

Table of Contents

	Page
Uranium Dioxide UO_2	1
1 Preparation	1
Overview	1
1.1 Oxidation of Uranium Metal	1
Oxidation of Uranium Metal with Oxygen	1
Oxidation of Uranium Metal with Steam	2
Oxidation of Uranium Metal with Carbon Dioxide or Carbon Monoxide	3
1.2 Reduction of Higher Uranium Oxides	4
Hydrogen Reduction of UO_3 and $\text{UO}_3 \cdot n\text{H}_2\text{O}$	6
Hydrogen Reduction of U_3O_7 and U_4O_9	8
Hydrogen Reduction of U_3O_8	9
Reduction with Hydrogen-Nitrogen Mixtures or Ammonia	10
Reduction with Methane, Carbon Monoxide, Carbon, or Sulfur	11
1.3 Reduction of Uranium Tetraoxide $\text{UO}_4 \cdot 2\text{H}_2\text{O}$	12
1.4 Reduction of Ammonium Diuranates (ADU) and Polyuranates	13
Precipitation Conditions	14
Thermal Decomposition and Reduction	15
1.5 Decomposition and Reduction of Ammonium Uranyl Carbonate (AUC)	20
1.6 Preparation From Uranium Halides, Uranium Oxide Halides, and Uranyl Halides	21
1.6.1 Preparation From Uranium Hexafluoride and Uranyl Fluoride	21
Preparation by Hydrolysis of UF_6 (ADU-type)	21
Preparation by Hydrolysis of UF_6 (AUC-type)	22
Preparation by Conversion of UF_6 to Uranyl Nitrate	24
Preparation by Hydrolysis of UF_6 via Fluoro Complexes	24
Preparation by Dry Conversion of UF_6	24
Preparation by Decomposition and Reduction of Uranyl Fluoride	29
1.6.2 Preparation from Uranium(IV) Chloride, Uranium(IV) Oxide Chloride, and Uranyl Chloride	30
1.6.3 Preparation from Uranium(IV) Oxide Bromide and Uranyl Iodide	31
1.7 Decomposition and Reduction of Other Inorganic Uranium Salts	31
1.7.1 Decomposition and Reduction of Uranyl Nitrate	31
1.7.2 Decomposition and Reduction of Uranyl Phosphate	32
1.7.3 Decomposition and Reduction of Uranyl Sulfate	33
1.7.4 Decomposition and Reduction of Uranium Sulfite	34
1.8 Preparation by Decarboxylation of Uranium Compounds of Carbonic Acids	34
1.8.1 Preparation from Uranium Formates	34
Preparation from Uranium Tetraformate and Uranium(IV) Oxide Formate	34
Preparation from Uranyl Diformate	34
1.8.2 Preparation from Uranium Acetates	35
Preparation from Uranium Tetraacetate and Uranium(IV) Oxide Acetate	35
Preparation from Uranyl Diacetate	35

1.8.3 Preparation from Uranium Oxalates	36
Preparation from Uranium(IV) Oxalate	36
Preparation from Uranyl Oxalate	36
Preparation from Uranyl Mesooxalate	37
1.9 Hydrometallurgical Preparation	37
1.10 Deposition of Coarse Crystalline UO_2 Powder	38
1.10.1 Electrolytic Deposition from Alkali Chloride Melts	38
1.10.2 Preparation of Single Crystals	40
1.11 Preparation of UO_2 Microspheres	42
1.11.1 Preparation of UO_2 Microspheres by Sol-Gel Technique	42
Preparation of UO_2 Sols	42
Precipitation of UO_2 Spheres by Gelation	46
Calcination and Sintering of Dried Spheres	48
1.11.2 Preparation of UO_2 Microspheres by Gel-Supported Precipitation or Precipitation from Uranium(VI) Solution	48
2 Production of Uranium Dioxide Pellets and Other Shapes	65
2.1 Introduction. Process Overview	65
2.2 Binders and Lubricants for Pellet Production	70
2.3 Pressing of the Pellets	73
2.4 Sintering of the Pellets	75
2.4.1 Phenomenological Description of the Parameters of Sintering	75
2.4.2 The Kinetics of Sintering	83
Fundamentals	83
Studies of the First Sintering Stage	85
Studies of the Second and Third Stages of Sintering	88
3 Crystallographic Properties	97
3.1 Phase Transitions	97
Antiferromagnetic Ordering in the Low Temperature Region	97
Transition in the High Temperature Region	98
Transition at High Pressures	98
3.2 Habit. Surface Structure	100
3.3 Crystal Structure	103
3.3.1 Crystal Structure and Bonding of Stoichiometric Uranium Dioxide	103
3.3.2 Crystal Structure of Hyperstoichiometric Uranium Dioxide	105
3.3.3 Crystal Structure of Hypostoichiometric Uranium Dioxide	110
3.3.4 Lattice Constants	112
Effects of the O/U Ratio