-time fuel of the thorium fuel cycle by extracting the dissolved spent fuel with TBP under such conditions that only the uranium is extracted, while the thorium and protactinium remain in the aqueous raffinate, along with the products of fission and ^{232}U decay. It was intended that, after an additional cooldown period to allow conversion of ^{233}Pa to ^{233}U , the raffinate from the interim ^{233}U process would be reworked through the Thorex process to recover and partition the thorium and the built-in ^{233}U .

The simplified schematic of the interim ^{233}U process is shown in Fig. 10.4. The fuel solution obtained by dissolving the spent thorium-uranium fuel is adjusted to a 0.2 N acid-deficient feed containing 1.5 M thorium nitrate and 0.5 M aluminum nitrate, along with uranium, protactinium, fission products, decay products of ^{232}U , and the fluoride catalyst of the dissolvent. This feed solution is extracted with a

Figure 10.4. Interim Uranium-233 Process Schematic.

1.5 percent solution of TBP in Amsco, while being scrubbed with an acid-deficient 1.0 M aluminum nitrate solution. At the low TBP concentration, only uranium is extracted into the organic phase, while thorium and protactinium remain in the aqueous phase. The aqueous raffinate is sent to storage to allow the protactinium to decay to ^{233}U . Following this decay, the aqueous raffinate is put through the Thorex process to recover separately the built-in ^{233}U and the thorium.

As shown in Fig. 10.4, the organic phase containing the uranium flows from the top of the extraction column into the bottom of the stripping column where the uranium is stripped into 0.05 M aqueous nitric acid. The stripped organic extractant is recycled to the extraction column. As required, the TBP extractant is purified to free it of degradation products that interfere with its extracting capability. The uranium in the aqueous phase from the stripping column is subjected to tail-end purification, as required. The resulting solution is evaporated to yield a concentrate of the ^{233}U -uranyl nitrate product. The nitric acid from the evaporator is recycled back into the process.

(3) **HEXONE ^{233}U PROCESS.** This process is applicable for recovering ^{233}U from long cooldown-time fuel of the thorium fuel cycle by means of hexone extractant, while thorium remains unextracted in the

aqueous raffinate, along with the products of fission and of decay of ^{232}U . The hexone does not extract protactinium. Consequently, the cooldown time of the spent fuel must be long enough to convert ^{233}Pa into ^{233}U .

As indicated in the simplified schematic of Fig. 10.5, the dissolved spent $\text{ThO}_2\text{-UO}_2$ fuel is adjusted to a 0.2 N acid-deficient feed containing 1.5 M thorium nitrate and 0.1 M aluminum nitrate. Aluminum nitrate in the feed is present only to complex the fluoride catalyst the dissolvent. The thorium nitrate, which remains unextracted serves as the primary salting-out agent for the extraction of the ^{233}U . The feed enters near the middle of the extraction column and is extracted with 100 percent hexone, which flows upward from the bottom of the extraction column. A 0.2 N acid-deficient scrubbing solution of 1 M aluminum nitrate enters the top of the extraction column and flows downward to issue from the column bottom with the extracted feed solution as the aqueous raffinate. The uranium-free aqueous raffinate, which contains the thorium, fission products, ^{232}U decay products, fluoride catalyst, and the aluminum nitrate salting-out agent, is held in storage for later recovery of the thorium.

The uraniferous organic phase from the top of the extraction column passes to the bottom of the stripping column and flows upward against a 0.04 M aqueous nitric acid stripping solution. The ^{233}U is

Figure 10.5. Hexone Uranium-233 Process Schematic.

stripped from the hexone, which is recycled to the extraction column. As required, the hexone is purified to free it of degradation products that interfere with its use as an extractant. The aqueous solution of the ^{233}U from the bottom of the stripping column is evaporated to yield the concentrated 233-uranyl nitrate product. The nitric acid from the evaporator is recycled back into the process.

3.2 Nonaqueous Separation Processes

Nonaqueous separations comprise two types of processes: halide volatility and pyrochemical. With the notable exception of the fluoride volatility process, the nonaqueous separations, despite effectively eliminating the significant fission-product neutron poisons, do not yield as high beta-gamma decontamination factors as the aqueous separations. However, in reprocessing spent fuel of the thorium fuel cycle, a relatively low decontamination factor is not a matter of concern, provided that the reprocessed fuel is freed of the neutron poisons that would interfere with breeding. Even if the reprocessing of spent $\text{ThO}_2\text{-UO}_2$ fuel yielded a high decontamination factor, the rapid regrowth of the gamma radiation field of the recovered ^{233}U , due to the buildup of ^{232}U decay products, would require remote handling.

The nonaqueous separation processes have the following advantages:

1. The nonaqueous separations are carried out under nonmoderating conditions. Thus, criticality problems associated with aqueous reprocessing are eliminated.
2. The nonaqueous process reagents are, in general, inorganic and thus subject to less radiation damage than the organic extractants used in aqueous reprocessing.
3. The nonaqueous separations are simple in concept and require few reprocessing operations.
4. The wastes from nonaqueous separations are solid and of small volume. Thus, the problem of disposing of radioactive wastes from nonaqueous separations is less severe than that of disposing of liquid radioactive wastes from aqueous fuel reprocessing.

By contrast, nonaqueous separation processes have the following disadvantages:

1. Nonaqueous separations are carried out at elevated temperatures under highly corrosive conditions. Consequently, the materials-construction problems in nonaqueous separations are more severe than in aqueous separations.
2. Although abundant data are available on the performance of large scale solvent extraction operations in reprocessing nuclear fuels, no such data are available on nonaqueous separations. None of the nonaqueous separations has progressed beyond the pilot plant stage, and few have progressed as far as pilot plant operation. A single

exception to this is the direct production and handling of uranium hexafluoride, with which there is considerable experience from large scale isotopic separations in diffusion plant operations.

(a) *Halide Volatility Separations*

From the first recognition of the need to reprocess spent reactor fuel, effort has been devoted to developing actinide separation processes based on the volatility of the chlorides and fluorides of the heavy elements. Underlying this developmental effort is the industrial experience with fractional distillation in separating volatile materials. Table 10.2 lists the melting-point and boiling-point data for the chlorides and fluorides of elements significant in reprocessing spent fuels of the thorium fuel cycle, including the driver fuel of the prebreeder cycle.

(1) CHLORIDE VOLATILITY SEPARATION. There are far more volatile metal chlorides than volatile metal fluorides. Thus, more of the fission products and structurals (e.g., zirconium, trivalent iron, and tetravalent tin) can be volatilized as chlorides than as fluorides. The numerous volatile transition metal chlorides yield overlapping vapor pressure ranges with the actinide chlorides. As a result, separation of the uranium as a mixture of volatile uranium pentachloride and volatile uranium hexachloride is hindered by the overlapping ranges of the volatile structural and fission product chlorides.

Laboratory-scale experimental studies (Gens, 1965; Hirano and Ishihara 1969; Ishihara and Hirano, 1965; Hariharan et al, 1969) have been carried out on the recovery of uranium from spent oxide fuels by chloride volatility separation. The fuels were chlorinated at elevated temperature by carbon tetrachloride vapors mixed with chlorine and an inert gas, or by carbon tetrachloride vapors mixed only with an inert diluent gas, to yield volatile pentachloride and hexachloride of uranium and the volatile chlorides of some of the fission products and structurals. The volatilized chlorides were adsorbed at reduced temperature on barium chloride or alumina, where the chlorides of the fission products and structurals were held. The uranium was recovered by desorbing it from the barium chloride or alumina at elevated temperature in a stream of the chlorine-containing reactant gas. The hot reactant gas prevented disproportionation of the uranium chlorides, and it maintained volatility of the chloride by keeping the uranium at its higher valency. The nonvolatile thorium tetrachloride formed by the chlorination reaction remained with the nonvolatile chlorides of the fission products (alkali metals, alkaline earths, and lanthanides) and of the structurals. These experimental results indicate the possibility of employing chloride volatility as the basis for actinide separation in reprocessing spent fuel of the thorium

TABLE 10.2—MELTING POINT AND BOILING POINT DATA OF SIGNIFICANT CHLORIDES AND FLUORIDES

Compound	Chlorides		Compound	Fluorides	
	M. Pt. (K)	B. Pt. (K)		M. Pt. (K)	B. Pt. (K)
UCl ₃	1115	1683	UF ₃	~1775	decomposes
UCl ₄	863	1065	UF ₄	1233	1693
UCl ₅	800	<975	UF ₅	<675	---
UCl ₆	451	645	UF ₆	338	329(S)
PaCl ₅	574	---	PaF ₅	---	<725
PuCl ₃	1306	2313	PuF ₃	1698	2550
ThCl ₄	1043	1194	PuF ₄	1310	---
ThCl ₅	710	604(S)	PuF ₆	324	335
ThCl ₆	483	519	ThF ₄	1383	---
MoCl ₂	1003	1673	ZrF ₄	1191	1176(S)
MoCl ₅	467	541	NbF ₅	290	308
MoCl ₆	---	630(S)	MoF ₆	290	308
SbCl ₃	346	494	SbF ₃	565	592
Cl ₃	---	337(S)	IF ₅	282	373
eCl ₄	497	661	TeF ₄	403	557
eCl ₂	950	1299	TeF ₆	---	238(S)
eCl ₃	577	592	FeF ₂	1375	~2075
iCl ₂	1274	1246(S)	FeF ₃	~1275	~1375
oCl ₂	997	1323	NiF ₂	~1275	~1875
rCl ₃	1423	1573(S)	CoF ₃	~1475	~1575
uCl ₃	873	decomposes	CrF ₃	~1375	~1675
hCl ₃	1221	decomposes	RuF ₅	374	586
iCl ₂	520	896	RhF ₄	---	1025
iCl ₄	240	387	RhF ₅	---	>575
iCl ₂	1235	2103	PdF ₃	---	~875
Cl ₂	1146	2273	SnF ₂	>875	>1475
eCl ₃	1095	2203	SnF ₄	---	927(S)
Cl ₃	1143	2218	BaF ₂	1558	2490
			SrF ₂	1623	2733
			CeF ₃	1597	2573
			CeF ₄	1733	decomposes
			LaF ₃	1673	2573

is sublimation temperature.

el cycle. However, much developmental work remains. At present practical chloride volatility separation exists for uranium recovery from spent fuel.

As shown from the data of Table 10.2, the chlorides of metals in their higher valence states are generally volatile, while the chlorides of metals in their lower valence states are generally nonvolatile. Chlorinating $\text{ThO}_2\text{-UO}_2$ fuel with carbon tetrachloride or chlorine oxidizes uranium to its higher valence states to yield volatile uranium pentachloride and volatile uranium hexachloride. Zirconium, iron, molybdenum, and tin are also oxidized by the chlorination to their higher valence states, where they form volatile chlorides which distill with the volatile uranium chlorides. On the other hand, hydrochlorination, if it attacks $\text{ThO}_2\text{-UO}_2$ at all, reduces the uranium of the fuel from tetravalency to trivalency, thus forming nonvolatile uranium trichloride. However, hydrochlorination still converts the zirconium of the Zircaloy cladding to volatile zirconium tetrachloride. The Zircex process and the salt melt hydrochlorination process, applicable for removing Zircaloy cladding from thorium-uranium fuel, are based on the hydrochlorination reaction. In both these processes, the Zircaloy cladding is removed by hydrochlorinating its zirconium to volatile zirconium tetrachloride, which is removed by distillation. In the Zircex process, the $\text{ThO}_2\text{-UO}_2$ fuel is not attacked, but remains as the nonvolatile oxide mixture. In the salt melt hydrochlorination process the uranium of the $\text{ThO}_2\text{-UO}_2$ fuel does undergo attack, being reduced by the hydrochlorination to yield nonvolatile uranium trichloride.

(2) FLUORIDE VOLATILITY PROCESS. The development of the fluoride volatility process has received concentrated efforts for its potential application to reprocessing fast breeder fuels (Jonke et al, 1969; Cathers et al, 1962; Cathers et al, 1958; McNeese, 1963; Steindler et al, 1969). The recovery and decontamination of uranium by the fluoride volatility process depend upon the unique volatility characteristics of uranium hexafluoride, which sublimates at 329 K under atmospheric pressure and has its triple point at 337 K and 0.15 MPa. Also, uranium hexafluoride reversibly forms an adduct with crystalline sodium fluoride. The adduct, formed at temperatures up to 300 K, dissociates at 673 K in a fluorine atmosphere in accordance with the following equation:

The fluorine atmosphere is required to suppress the decomposition of the adduct by the following reaction, which would leave the uranium irreversibly adsorbed on the sodium fluoride surface:

The fluorides of other metals react irreversibly with the sodium fluoride and are not evolved by heating. This difference between the adsorption on sodium fluoride of uranium hexafluoride and other metal fluorides is exploited in purifying uranium hexafluoride.

Fluorination is normally carried out with fluorine gas, which may be admixed with nitrogen or some other inert gas. Additional fluorinating agents are bromine trifluoride (BrF₃, melting point 282 K, boiling point 399 K), bromine pentafluoride (BrF₅, melting point 213 K, boiling point 314 K), chlorine monofluoride (ClF, melting point 117 K, boiling point 173 K), and chlorine trifluoride (ClF₃, melting point 197 K, boiling point 285 K). These interhalogen fluorinating agents are more easily handled and fluorinate more smoothly than fluorine gas. The presence in the reaction mix of a group V element fluoride, e.g., SbF₅ added as Sb₂O₃, enhances the activity of the interhalogen fluorinating agent.

Of the several versions of the fluoride volatility process under development, the fused salt fluoride volatility procedure, FSFVP (Bannasch et al, 1969) and the fluidized bed fluoride volatility procedure, FBFVP (Anastasia et al, 1965; Anastasia et al, 1967; Philenskias, 1968), are best adapted to reprocessing ThO₂-UO₂ fuel. Before subjecting the ThO₂-UO₂ fuel to either of these procedures, the fuel is de-clad. In the case of Zircaloy-clad ThO₂-UO₂ fuel, the cladding can be removed by the Zirflex process, the Zircex process, the salt melt hydrochlorination process, or by dissolution in molten zinc. Alternatively, the cladding can be removed mechanically by means of the impact shearing technique (Parks et al, 1978; Winsch et al, 1980; Magan et al, 1981; Levitz et al, 1981). In this technique, the fuel is sheared into short cuts, with the cut length equal to about half of the fuel rod diameter. By this method of shearing, the fuel, which is comminuted to a powder and dislodged from the cladding hull rings, can be recovered free of the Zircaloy cladding hulls by sieving. In its comminuted state, the ThO₂-UO₂ fuel is in ideal condition for dissolution in the fused salt for FSFVP processing or for suspension as a fluidized bed for FBFVP processing. The fused salt mixture, with an optimum composition of LiF:NaF:ZrF₄ = 25:25:50 mole percent and at a temperature of 873 K, is able to dissolve the Zircaloy cladding. However, loading the fused salt with Zircaloy alters its composition and causes operational problems.

The comminuted ThO₂-UO₂ fuel, dissolved in the fused salt mixture suspended as a fluidized bed, is first hydrofluorinated with dry

hydrogen fluoride gas to nonvolatile thorium tetrafluoride and non-volatile uranium tetrafluoride in accordance with the following reactions:

The hydrogen fluoride gas, which is sparged into the fused salt or recirculated through the fluidized bed, converts the thorium to its final tetrafluoride state, but it is not able to oxidize the uranium to its highest valence state to yield the volatile uranium hexafluoride. However, because fluorinating agents are expensive and hydrogen fluoride is comparatively inexpensive, the hydrofluorination with hydrogen fluoride is carried out to satisfy economically all the fluoride requirements of the thorium and two-thirds of the fluoride requirements of the uranium. Following the hydrofluorination with hydrogen fluoride, the reaction mix is fluorinated by means of fluorine gas, admixed with nitrogen at a concentration of 50 volume percent or greater of fluorine gas, or by means of another fluorinating agent, or mixture of agents to volatilize uranium from the reaction mix as uranium hexafluoride. The following equations illustrate the reactions of the various agents in carrying out the fluorination of the uranium tetrafluoride of the reaction mix to convert it to volatile uranium hexafluoride:

The fission products that are fluorinated to volatile fluorides are volatilized along with the uranium. In general, fission products of periodic groups I, II, III (including the lanthanides), and IV (excluding germanium) form nonvolatile fluorides under the fluorinating conditions, while fission products of periodic groups V, VI, VII, and VIII form volatile fluorides. In periodic group VIII, palladium is borderline; under the fluorinating conditions it forms palladium trifluoride, which volatilizes at about 873 K. Among the actinides of inter-

est, thorium does not form a volatile fluoride; however, under proper fluorinating conditions, protactinium, uranium, and plutonium all form volatile fluorides.

Figure 10.6 is the simplified schematic of the fluidized bed fluoride volatility procedure operating on declad, comminuted thorium-uranium fuel with a cooldown time long enough to convert its ^{233}Pa content into ^{233}U . The comminuted fuel, as a fluidized bed at 873 K, is first hy-

drofluorinated with dry hydrogen fluoride gas, and then fluorinated with fluorine gas (or an alternative fluorinating agent). The uranium of the fuel is volatilized as the hexafluoride and, along with any volatilized fission products, ^{232}U decay products, and system corrosion products, is swept into the sodium fluoride absorbing column maintained at 673 K. The thorium, converted to the nonvolatile thorium tetrafluoride, remains in the fluidized bed fluorinator, along with the unvolatilized fission products, ^{232}U decay products, and fluorinator corrosion products.

In the adsorber, under proper conditions, all of the impurities in the volatilized uranium hexafluoride, except the noble fission gases and any diluent gas admixed with the fluorinating gas, are irreversibly adsorbed on the sodium fluoride crystals. Because of the very high volatility of tellurium hexafluoride (TeF_6 , sublimation temperature

Figure 10.6. Fluidized Bed, Fluoride Volatility Process Applied to Thorium-Uranium Fuel.

238 K) the sodium fluoride adsorption column should be sized to yield sufficient retention time for the flowing gas stream to ensure adsorption of the tellurium impurity. From the adsorber, the mixture of uranium hexafluoride and its fixed gas impurities flow to the condenser, which is held below the sublimation temperature (329 K) of the uranium hexafluoride. Here the uranium hexafluoride is desublimed as the solid product. The uncondensed noble fission gases and any fluorinating agent diluent gas pass through the condenser disposal. The condenser temperature is not low enough to condense any tellurium hexafluoride that may remain as an impurity in the fixed gases leaving the adsorber. This tellurium hexafluoride impurity passes from the condenser with the fixed gases and does not appear as an impurity in the uranium hexafluoride product.

The ^{233}U hexafluoride product from the fluoride volatility process is obtained in a state of high purity, free of fission products and temporarily free of ^{232}U decay products. The unvolatilized thorium (including the ^{228}Th of the ^{232}U decay chain), which remains in the form of thorium tetrafluoride in the fluorinator, retains the long-lived fission products of the alkali metals, alkaline earths, rare earths, and transition metals that do not form volatile fluorides. This undecontaminated thorium tetrafluoride residue, with a high level of fission product neutron poisons, is held for further reprocessing.

(b) Pyrochemical Separations

Pyrochemical reprocessing of spent fuels is based on the extension of metallurgical purification methods to fuel reprocessing. These purification methods include the following:

1. Metal melting under slags (synthetic or formed by self-slugging or by oxidative slugging) in which the fission product impurities are concentrated for separation from the actinide fuel metals.
2. Metal distillation to separate the fission product impurities from the actinide fuels or to separate the actinide fuels from each other.
3. Liquid metal extraction to remove fission product impurities from the molten fuel metal by extraction with an immiscible molten metal extractant, in a manner analogous to organic solvent extraction.
4. Pyrochemical redox reactions by which the oxidation state of a selected constituent of the fuel is adjusted to interconvert the constituent among the oxide, metallic, or salt (i.e., slag) states, as required. By this means, one is able to reduce selectively the actinide

fuel components and the fission products nobler than the actinide fuel components to the metallic state, while separating the less noble fission products as a molten salt slag. Then, to complete the purification, one can selectively oxidize the metallic actinide fuel components to a molten salt slag, while separating the fission products nobler than the actinide fuel components in the form of the molten metals dissolved, if required, in a suitable metal diluent.

Pyrochemical reprocessing is under development primarily for continuously reprocessing the metallic fuel of the liquid metal fast breeder reactor (LMFBR). Application of pyrochemical reprocessing to spent thorium-uranium fuel requires reduction to the metallic state of the thorium-uranium oxide fuel. A pyrochemical reprocessing procedure has been proposed for spent thorium-uranium fuel (Chiotti, 1962). Figure 10.7 presents the schematic of the proposed process. In accordance with this schematic, the pyrochemical reprocessing of $\text{ThO}_2\text{-UO}_2$ fuel is carried out in a series of six steps (the first five of which can be performed in a single properly designed vessel) as follows:

1. The Zircaloy cladding is dissolved from the sheared thorium-uranium fuel rods by means of molten Zn at 1023 K, leaving the ceramic fuel unattacked. The solution of Zircaloy in Zn is poured off, and the fuel is rinsed with molten Zn.

Figure 10.7. Pyrochemical Process Schematic for Spent Thorium-Uranium Fuel.

2. To the dechlorinated thorium-uranium fuel under a molten salt bath of LiCl , MgCl_2 , MgF_2 , and MgO at 873 K is added molten Zn-3 percent Mg alloy. Thorium-uranium is reduced to the intermetallic compound (Th, U) $\text{Zn}_{8.5}$ which remains with the metal phase. The noble metal fission products also pass into the metal phase, while the alkali, alkaline earth, and lanthanide fission products pass into the salt phase. The supernatant salt phase (specific gravity ~ 2) is decanted from above the metal phase (specific gravity ~ 7.5), and the metal phase can be rinsed several times with fresh portions of the salt bath, leaving finally a fresh portion of the molten salt above the metal phase.

3. Zinc chloride is stirred into the vessel still at 873 K to oxidize the U and Th metals to the chlorides, which quantitatively pass into the salt phase, leaving the unoxidized Mo, Nb, and noble metal fission products in the metal phase. The phases are allowed to separate, and the metal phase is drained off.

4. Molten Zn-3 percent Mg alloy is stirred into the molten salt containing the U and Th as the chlorides to reduce them again to the metals. After the phases are allowed to separate, the salt phase is poured off, and the Zn-3 percent Mg alloy is distilled off at 1023 K under vacuum to leave a sponge of U-Th alloy.

5. To the U-Th sponge is added pure molten Mg, in which at 873 K the Th is highly soluble, while the U is highly insoluble. The U settles to the bottom of the vessel as metal crystals. The U is filtered out and "dried" free of Mg by distilling off the Mg at about 1023 K under vacuum. The U can be recovered in the form of the resulting metal crystals (containing about 0.4 percent Th) or the U metal can be readily converted to UO_2 by retorting in air.

6. The Th in the form of its 40 percent solution in Mg can be cast into pigs and held in storage. However, if desirable, it can be recovered as the metal (containing 0.005 percent U) by vacuum-distilling off the Mg at about 1023 K, or the Th metal can be readily converted to ThO_2 by retorting in air.

The simplicity of pyrochemical techniques favors their exploitation. However, there are still unsolved problems associated with the temperatures and highly corrosive conditions involved.

10.4 TREATMENT OF WASTES FROM REPROCESSING SPENT ThO_2 - UO_2 FUEL

10.4.1 Characterization of Reprocessing Wastes

The radioactive wastes from reprocessing spent thorium-uranium fuel are gaseous, liquid, and solid. These may be further subdivided into

low-level, intermediate-level, and high-level wastes. Assuming a cooldown time of approximately six months to allow conversion of ²³³Pa to ²³³U, the main gaseous fission product activities in the reprocessing waste are ⁸⁵Kr and ¹²⁹I, which are released from the fuel during its decladding and dissolution. Some volatilized ¹⁰⁶Ru accompanies these gases. Typical solid radioactive wastes are the end cropings, sheaths, and grids from decanning the fuel rods, the cladding metal from mechanical decladding, and the solidified zirconium tetrachloride from hydrochlorination processes used to remove the Zircaloy cladding. Solid radioactive wastes result from the fluoride volatility process and from the pyrochemical process used to remove the Zircaloy cladding.

On the basis of a 33000 MWD/tonne burnup, it is estimated (Blomeke and Bond, 1976) that each tonne of spent ThO₂-UO₂ fuel subjected to aqueous reprocessing generates 5175 liters of high level liquid waste, with a concentration of 5.6 grams of fission products per liter, plus significant concentrations of the transuranics. In addition, the aqueous wastes contain dissolved structurals and the reprocessing chemicals. The distribution of the principal nongaseous fission products in the waste at 1 year and at 20 years after reactor shutdown has been approximated (Saddington, 1961) as shown in Table 10.3. Twenty years after shutdown, the total activity of the fission product waste is only 10 percent of its total activity 1 year after shutdown. In

TABLE 10.3—PRINCIPAL RADIOACTIVE FISSION PRODUCTS
IN REPROCESSING WASTE

Isotope	Half Life	Percent Total β , γ -Activity	
		after 1 Year	after 20 Years
^{137}Ce	30 a	9.3	55
^{90}Sr	20 a	9.0	44
^{106}Ru	1 a	12.0	
^{144}Ce	279 d	51.3	
^{147}Pm	2.6 a	17.9	1
^{151}Sm	73 a	0.4	
^{125}Sb	2.7 a		
^{155}Eu	1.8 a		
		99.9	100

this discussion, it is assumed that the radioactive reprocessing wastes are generated from the spent thoria-urania fuel with a cooldown time of about one year.

10.4.2 Treatment of Gaseous Reprocessing Wastes

The gaseous wastes generated during reprocessing operations are mainly the radioactive fission gases ^{85}Kr and ^{129}I , along with significant concentrations of radioactive aerosols, including ^{106}Ru as the tetroxide. In addition, the reprocessing gas contains hydrogen, oxides of nitrogen and carbon, and acid fumes, as well as nonradioactive halogens and noble gases, along with considerable air. For every 100,000 MWD of nuclear energy, 1.74 kg of ^{129}I is generated. However, due to its long half life, the specific activity of ^{129}I is low. Thus ^{129}I is not a major contributor to the activity of the expelled gas. Nevertheless, because of the biological hazard of ^{129}I , extensive studies (Davis et al, 1976; Morgan et al, 1978) have been carried out on the removal of this isotope from the expelled gas.

In the waste treatment of the typical gas from reprocessing spent thoria-urania fuel, the gas is first compressed in a short-time holding tank where the nitric oxide, NO , of the gas reacts rapidly with oxygen to form acidic nitrogen dioxide, NO_2 . During this holding period, the gas is scrubbed with aqueous caustic soda to remove nitrogen dioxide, carbon dioxide, and the acid fumes. In addition, the caustic soda scrubbing removes most of the ^{129}I , the bromine and chlorine, and the aerosol of ruthenium-106 tetroxide from the expelled gas.

To reduce even further the concentration of ^{129}I , the gas can be subjected to one of the following processes:

1. In the silver reactor process, the gas, preheated up to 468 K, is contacted with aqueous silver nitrate in a packed tower where ^{129}I and other halogens in the gas are precipitated as the silver halides, which remain on the packing surface. By this means, 99.9 percent of ^{129}I is removed. The column packing must be guarded against exposure to ammonia fumes which, under suitable conditions, can convert silver halide on the packing surface to explosive fulminate of silver.

2. In the iodox process, the gas is passed through concentrated nitric acid to convert the iodine to a precipitate of anhydroiodic acid, HI_3O_8 . This product is separated and reacted with barium hydroxide to form highly insoluble barium iodate, as follows:

Mixed with portland cement for disposal, the insoluble barium iodate forms a grout that is stable against leaching of the iodine.

3. In the mercuric iodate process, the gas is contacted with mercuric nitrate to convert the iodine to a precipitate of mercuric iodate, Hg(IO₃)₂. This product is separated and reacted with aqueous caustic soda to yield mercuric hydroxide (insoluble in aqueous caustic soda but soluble in nitric acid) and moderately water-soluble sodium iodate. The mercuric hydroxide is converted back to mercuric nitrate and recycled. The sodium iodate is reacted with barium hydroxide to yield the highly insoluble barium iodate, which is made into a grout with portland cement for disposal.

Following removal of the iodine, the gas still contains nitrous oxide. To eliminate N₂O, the gas is passed through a catalytic converter, where the nitrous oxide and also the oxygen residual in the gas are reacted with hydrogen on a palladium catalyst to yield nitrogen gas and water vapor. The gas is freed of the water vapor by flowing it through a condenser and then through alumina dryers to result in a dewpoint of 223 K.

According to previous waste treatment procedures, the dried residual expelled gas was sent through a series of filters, the final one being a high efficiency filter capable of removing 99.99 percent of the particles in the submicron range. The filtered gas was finally discharged to the atmosphere through a stack to assure adequate dispersion of its ⁸⁵Kr content. The Nuclear Regulatory Commission mandates that the ⁸⁵Kr be held for decay. Accordingly, before dispersion of the iodine-free, low dewpoint, filtered gas to the atmosphere, the gas is passed through a cryogenic absorber-distillation system, cooled by liquid nitrogen, where the ⁸⁵Kr is separated and compressed into storage tanks and held for decay. The remainder of the treated and filtered gas is then released to the atmosphere.

0.4.3 Treatment of Liquid Reprocessing Wastes

Liquid reprocessing effluents are generally collected separately as low-level, intermediate-level, and high-level wastes. The low-level liquid wastes are collected in large volumes, tens of thousands of liters per day. These low-level wastes have extremely low solute concentrations (mainly water hardness salts) and have beta-gamma activity concentrations of only fractions of a millicurie per liter. The intermediate-level liquid wastes are of smaller volumes but of greater solute concentrations than the low-level liquid wastes, and have

beta-gamma activity concentrations in the range of millicuries per liter. The dissolved salt content of intermediate-level liquid wastes is normally too high for ion exchange cleanup. The high-level liquid wastes are smallest in amount, a few thousand liters per day, but are very high in solute concentration and in beta-gamma activity concentration, which may range as high as several hundred curies per liter. In treating the liquid reprocessing wastes, it is usual to concentrate the intermediate-level liquid wastes by evaporation. The concentrate is handled as high-level liquid waste and the condensate as low-level liquid waste. Thus, for liquid reprocessing waste treatment purposes, the treatment procedures are generally devised for low-level and high-level liquid wastes only.

(a) Low-Level Liquid Reprocessing Waste Treatment

The low-level liquid reprocessing wastes consist largely of water not used in the reprocessing proper, but which may become contaminated under abnormal or accidental conditions. Large volumes and very low concentrations of solute and activity characterize these wastes. The treatment procedures for the low-level liquid reprocessing wastes must be economically applicable to the large volumes, but are required to have only moderate decontaminating effectiveness.

The various processes used in treating the low-level liquid reprocessing wastes are:

1. Disposal to the earth or, with the required proper dilution, to a body of water, without prior treatment or retention.
2. Retention in lagoons to allow time for the activity to decay before discharge to the environment.
3. Bacteriological holdup prior to disposal to the environment. In this process the low-level liquid waste is trickled through sand filters or held for a while in oxidation ponds in contact with bacteria and algae whose metabolic processes retain the activity and allow it to decay.
4. Flocculation with alum or phosphate, followed by settling and filtration, with disposal of the clarified liquid to the environment.
5. Hydraulic fracturing, in which the liquid waste is mixed with a setting agent and injected under pressure deep into bedded rock. The injection pressure causes the liquid waste to flow into the bedding planes where it sets up and remains. This method of disposal is applicable only in special geologic locations.
6. Mixed bed ion exchange, in which the deionized effluent is released to the environment. The exhausted resin is disposed of as solid radioactive waste.

7. Adsorption on montmorillonite clay. The fission products are retained on the ion exchange sites of the clay, and the contamination-free effluent is discharged to the environment. The clay is sintered at 1273 K to fix the activity on it, and the clay is then disposed of at a burial site.

8. Electroosmosis, in which the osmosed liquid is released to the environment; the raffinate, containing the concentrated activity, is treated as high-level liquid reprocessing waste.

(b) High-Level Liquid Reprocessing Waste Treatment

The high-level liquid reprocessing wastes from aqueous reprocessing operations on spent $\text{ThO}_2\text{-UO}_2$ fuel contain practically all of the fission product activity. In the United States, approved facilities and procedures for solidifying high-level liquid wastes and final repositories for solidified storage await government resolution. Meanwhile, high-level liquid wastes are treated and stored in tanks. This section discusses high-level liquid waste storage and its projected conversion to a solid form for permanent storage.

Practically all of the high-level liquid reprocessing wastes that have been generated over the years in the United States are being held in underground tanks. Some have capacities as great as 3800 cubic meters (1,000,000 gal). Provision is made for removing the radiolytic hydrogen and oxygen gases and the decay heat. Tanks that store acidic wastes are made of stainless steel or stainless-steel-lined concrete to withstand the corrosive conditions (Legler and Bray, 1976). If the wastes are neutralized, they can be stored in less expensive carbon steel or carbon-steel-lined concrete tanks. However, precipitates in the tanks, from neutralizing the high-level wastes, form sludges that settle to the bottom. There, the sludges concentrate the fuel into a criticality problem and also intensify decay heating, which causes the liquid to bump during boiling. Decay heat can be removed in a number of ways: (1) by providing cooling coils in the tank bottom; (2) by dissipating it into the soil surrounding the tank; (3) by flowing water through a vapor space cooling coil to condense and reflux the vapor generated in the tank; (4) by letting the vapor escape from the tank, with consequent concentration of the high-level liquid waste in the tank.

Research and development studies have as their objective the reduction of high-level liquid waste to a small, solid, nonradioactive volume which can be stored indefinitely. The reduction in volume is effected by evaporation, followed by calcining in fluidizing air or in a crucible or kiln. Fixation of the radioactivity in nonleachable solid

form is carried out by incorporating the calcined high-level waste in glass, vitrified clay, portland cement, urea formaldehyde resin, asphaltum, or a metal (lead alloy) matrix. The stabilized high-level reprocessing waste in nonleachable solid form is enclosed in corrosion resistant packaging for permanent disposal.

10.4.4 Handling of Solid Reprocessing Wastes

(a) Low-Level and Intermediate-Level Solid Wastes

An accumulation of low-level and intermediate-level radioactive solid wastes at the reprocessing facility for spent thorium-uranium fuel must be disposed of by burial in accordance with established procedures. The burial of low-level and intermediate-level solid wastes, packaged in appropriate containers, may be under the earth or on its surface, depending upon the level of the activity in the containers, the method of packaging, and the requirements of the disposal site.

The low-level solid wastes include tools, gloves, cloths, plastics, and a variety of materials that become contaminated with low levels of radioactivity in the normal operation of the reprocessing facility. As required, these low-density materials are compacted during packaging for disposal.

Included among the intermediate-level solid wastes are the metallic structurals and cladding sections from mechanically decanning and decladding the spent $\text{ThO}_2\text{-UO}_2$ fuel. The intermediate-level solid wastes include also the fluorozirconate residue from evaporating Zircalox decladding solutions and the solidified zirconium tetrachloride product from removing Zircaloy cladding by the Zircex process or by the salt melt hydrochlorination process. In addition, the ion-exchange resins, the sintered-montmorillonite adsorption clays, the filtered-out alum or phosphate flocs, and the other solid materials that concentrate the activity from the low-level liquid wastes are included among the intermediate-level solid wastes.

The low-level and intermediate-level solid wastes are mixed, as required, with portland cement, urea formaldehyde resin, asphaltum, or other suitable material and enclosed in an adequately shielded metal container suitable for burial. Portland cement is the commonly used "solidifying" material in the United States, though urea formaldehyde resins are finding use. Asphaltum finds considerable use in Europe, but is being evaluated in the United States.

Transportation of the packaged low-level and intermediate-level solid waste to an off-site burial facility is in accordance with the following requirements:

1. Title 49, Parts 100 to 199 of the Code of Federal Regulations. These regulations specify the packaging, labeling, and transportation of radioactive materials.
2. Review of Department of Transportation (DOT) Regulations for Transportation of Radioactive Materials.
3. State laws and regulations and local ordinances that regulate the movement of radioactive shipments through tunnels and port eas, across bridges, and along specific roadways.

(b) High-Level Solid Wastes

In addition to the low-level and intermediate-level solid wastes, high-level solid radioactive wastes result from reprocessing spent thorium-uranium fuel and ultimately must be disposed. Regulations for the permanent disposal of high-level wastes, which are concentrates of the fission products and transuranics from the reprocessing operations, are not yet established. High-level solid wastes result from the fluoride volatility and pyrochemical spent fuel reprocessing operations and from concentrating the high-level liquid wastes from aqueous reprocessing operations. Procedures for treating these high-level solid wastes and arrangements for disposing of the treated wastes are being formulated. Tentative planning, based on accumulated data from numerous studies, calls for calcining the wastes and incorporating them in a suitable nonleachable solid form, such as in a glass or metal matrix. The wastes, thus stabilized, are sealed in corrosion-proof, shielded containers and placed in permanent underground storage in dry repositories, such as mined permian salt domes.

0.5 SUMMARY

The role of fuel reprocessing in the thorium fuel cycle was discussed in this chapter. The head-end operations comprise mechanical or chemical decladding of the thorium-uranium fuel and, in the case of aqueous reprocessing, the dissolution of the fuel and the scavenging treatments for preliminary decontamination of the fuel solution. In the case of aqueous reprocessing of the fuel after a short cooldown time, the head-end operations also include processing to separate out the ²³³Pa.

Decladding is usually preceded by shearing. If the shear cuts are short (no more than 60 percent of the cladding diameter) the powdered fuel can be removed from the cladding rings by sieving. Decladding can be effected by dissolving the Zircaloy cladding (Zirflex process) or by volatilizing it (Zircex process) from the ceramic fuel. Alternatively,

the thoria-urania fuel can be dissolved from the short-sheared cladding rings in an aqueous solution (Thorex dissolvent) amenable to solvent extraction.

Following the head-end operations, the fuel values are recovered free of fission product neutron poisons by separation operations. Solvent extraction is used to recover the fuel values from aqueous solution. Established solvent extraction processes for the $\text{ThO}_2\text{-UO}_2$ fuel are the Thorex and interim ^{233}U processes which use TBP as the extractant, and the hexone ^{233}U process, which uses hexone as the extractant. Separation and recovery of the uranium can also be effected by volatilizing it as the hexafluoride, taking advantage of the different volatilities of the fission products and of the nonvolatility of thorium fluoride. Procedures have been developed for recovering the uranium and thorium by pyrochemical separations, using molten salts and metals. However, the main separation method for the recovery of the fuel values during reprocessing is solvent extraction from aqueous solution.

Waste treatment and disposal operations associated with thoria-urania fuel reprocessing are applicable to radioactive wastes in the form of gases, liquids, and solids. Procedures are employed to avoid the efflux to the atmosphere of radioactive gases (mainly ^{85}Kr and ^{129}I). The treatment of radioactive liquids to avoid contaminating the environment is based upon the levels of the activity concentrations. Large-volume, high-level liquid waste is held in tank storage. Low-level solid wastes can be disposed of by burial. Procedures for treating high-level solid wastes for disposal in nonleachable form are being actively developed.

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554 THORIUM DIOXIDE: PROPERTIES AND NUCLEAR APPLICATIONS

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SUMMARY TABLE: PROPERTIES OF ThO₂

Except as otherwise indicated, the values tabulated below represent best-estimate experimental determinations and are for polycrystalline ThO₂, 100 percent of theoretical density, at a temperature of 298 K. Corrections for variations from these conditions, including effects of composition, are discussed in the text.

<i>Property</i>	<i>Value</i>
Lattice Properties	
Crystal Structure	Face-centered-cubic (CaF ₂ -type)
Space Group	Fm3m
Lattice Parameter (a ₀)	0.55975 nm
Interatomic Distances	
Th-Th	0.3958 nm
O-O	0.2799 nm
Th-O	0.2424 nm
Theoretical Density (ρ)	10.00 Mg/m ³
Molar Volume (V)	26.4 × 10 ⁻⁶ m ³ /mol
Lattice Energy (U) at Zero K	-10096 kJ/mol
Mechanical Properties	
ELASTIC PROPERTIES	
Young's Modulus (E)	249.1 GPa
Shear Modulus (G)	96.9 GPa
Bulk Modulus (K)	192.8 GPa
Poisson's Ratio (μ)	0.285
Knoop Hardness Number (for 95% TD)	700 KHN
Modulus of Rupture (S)	164 MPa for ASTM #9

Property	Value
Fracture Toughness (K_{IC})	1.07 MPa·m ^{1/2}
Mean Crush Strength (of LWBR pellets)	566 MPa
Thermal Creep Rate ($\dot{\epsilon}_s$)	$\dot{\epsilon}_s = 14.75 \sigma^{1.47} \exp\left[\frac{-404 \text{ kJ/mol}}{RT}\right] \text{ hr}^{-1} (\sigma \text{ in MPa})$
Thermal Properties	
Melting Temperature (T_m)	3640 K
Linear Thermal Expansion Coefficient (α_l)	$8.43 \times 10^{-6}/\text{K}$
Percent Linear Thermal Expansion ($\frac{\% \Delta L}{L_0}$)	$\frac{\% \Delta L}{L_0} = -0.2426 + 7.837 \times 10^{-4} T + 9.995 \times 10^{-8} T^2$
Transition Temperature (T_r)	2950 K
Debye Temperature (θ_D)	~480 K
Einstein Temperature (θ_E)	~290 K
Vapor Pressure (thorium-bearing species)	$\log P(\text{atm}) = 8.26 - \frac{35,520}{T}$
Emittance ϵ (at 10.6 μm above 1500 K)	0.9
(at 0.63 μm above 1500 K)	0.87
Thermodynamic Properties	
Heat of Formation (ΔH_f)	-1226.9 kJ/mol
Free Energy of Formation (ΔG_f)	-1169.3 kJ/mol
Heat of Fusion (ΔH_m)	90.8 kJ/mol
Heat of Sublimation (ΔH_s)	671.5 kJ/mol
Heat of Vaporization (ΔH_v)	580.7 kJ/mol
Standard Entropy (S_{298})	65.2 J/mol·K
Heat Capacity at Constant Pressure (C_p)	61.74 J/mol·K

Heat Capacity at Constant Volume (C_V)	60.79 J/mol·K
Adiabatic Compressibility (β_T)	$5.202 \times 10^{-12} \text{ m}^3/\text{J}$
Isothermal Compressibility (β_S)	$5.283 \times 10^{-12} \text{ m}^3/\text{J}$
Fracture Surface Energy (γ)	2.5 J/m ²
Surface Energy (γ) (Born-Haber cycle calculation)	1.15 J/m ²

Transport Properties

Oxygen Self-Diffusion Coefficient (D_O^S) (1484—1919 K)	$5.73 \times 10^{-6} \exp\left[\frac{-209 \text{ kJ/mol}}{RT}\right] \text{ m}^2/\text{s}$
Thorium Self-Diffusion Coefficient (D_T^S) (2123—2323 K)	$3.5 \times 10^{-5} \exp\left[\frac{625.5 \text{ kJ/mol}}{RT}\right] \text{ m}^2/\text{s}$
Uranium Diffusion in ThO ₂ (D_U^T) (1913—2473 K)	$5.0 \times 10^{-5} \exp\left[\frac{-627.6 \text{ kJ/mol}}{RT}\right] \text{ m}^2/\text{s}$
Surface Diffusion Coefficient (D_S) (1873—2773 K)	$5.21 \times 10^5 \exp\left[\frac{-593.7 \text{ kJ/mol}}{RT}\right] \text{ m}^2/\text{s}$
Thermal Diffusivity (α)	$6.2 \times 10^{-6} \text{ m}^2/\text{s}$
Thermal Conductivity (λ)	14.52 W/m·K and 2.03 W/m·K at 2950 K
Electrical Conductivity (σ)	0.05 S/m at $P_{O_2} = 1 \text{ atm}$ at 1273 K
Ionic Conductivity (σ_{ionic})	0.003 S/m at $P_{O_2} = 10^{-12} \text{ atm}$ at 1273 K
Thorium Transport Number (t_{Th})	10^{-7}
Oxygen Transport Number (t_O)	1.0 at $P_{O_2} = 10^{-12} \text{ atm}$ at 1273 K

Property	Value
Optical Properties	
Refractive Index (n)	2.105 at 589 nm wavelength
UV Absorption Edge	213 nm (5.82 eV)
Magnetic Susceptibility (χ_m)	$-15 \times 10^{-6}/\text{mol}$

Appendix B

CONVERSION TABLE

This work has adhered to SI units for the most part. Some exceptions have been made, such as in figures reproduced directly from original sources. No attempt is made in the following table to provide a complete set of conversion factors either to, or from, all SI units. Only those used most frequently in this book are included.

<i>To convert from</i>	<i>to</i>	<i>multiply by</i>
atmosphere	pascal (Pa)	1.013×10^5
bar	pascal (Pa)	1.0×10^5
fission unit	10^{20} fissions/cm ³	1
	percent burnup (pure ThO ₂)	0.438
	MWD/MTM	4072
GPa (gigapascal)	psi	0.145×10^6
	kilobars	10
	dyne/cm ²	10^{10}
J (joule)	cal	0.239
J/mol·K	cal/mol·K	0.239
kPa (kilopascal)	atmosphere	9.87×10^{-3}
MPa (megapascal)	ksi	0.145
Mg/m ³	g/cm ³	1
N (newton)	dyne	10^5
	angstrom	10
psi	pascal (Pa)	6.895×10^3
TPa·s (terapascal second)	psi·hr	40290
	poise	1×10^{-8}
W/m·K	cal/cm·s·°C	0.239×10^{-2}
	Btu/hr·ft·°F	0.577
eV/atom	kJ/mol	96.488
eV (energy)	nm (wavelength)	divide 1239.85/eV

GENERAL PHYSICAL CONSTANTS

Gas Constant $R = 8.314 \text{ J/mol}\cdot\text{K}$

Planck's Constant $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

Avogadro's Number $N = 6.023 \times 10^{23}/\text{mol}$

Boltzmann's Constant $k = 1.38 \times 10^{-23} \text{ J/K}$

Elementary Charge $e = 1.602 \times 10^{-19} \text{ C}$

INDEX

A

- Absorptance, 99
- Absorption
 - bands in ThO_2 , 86
 - coefficient, 99
 - cross section (see Cross section, absorption)
 - edge, ultraviolet, 89, 91, 95, 558
 - of photons, 294
 - peaks in ThO_2 , 88
 - spectra
 - of ThO_2 , 88
 - of $\text{ThO}_2\text{-UO}_2$, 92
 - of UO_2 , 93
- Acoustic mode, 207
- Actinium series, 26, 78, 480
- Activation energy
 - for diffusion, 246—252
 - of oxygen in ThO_2 , 246
 - of oxygen in UO_2 , 246
 - of oxygen in PuO_2 , 246
 - of thorium in ThO_2 and $\text{ThO}_2\text{-UO}_2$, 252, 335
 - of uranium in ThO_2 and $\text{ThO}_2\text{-UO}_2$, 252, 335
 - for electrical conductivity, 285—288
 - of doped ThO_2 , 285
 - of ThO_2 , 285, 288
 - of $\text{ThO}_2\text{-UO}_{2+x}$, 288
 - fission gas diffusion, 499
 - for formation of a Frenkel pair, 84, 248
 - for formation of Schottky defects, 84, 174
 - for grain-boundary diffusion from sintering kinetics, 413
 - for ionic conductivity, 283
 - for n-type conduction, 283
 - for p-type conduction, 283
 - for steady-state creep
 - in ThO_2 , 337
 - in UO_2 , 340
 - for volume diffusion from sintering kinetics, 413
- Active powder, 361, 412
- Activity coefficients
 - for UO_{2+x} in $(\text{Th,U})\text{O}_{2+x}$, 222
 - for PuO_{2-x} in $(\text{Th,Pu})\text{O}_{2-x}$, 224
- Additives, as sintering aids, 153
- Adsorboluminescence, of doped thoria, 95
- Adsorption
 - heat of (see Heat)
 - of CO_2 on ThO_2 , 236
 - of water vapor on ThO_2 , 234—236
- ADU process, 361
- Advanced Water Breeder Applications (AWBA), 19, 401, 438, 455, 494, 496
- Agglomeration, 419, 420
- Aliovalent ions
 - additions to ThO_2 , 124, 146—155
 - as dopants, 94—96
 - as impurities, 88, 89, 267, 276
- Alpha
 - decay, 3, 27, 510
 - particles, radiation damage from, 439, 440
 - ray spectrometry, 251, 254, 257
- Aluminum, as cladding material, 513
- AM-350, as LWBR grid material, 14
- Ambipolar (see Thermal conduction)
- Ammonium diuranate, 361
- Anharmonicity, lattice, 76
- Anion
 - interstitials, 84
 - vacancies, 84
- Anisotropy factor, 69, 319—321
- Annulus, of $\text{ThO}_2\text{-UO}_2$, microstructure of, 438
- Antiferromagnetism, UO_2 at low temperatures, 109
- Aqueous reprocessing, fuel dissolution for, 521, 522
- Athermal
 - creep, 333—336
 - impurity contribution to thermal conductivity, 293
- Atomic
 - bonding, 77, 113

Atomic—Continued

- mass, 25, 72, 476
- number, 25, 126, 476
- radii, 77, 125, 147
- structure, 80, 81

B

- Ball milling, 371, 372
 - as source of impurities, 397, 398
 - to increase tap density, 379, 381
- Band gap, 89, 295
- Barn, 30
- Beta decay, 327, 510
- Binary compounds of thorium dioxide, 156, 157
- Binary phase diagrams (see Phase diagrams)
- Binding energy per nucleon, 43
- Bismuth 212, decay scheme for, 29
- BISO fuel elements, 12
- Blanket modules, 13
- Bohr magneton, 109
- Boiling point, estimated for ThO_2 , 187
- Bonding, 77, 113
 - covalent, 79, 144
 - ionic, 78, 79, 113, 144
- Bond strength, 113
- Born-Haber cycle, 82
- Boron, as burnable poison, 5, 13
- Bragg angles, 73
- Bravais lattices, 72
- Breeding, 1, 16, 24, 437
- Brittle fracture, 350, 355
- Brouwer diagram, 268, 269
- Bulk
 - density, 2, 19, 113, 152, 366
 - modulus, 320—329, 357, 555
 - viscosity, 470
- Burgers vector, 86
- Burnup, maximum in LWBR fuel, 15
- Boiling water reactor (BWR), 5

C

- CaF_2 crystal structure, 71, 74, 79, 89, 113, 485
- Canadian Deuterium Uranium (CANDU) Reactor, 18
- CaO
 - as dopant in ThO_2 , 85, 94, 278
 - as sintering aid for ThO_2 , 153
 - effect on electrical conductivity of ThO_2 , 280, 281
 - solubility in ThO_2 , 153, 154

- Capture cross section (see Cross section)
- Carbowax, as binder, 419
- Center temperature, 503
- Central void, 445, 503
- Cesium release, 480, 485, 488, 499
- Charge carriers, 264
- Chemisorption, of water vapor on ThO_2 , 235
- Cladding
 - removal of, for fuel reprocessing, 514—520
 - Zircaloy, for ThO_2 - UO_2 fuel, 5, 14, 20
- Coefficient of thermal expansion (see Thermal expansion)
- Cohesive energy (see Lattice energy)
- Color centers, 85, 95
- Columnar grains, 443—445
- Comminution processes, 372
- Compatibility behavior, 232
- Compressibility
 - adiabatic, 202—204, 557
 - isothermal, 202—204, 557
- Compton scattering, thorium cross section for, 66
- Conductance
 - electrical (see Electrical conductance)
- Conductivity
 - electrical (see Electrical conductivity)
 - thermal (see Thermal conductivity)
- Congruent
 - melting, 181
 - vaporization, 183, 184
- Conversion ratio for near-breeders, 24
- Coordinate system
 - center-of-mass, 33
 - laboratory, 33
- Coordination number, 71, 125, 143
- Coring of pellets
 - measures taken to prevent, 424
 - origin of, 424
- Correlation factor, in diffusion, 289
- Covalent bonding (see Bonding, covalent)
- Creep
 - athermal, 470
 - compressive, 333, 334
 - deformation, 333—337
 - diffusional, 335
 - effect of CaO additions on creep of ThO_2 , 338
 - effect of composition on creep of ThO_2 , 337, 338
 - effect of grain boundaries on creep of ThO_2 , 336
 - fission-induced mechanism for, 469, 470, 474

Creep—Continued

- in-pile, of UO_2 and $\text{ThO}_2\text{-UO}_2$, 470
- Nabarro-Herring, 335
- radiation-induced, 469—472
- steady state, 334, 336
- thermal, 335, 556

Cross section

- absorption, 31
- ssion, 45, 47
- neutron capture, for
 - ^{233}Pa , 30—34, 44
 - ^{239}Pu , 30—34, 44
 - ^{241}Pu , 30—34, 44
 - ^{233}U , 30—34, 44
 - ^{235}U , 30—34, 44
- neutron scattering, elastic, 55, 61
- neutron scattering, inelastic, 55, 60
- photon-nucleus reaction, 65
- resonance capture for ^{232}Th , 34, 36
- thermal capture for ^{232}Th , ^{238}U , 34, 35
- thorium-gamma ray reactions, 62
- versus energy, 41, 46, 47

Crystallite, definition of, 393

Crystallite size, measurement of, 393—395

Crystals

- growth of, 377, 378
- structure of, 70, 81
- CsBr , 480, 499
- CsI , 480, 499
- cube directions, 330, 331, 344
- Curie constant, 105, 112
- Curie-Weiss law, 105, 110

D

Darken equation, 244

Debye temperature, 207—209, 293, 556

Debye-Waller factor, 76

Damping, 514

Decay chains, 26

Declassing, 514—520

by chemicals, 517—520

by shearing, 515, 516

Defected fuel rods

- behavior of, 439, 440, 456—462, 480
- neutron radiographs of, 458, 460

Defects

- anti-Frenkel, 82, 83, 265
- concentration of, 94
- electronic, 265
- energies of formation of, 84, 174, 248
- Frenkel, 77, 83
- impurity, 85
- induced by irradiation, 85

Defects—Continued

- interstitial, 83
- ionic, 265
- line, 86
- notation for, 265, 267
- point, 83
- Schottky, 83

Degassing of pellets, 425

Delayed neutron data

- for fissile isotopes, 50
- for ^{232}Th , 49
- for ^{238}U , 49

Delayed neutrons, energy spectra for, 45,

54, 56

Densification

- and sintering, 411
- and swelling at low temperature, 450—455
- in-reactor, 445, 453
- mechanistic models for, 340, 358, 445—453

Densities of $\text{ThO}_2\text{-UO}_2$ solid solutions,

- 113—180
- as functions of temperature, 181

Density

- bulk, of powders, 379
- change with temperature, for
 - ThO_2 , 181
 - UO_2 , 181
- tap, of powders, 379
- theoretical, for
 - ThO_2 , 72—74, 129, 379, 555
 - UO_2 , 74, 379

Desintering, 416

Diamagnetism, 71, 104, 110

Diffraction

- neutron, 75
- X-ray, 72, 83, 122, 142

Diffuse transition, 69, 85, 190, 191

Diffusion

- apparent, 244
- chemical, 244
- defect, 244, 474
- extrinsic, 244, 248
- grain boundary, 244, 259
- inter, 244
- intrinsic, 244, 247, 248
- lattice, 244
- of actinides in ThO_2 and $\text{ThO}_2\text{-UO}_2$, 259, 335
- of oxygen in ThO_2 , 245—250
- of thorium and uranium in ThO_2 , 251, 254, 255, 335
- of thorium and uranium in $\text{ThO}_2\text{-UO}_2$, 257—259, 335

Diffusion—Continued
 self or tracer, 243, 244
 short circuit, 243, 253, 259
 surface, 244, 261—264
 thermal, 245
 volume, 245, 253
 Diffusion coefficient
 apparent, 253
 bulk, 244
 effect of atmosphere on, 249
 effect of grain boundaries on, 249
 for oxygen in ThO_2 , UO_2 , and PuO_2 , 246
 for thorium in ThO_2 and $\text{ThO}_2\text{-UO}_2$, 252
 for uranium in ThO_2 and $\text{ThO}_2\text{-UO}_2$, 252
 grain-boundary, 260
 lattice, 244
 self, 244
 surface, 244, 261—264
 volume, 244
 Diffusivity path, 243
 Dilatometric measurements of thermal expansion
 of ThO_2 , 169, 170
 of $\text{ThO}_2\text{-UO}_2$, 175
 of UO_2 , 174
 Dilute solution model for electrical conductivity, 265—267
 Dimensional
 changes, 438, 439, 451
 stability, 10, 19, 69, 445, 503
 Disintegration rate of ^{208}Tl , 32
 Dislocations, 86, 335, 336, 411, 417, 492, 493, 497—503
 Dislocation term in thermal conductivity expression, 298, 299
 Disproportionation reactions for
 CO, 403
 ThO, 122
 U^{+4} in UO_2 , 301
 Dissolution reactions, 232
 Doppler broadening, 33
 Dry pressing, 397, 399, 420, 421
 Duplex fuel pellets, 401, 438, 456

E

Effusion measurements, 183
 Einstein temperature for ThO_2 , 209, 556
 Elastic
 constants
 of single crystals of ThO_2 and UO_2 , 320

Elastic—Continued
 of polycrystalline ThO_2 and UO_2 , 321—325
 moduli, temperature dependence of, 322, 323, 328, 329
 properties, 320—329
 Electrical conductance
 of ThO_2 , vs O_2 partial pressure, 277
 Electrical conductivity
 and defect equilibria, 264—269
 and diffusion, 288—290
 as function of oxygen partial pressure, 272, 274, 275, 279
 in pure and doped ThO_2 , 270—285
 ionic, of $\text{ThO}_2\text{-Y}_2\text{O}_3$ and $\text{ThO}_2\text{-CaO}$, 274, 280, 281
 n-type, 264, 265, 276, 280
 of ThO_{2-x} , 285—287
 of $\text{ThO}_2\text{-UO}_{2+x}$, 285—287
 of UO_2 , 285—287
 p-type, 264, 265
 total AC, vs O_2 partial pressure and fugacity, 283, 284
 Electrolyte, use of ThO_2 in galvanic cells, 2
 Electron
 configuration, 70, 80, 113
 shell, 86, 113
 Electronic contribution to thermal conductivity (see Thermal conduction)
 Elk River Reactor, 5
 Ellingham plot, 227, 228, 480
 Emissivity (see Emittance)
 Emittance
 of ThO_2 above 1500 K, 103, 556
 of $\text{ThO}_2\text{-CeO}_2$ solid solutions, 101
 spectral, as a function of wavelength for thorium, 102
 total, of polycrystalline ThO_2 vs temperature, 100
 Energy
 band gap, 89
 spectra
 of delayed neutrons, 53
 of prompt neutrons, 52
 yield from fission reactions, 51
 Enthalpy
 anomaly, effect on thermal conductivity, 311
 assessments of UO_2 data, 188—192
 excess at high temperatures, 189—192
 low-temperature data for ThO_2 , 192
 measurements for ThO_2 , 192—196

Enthalpy—Continued
 measurements for $\text{ThO}_2\text{-UO}_2$,
 198—201
 of fusion, 129
 of mixing, 226

Entropy, standard for ThO_2 , 556

Equilibrium oxygen pressure, 121

Eta

definition of, 23
 dependence on neutron capture cross
 section, 42
 vs neutron energy for ^{233}U , ^{235}U , and
 ^{239}Pu , 24

Eutectic temperature, 148

Expansivity (see Thermal expansion)

Extinction

coefficient, 97, 294
 constant, 97, 98

Extrusion, 401, 402

F

Face-centered-cubic, 2, 70—74, 79, 113

F-centers, 85, 95

Fertile

isotopes,
 ^{232}Th , 23
 ^{238}U , 23

materials, 23, 509

Fick's laws, 243—245

Fissile

inventory ratio, 113

isotopes,
 ^{233}U , 23, 24
 ^{235}U , 23, 24
 ^{239}Pu , 23, 24
 ^{241}Pu , 23, 24

materials, 23, 509

Fission

cross sections,
 for fissile isotopes, 47
 for ^{232}Th and ^{238}U , 46

density, 437, 447

fragment distribution, 472, 476, 479,
 480

gas bubbles, coalescence of, 474

gas release, 451, 476, 478, 491—494

correlation with grain growth, 496

effect of fuel burnup on, 495

effect of fuel density on, 491—494

effect of fission density on, 491

effect of temperature on, 491—494

product and energy yield, 50—55

product neutron poisons, 512

Fission—Continued

product yield for ^{232}Th and ^{233}U , 58, 59

products, 475—478

accumulation of, 477

chemical state of, 480—486

migration of, 487

physical state of, 479, 480

release of, 487, 488

rate, 447

reaction, energy yield from, 57

spike, formation of, 446, 470, 472

unit, 8, 15, 437

yield, 60, 489

for ^{233}U , 437, 475—478

for ^{235}U , 437, 475—478

Fluorescence

in ThO_2 , 94, 95, 113

in $\text{ThO}_2\text{-CaO}$, 94

in $\text{ThO}_2\text{-Y}_2\text{O}_3$, 96

Fluorite structure

of ThO_2 , 70—74

of UO_2 , 70—74

stability limit criterion for ionic model
 of, 78, 144

Fracture

strength, 344

surface energy, 233, 234

toughness, 440, 555

Free energy

of formation of oxides (see Gibbs free
 energies)

of formation of ThO_{2-x} and ThO_2 , equa-
 tions for, 206, 216

of mixing, 224

Freeze-Dry Process, 375, 376

Frenkel

defect, 77, 83, 189, 248, 275

disorder, 77, 84

formation energy of, 84, 248

Fuel

cycle, $\text{Th-}^{233}\text{U}$, 24

element test, 494—498

pellet fabrication, 397—402

performance,

effects of material properties on, 19,
 20

rods

defected (see Defected fuel rods)

dimensional changes due to irradia-
 tion, 455

fission gas release from, 491—497,
 503

irradiation testing of, 494—498

$\text{ThO}_2\text{-UO}_2$, 494—498

Fuel—Continued

- swelling, 450, 451
 - due to fission gas, 488—490
 - due to solid fission products, 486

Fusion

- heat of, estimated for ThO_2 , 183
- heat of, measured for UO_2 , 183
- molar entropy of, 183

G

Gamma ray spectrometry, 255

Gaussian profile, 87

Gas bubbles

- nucleation, growth, and migration of, 487—493

Generation of ^{232}U , 5, 509

Gibbs

- free energies, of formation of fission product and actinide oxides, 481
- phase rule, 120

Grain growth, 155, 339

and fission gas release, 498—502

discontinuous, 416

driving force for, 410

during sintering, 414

exaggerated, 416

inhibition of, 410

kinetics of, 410, 417, 418

normal, 327, 334, 350, 353, 410

picture framing in ThO_2 pellets, 417, 422—424

Gray absorber, 294

Grüneisen parameter for

 ThO_2 , 209—212 UO_2 , 209—212

H

Halide volatility separation, 534—540

Hardness, 344—350, 357

effect of composition, 347, 349

effect of porosity, 345—349

effect of temperature, 345—349

Knoop, 345, 346

Meyers index of, 347

Mohs, 350

Rockwell A, 345

Vickers, 345—347

Heat capacity

at constant pressure, for ThO_2 , 194, 205

at constant volume, 201—203, 205, 557

Heat capacity—Continued

at low temperatures for ThO_2 , UO_2 , and NpO_2 , 193for ThO_2 at high temperatures, 195, 205for UO_2 at high temperatures, 188, 192, 205for ThO_2 - UO_2 solutions, 200, 201

Heat of

combustion of thorium, 203

formation of ThO_2 and ThO_2 - UO_2 , 206, 556

fusion, 182, 183, 556

immersion in H_2O of ThO_2 , 234, 235sublimation of ThO_2 , 184, 185, 503, 556vaporization of ThO_2 , 184, 185, 556

Heat transfer, in oxide ceramics, 292

Heavy Water Suspension Reactor (HWSR), 18

Helium, as coolant, 10

Hertzian indentation, 233

Heterogeneous isotopic exchange, 245

Hexone- ^{233}U process, 531, 532

High diffusivity paths, 243

Hole concentration, 266

Homogeneity, 371, 372

Homologous temperature, 77, 335, 345, 347, 348, 350, 357

Hot pressing

and creep rate, 344

ex-reactor, 340—344

fabrication of low density ThO_2 pellets by, 401

in-reactor, 440, 445, 471, 472

High-temperature Gas-cooled Reactor (HTGR), 10—12, 362, 494

Huttonite, 3

Hydrofluorination, 538

Hydrosols of

 ThO_2 , 362, 374 ThO_2 - UO_2 , 374Hypostoichiometric ThO_2 ,

congruently vaporizing composition for, 118

lower phase boundary for, 118—120

Hypostoichiometry

of ThO_{2-x} , thermodynamic properties

of, 212—214

of UO_{2-x} , 214

Hyperstoichiometry

of ThO_2 - UO_{2+x} , 91, 131—136, 480of UO_{2+x} , 85, 131, 136

I

- Ideal solution, 125, 129, 480
 model of electrical conductivity, 271
- Inclusions
 as fission products, 480—486, 503
 metallic, 482, 484, 486, 503
 nonmetallic, 480, 484
 congruent vaporization, 118, 183, 184
 index of refraction, 96, 98, 113, 558
- Indian Point Reactor, 7—10
- Infrared (and near-infrared) absorption spectra
 of ThO_2 , 87, 89, 90
 of $\text{ThO}_2\text{-UO}_2$, 91—94
 of UO_2 , 89
- In-pile measurements
 of creep of ThO_2 and $\text{ThO}_2\text{-UO}_2$, 469, 470, 474
 of thermal conductivity of $\text{ThO}_2\text{-UO}_2$, 474, 489, 503
- Interatomic distances
 in ThO_2 , 72, 555
 in UO_2 , 70, 72
- Interstitial
 atoms, 74, 75, 440, 442
 oxygen, 81
 positions, 70
- Iodine, release from fuel, 488, 499—502
- Ionic
 bond, 79
 conductivity, 278
 and diffusion, 288—290
 mobility, 265, 288
 radius, 77, 125, 126, 147
 transport number, 265
- Ionicity, 78, 79
- Ionium (^{230}Th), 26
- Irradiation, effects of
 creep, 469, 470, 474
 densification of fuel, 445, 446, 451—453
 on dimensional changes of fuel rods, 451—456
 on lattice parameter of UO_2 , 441
 on melting point of UO_2 , 462—467
 on microstructural changes in fuel, 443—445, 487
 on thermal conductivity of $\text{ThO}_2\text{-UO}_2$, 474, 489
- Isopiestic techniques, 118
- Isostatic pressing, 340, 344, 401
- Isostructural compounds, 4, 69, 70, 157, 344
- Isotopes
 fertile, 23
 fissile, 23
 radioactive, 27, 28
 stable, 27, 28
- Isotopic
 abundance, 25
 exchange, 245, 247
 tracer, 245
- Isotropy, 319—321

K

- Kilorod project, 361, 362
- Knoop hardness number, 345, 346, 555
- Knudsen effusion, 183
- Kröger-Vink notation, 265, 267
- Krypton, release from fuel, 487

L

- Lambda transition, 69, 85, 190, 191
- Lambert-Beer law, 97
- Lanthanide sesquioxides, 146—155, 162
- Lattice
 cubic, 69—72
 defects and thermal expansion, 169
 defects, classification of, 82, 83
 directions, 86
 disorder
 Frenkel type, 77, 83
 Schottky type, 84
 energy, 81, 82, 555
 imperfections, 82—86
 parameter,
 of ThO_2 , 70, 74, 109, 126, 128, 555
 of $\text{ThO}_2\text{-UO}_2$ compositions, 74, 136—139
 of UO_2 , 70, 74, 109, 126, 128
 properties, 555
 thermal vibration of, 75—77
- Law of Gladstone and Dale, 122
- Leaching of thorium and uranium ores, 363
- Lethargy, 42
- Line defects, 86, 335, 336, 492, 493
- Liquidus, for $\text{ThO}_2\text{-UO}_2$ compositions, 129—131
- Loeb equation, 296
- Lorenz number, 295

Light Water Breeder Reactor (LWBR),
13—18, 437, 438, 476, 494
LWBR reference process, 361, 397—399,
407—426
Luminescence behavior of thoria-yttria
effect of oxygen vacancies on, 96

M

Magnetic
properties of ThO_2 , UO_2 , and
 $\text{ThO}_2\text{-UO}_2$, 103—113
susceptibility, 104—109
at low temperature, 107
molar, of ThO_2 , 104, 105
of oxidized $\text{ThO}_2\text{-UO}_2$, 110—113
Mass action equilibria, 138—140, 266
Mass number, 476
Maxwell-Boltzmann distribution, 31, 34
Maxwell-Eucken equation, 296
Melting
congruent, 118
volume change on, for UO_2 , 175, 176
Melting point
effect of irradiation on, for UO_2 , 182,
462, 464—467
of ThO_2 , 117, 129, 131, 180, 556
of UO_2 , 131, 181
of $\text{ThO}_2\text{-UO}_2$ solutions, 129—131, 182,
200
Metamictization, 69, 442, 474
Metastable, 122, 136
Meyers hardness index, 347
Micronizing
as comminution method, 372
of ThO_2 powder, 398, 399
of $\text{ThO}_2\text{-UO}_2$ powders, 372, 419
Microspheres
fertile, 10—12
fissile, 10—12
kernels, 10
preparation of, 361, 373, 374
Microstructural changes
effects of thermal gradients on,
443—445
due to irradiation, 461—464
during sintering, 408, 409
Migration of pores (see Pores, migration
of)
Miller indices, 72
Moderating materials, 23
Modulus
of elasticity, 326

Modulus—Continued
of rupture, 352—357, 555
Young's, 322—329, 356, 357, 555
Mohs hardness scale, 350
Molar volume of ThO_2 , 555
Molten Salt Breeder Reactor (MSBR), 18
Monazite, 4, 363
Monotectic temperature, 118
Monoxide, 121, 122
Monte Carlo technique, 35

N

Néel Temperature, 110
Nernst-Einstein equation, 288
Neumann-Kopp rule, 198
Neutrino, 50
Neutron
capture in protactinium, 40
capture cross section for fissile isotopes,
30, 42, 43
energy range, 23
diffraction measurements, 74, 75
radiographs,
of defected fuel rods, 458—460
scattering measurements, 84
yield (total) from fission vs neutron en-
ergy, 24, 48
Nonnuclear uses of ThO_2 , 2
Nonstoichiometry, 118—120, 131—143
n-type conductivity (see Electrical con-
ductivity)
Nuclear performance of thorium, 4, 5, 63,
64
Nuclide half lives for,
Thorium series, 27
Uranium series, 28

O

Octahedral
directions, 320, 331, 344
interstices, 70
Optical
absorption (see Absorption spectra)
constants, 90, 96
density, 96—99
interferometry measurements, 168
mode, 207
properties, 86—99
transmission, 96—99
Oxidation of $\text{ThO}_2\text{-UO}_2$, 131—136, 231

Oxygen

- diffusion (see Diffusion)
- displacement of ions in ThO_2 vs temperature, 75—77
- interstitials, 265
- partial pressures, 121
 - and electrical conductivity, 268
- potentials,
 - and activity coefficients, 218—226
 - and free energies of formation, 227
 - and vapor pressures, 227—230
 - for fission product oxides, 480—482
 - for ThO_{2-x} , 213, 214
 - for $(\text{Th}, \text{U})\text{O}_{2+x}$, 219—223
 - for $(\text{Th}, \text{Pu})\text{O}_{2-x}$, 222, 223
 - for UO_{2+x} , 220
- to uranium ratio, 131—136, 138—140
- vacancies, 83, 84, 118—120, 265
- singly charged, 121
- doubly charged, 121, 266

P

- ^{233}Pa , neutron capture in, 40
 - recovery of, 523
- pair production, thorium cross section for, 66
- paramagnetism, 104, 109, 111
- partial molar quantities
 - enthalpies of solution of oxygen in ThO_{2-x} , 216
 - entropies of solution of oxygen in ThO_{2-x} , 216
- particle size
 - distribution of, 391—393
 - methods of measurement of, 391—393
 - of ThO_2 powders as a function of thorium oxalate precipitation temperature, 316
 - resin, fabrication of, 373—375
- Passive Bottom Reactor, 10
- peritectic temperature, 148
- perovskite, 157
- phase
 - boundary, 118, 120, 123, 129—131, 142
 - equilibria, 138—140
 - metastable, 122, 136
 - transition, 69, 85, 132
- phase diagrams
 - $\text{PuO}_2\text{-UO}_2\text{-O}$, 141, 143
 - Th-O binary, 119, 120
 - ThO_{2-x} , 119, 120

Phase diagrams—Continued

- $\text{ThO}_2\text{-Dy}_2\text{O}_3$, 152
- $\text{ThO}_2\text{-Er}_2\text{O}_3$, 154
- $\text{ThO}_2\text{-Gd}_2\text{O}_3$, 151
- $\text{ThO}_2\text{-Ho}_2\text{O}_3$, 153
- $\text{ThO}_2\text{-La}_2\text{O}_3$, 148
- $\text{ThO}_2\text{-MgO-HfO}_2$, 161, 162
- $\text{ThO}_2\text{-Nd}_2\text{O}_3$, 149
- $\text{ThO}_2\text{-PuO}_2\text{-BeO}$, 163
- $\text{ThO}_2\text{-SiO}_2$, 159
- $\text{ThO}_2\text{-Sm}_2\text{O}_3$, 150
- $\text{ThO}_2\text{-UO}_2$, 130
- $\text{ThO}_2\text{-UO}_2\text{-SiO}_2$, 163
- $\text{ThO}_2\text{-Y}_2\text{O}_3$, 156
- $\text{ThO}_2\text{-Yb}_2\text{O}_3$, 155
- $\text{ThO}_2\text{-ZrO}_2$, 145
- $\text{ThO}_2\text{-ZrO}_2\text{-CaO}$, 160
- Phillips Ionicity, 78
- Phonon
 - conductivity, 292
 - interactions, 293
 - mean-free-path, 293
 - scattering, 293
 - wavelength, 293
- Photoelectric effect, thorium cross section for, 66
- Photofission of ^{232}Th , prompt and delayed neutron yields from, 66
- Photoluminescence of impurity-doped ThO_2 , 96
- Photon
 - conductivity, 293, 294
 - energy transfer process, 294
 - mean-free-path, 294
- Plastic
 - deformation, 330, 331, 357, 358
 - flow, 340, 350
- Point defects, 77, 82, 83
- Poisson's ratio, 203, 320, 321, 325, 329, 356, 555
- Polarons, 301
- Pores
 - closure of, as a result of irradiation, 443—445
 - migration of, 444
 - morphology of, 444
 - shape of, 444
 - size of, 334, 443—455
- Porosity
 - effect on mechanical properties, 321, 327, 332, 341, 350
 - effect on thermal conductivity, 296—298

Positive hole conduction, 265, 275

Powders

flame denitration procedure for preparation of, 377

freeze-dry process for fabrication of, 375, 376

morphology of, 381, 382

preparation of ThO₂

by pyrolysis of thermal oxalate, 364—368

by pyrolysis of other thorium compounds, 368

preparation of thorium oxalate, 364

preparation of UO₂, 369

preparation of ThO₂-UO₂, 369—373

by coprecipitation, 369—371

by mechanical mixing, 371—373

by sol-gel process, 373—375

Prebreeder, 10, 18, 437, 438

Precipitation

at grain boundaries, 336

of thorium oxalate, 364

of other thorium compounds, 368

Preferred orientation, 321

Pressurized water reactor (PWR), 13

Pretreatment in CO₂, 402—406, 421

Prompt neutrons, 45, 52

Pseudobinary, 143, 146, 149

p-type conductivity (see Electrical conductivity)

Pyrochemical separations, 540—542

Pyrolytic carbon, 10

²³⁹Pu, 23

²⁴¹Pu, 23

R

Radiant heat transfer, 293, 294

Radiation

damage, 439—442

annealing of, 439, 440

due to alpha particles, 439, 440

due to fission fragments, 440—442

transfer of heat by, 293, 294

Radii

covalent, 79

ionic, 77, 125, 126, 147

Radiothorium (²²⁸Th), 25

Radioactive decay, 27, 28

Radius ratio, 125, 144

Radon, stable configuration of, 80

Rare earth oxides, 3, 146—155, 162

Reactors

experience with ThO₂ and ThO₂-UO₂, 5—16

fast, 23

fueled with ThO₂ and ThO₂-UO₂, 5—16

new concepts of, 16—19

thermal, 23

types of, 5—19

Reduced mass, 91

Reflectance

for ThO₂, in near-infrared region, 102

for ThO₂ in visible region, 102

Reflector modules, 14

Refractive index (see Index of refraction)

Refractory nature of thorium dioxide, 4, 69

Regular solution, 225

Renninger peaks, 75

Reprocessing

effect of ²³²U on, 511, 512

of spent fuels, 509—550

waste, principal radioactive fission products in, 543

Resonance

integral, 38, 39

heterogeneous, 37

infinitely dilute, 37

peak, 32

resolved, 33

unresolved, 33

Rosseland absorption coefficient, 98

Rupture

modulus, 350—357

strength, 357

S

Scattering

amplitude for ²³²Th in neutron diffraction, 75

coefficient, 97

of neutrons, 75

of photons, 294

Scavenging, 523

Schottky

defect, enthalpy of formation of, 83, 174

disorder, 83

Secular equilibrium, 25, 26

Seed modules, 14—16

Self-shielding, 33

- Separation operations, 524—542
Shear modulus, 320—326, 357, 555
 effect of porosity on, 325, 326
 effect of temperature on, 328
Shippingport LWBR, 25, 40
Shippingport PWR, 13
Single crystals, preparation of, 377, 378
Sintering
 definition of, 408
 driving force for, 409
 kinetics of, 409
 mechanism of, 409
 of ThO_2 and $\text{ThO}_2\text{-UO}_2$, 408—418
 pore elimination during, 409, 414
 stages of, 409, 412—415
 thermodynamic aspects of (see Thermodynamics)
Slip, 330, 331, 350
Slip casting, 402
Sol-gel
 derived ThO_2 -base fuels, 331, 336
 microspheres, 12, 361, 362
 process, 361, 362, 373—375, 426
Solid solutions, 125—162
Solidus, for $\text{ThO}_2\text{-UO}_2$ compositions, 129—131
Solubility limit, for CaO in ThO_2 , 154
Solution
 departure from ideal, 125, 129, 222, 224
 ideal, 125, 129
 of oxygen in ThO_{2-x} , 117—121
 partial molar enthalpy of, 216
 partial molar entropy of, 216
 of oxygen in $(\text{Th}, \text{U}) \text{O}_{2+x}$, 131—140
 partial molar enthalpy of, 222
 partial molar entropy of, 222
 ordered, 156, 157
 regular, 225
Solvent extraction from aqueous solution, 524—533
 e group, 71, 555
 f group, 522, 523
Specific heat (see Heat capacity)
Spectra
 absorption, 86—94
 infrared, 90
 near infrared, 92, 93
 ultraviolet, 88
 visible, 88
Spectral emittance (see Emittance, spectral)
Sphere-cal process, 400
Sphere-pac process, 362
Stability
 in high-temperature water, 231, 232
 limit, criterion for ionic model of fluorite structure, 125, 144
 thermal, in air, 231
Stabilized ZrO_2 , 126
Stainless steel, as cladding material, 5, 488
Stefan-Boltzmann constant, 294
Sterotex, as die lubricant, 420
Strength
 and grain size, 357, 358
 effect of porosity on, 357, 358
Stretching force constant, 90
Structure, 2, 70—74, 79, 113
Sublimation
 behavior of $\text{ThO}_2\text{-UO}_2$ solid solutions, 186, 187
 heat of (see Heat)
Superionic state, 312
Superlattice peaks, 122
Surface
 diffusion (see Diffusion)
 energy, 232—234
 fracture, 234, 557
 of ThO_2 , 232—234
 of UO_2 , 232—234
 tension, 343, 445, 488, 489
Surface area of powders
 as a function of thorium oxalate precipitation temperature, 365
 by gas adsorption, 382
 by gas permeability, 385
 by microscopic measurements, 385
 effect of calcination temperature on, 386—388
 effect of micronizing on, 388
 effects of oxalate precipitation parameters on, 367
 estimates of by thoron emanation, 391
Susceptibility
 diamagnetic, 104, 105
 magnetic, 103—113, 558
 paramagnetic, 107—113
Swelling
 due to fission gas, 438, 442, 446, 450—455, 488—491
 due to solid fission products, 445, 450—455, 486

T

- Tellurium, release from fuel, 501
 ^{228}Th (see Radiothorium)
 ^{232}Th , as fertile isotope, 4, 23, 509
 Thermal analysis
 of calcination of thorium oxalate, 395, 396
 Thermal conduction
 ambipolar contribution to, 295, 301
 electronic contribution to, 295, 301, 307
 phonon interactions, 292, 293
 radiation contribution to, 293, 294
 temperature dependence of, 293
 Thermal conductivity
 as a function of porosity, 296—298
 effects of irradiation on, 467—469, 474, 489
 of ThO_2 , 302—312
 of $\text{ThO}_2\text{-UO}_2$, 302—312
 of UO_2 , 298—302
 estimated lower limits for ThO_2 and UO_2 , 309
 Thermal diffusivity
 of ThO_2 , 304, 308, 310
 of $\text{ThO}_2\text{-UO}_2$, 304
 Thermal expansion
 and lattice defects, 169, 174
 at low temperature for ThO_2 , 109, 110
 data for ThO_2 , 169, 170, 172, 173
 data for UO_2 , 173—177
 data for $\text{ThO}_2\text{-UO}_2$, 175
 instantaneous linear coefficient, 168
 instantaneous volume coefficient, 170, 171
 mean linear coefficient, 168, 556
 mean volume coefficient, 170, 171
 percent linear for ThO_2 and UO_2 , 178
 Thermal neutrons, 23
 Thermal radiative properties, 99—103
 Thermal shock, 355—357
 Thermoluminescence
 of pure ThO_2 , 94
 of ThO_2 doped with impurities, 94
 Thermodynamic functions for ThO_2 and UO_2 , 193, 197
 Thermodynamics of
 presintering and sintering in H_2 of ThO_2 and $\text{ThO}_2\text{-UO}_2$, 406—408
 pretreatment in CO_2 of ThO_2 and $\text{ThO}_2\text{-UO}_2$, 402—406
 $\text{ThO}_2\text{-UO}_2\text{-O}$ system, 217, 218
 Th-O system
 phase diagram of, 119, 120
 ThO
 disproportionation to Th and ThO_2 , 122
 metastability of, 121, 122
 preparation of, 121
 ThO_{2-x}
 lower phase boundary of, 119, 120
 $\text{ThO}_2\text{-CeO}_2$ solid solutions, emissivity of, 2, 101
 Thorex, 521, 522, 527—530
 Thorianite, 3, 350
 Thorite, 1
 Thorium,
 conversion to ^{233}U by neutron capture, 23
 discovery of, 1
 fuel cycle
 advantages and disadvantages of, 4, 5
 nuclear reactions of, 509—511
 isotopes, 3
 occurrence in nature, 3
 preparation of, 1
 series, 26, 27
 Thorium dioxide
 nonnuclear uses of, 2
 occurrence, 3
 preparation of, 364—369
 systems (see Phase diagrams)
 Thorium nitrate, 95
 Thorium oxalate, 72, 361
 precipitation of, 364
 pyrolysis of, 364
 Thorogumite, 4
 Thoron emanation
 use of to estimate surface areas of powders, 3, 156
 ThSiO_4 , 363
 ^{208}Tl , 26
 Transition
 first order, 190
 second order, 85, 190
 temperature
 for ThO_2 , 196, 200, 556
 for $\text{ThO}_2\text{-UO}_2$, 200
 for UO_2 , 196, 200
 Translucency, 96
 Transmittance, 97, 99
 Transmutation process, 27, 30, 467, 480
 Transpiration measurements, 214
 Transport number
 definition of, 265
 ionic, for $\text{ThO}_2\text{-CaO}$, 280, 282
 for $\text{ThO}_2\text{-Y}_2\text{O}_3$, 270, 273
 of oxygen ion in ThO_2 , 271, 557

Transport number—Continued
of thorium ion in ThO_2 , 271, 557
TRISO fuel elements, 12

U

^{232}U , as contaminant to ^{233}U , 5, 509
 ^{235}U , as fissile isotope, 23, 509
 ^{238}U , as fissile isotope, 475, 476
 ^{238}U , as fertile isotope, 4, 23, 476
Ultraviolet absorption edge, 95
Umklapp process (see Phonon interactions)
Unit cell edge of ThO_2 , 74, 113, 119, 122, 128, 146, 152, 153
Uranium
fuel cycle, 4
series, 26, 28

V

Vacancy, 17, 113, 248
Valence, 125, 127, 135, 136, 137—143
van der Waals equation, 490
Vaporization
congruent and incongruent, 120, 183, 184
heat of (see Heat)
of ThO_{2-x} at high temperatures, 120, 214—216
of ThO_2 , 183, 184
of $\text{ThO}_2\text{-UO}_2$, 186, 187
Vapor phase equilibration, 120
Vapor pressure
congruent vaporization, 120
equations for ThO_2 , 121, 183, 184
plot of, 185
Vapor species, 121
Vapour's law
Coefficients for fluorite-type oxide solid solutions, 124
discussion of, 122—125
Vickers hardness number, 345, 347
Viscosity, in reactor
of $\text{ThO}_2\text{-UO}_2$, 470
of UO_2 , 470
variation of with applied stress, 470
Vigot-Reuss-Hill approximation, 321
Voloxidation of declad thorium-urania, 520, 521
Volume change on melting, of UO_2 , 175, 176
Volume diffusion (see Diffusion)

W

Water vapor
adsorption of, on ThO_2 , 234, 235
Waste, radioactive
disposal of, 549
from reprocessing spent $\text{ThO}_2\text{-UO}_2$, 542—548
handling of, 548, 549
storage of, 549
treatment of, 542—549
Welsbach Gas Mantle, 2, 100
Wiedemann-Franz law, 295
Wiedemann's additivity law, 104

X

Xenon, release from fuel, 487
X-ray
diffraction data for ThO_2 , 73
measurements of thermal expansion, of ThO_2 , 169, 170
of UO_2 , 174
photoemission spectroscopy, 80
structure of ThO_2 , 69—72

Y

Yield (see Fission yield and Neutron yield)
Young's modulus, 120, 320—329, 356, 357, 555
effect of porosity, 325
effect of temperature, 323
of single crystal and polycrystalline ThO_2 , 320
of single crystal and polycrystalline UO_2 , 320
of $\text{ThO}_{1.997}$, 120

Z

Zircaloy cladding
aqueous dissolution of, 517, 518
attack by iodine, 501, 502
removal by gaseous hydrochlorination, 518
removal by molten zinc, 518
removal by salt melt hydrochlorination, 519
Zircon, 4, 474
Zirconium dioxide, 117, 124, 126, 143, 162, 461

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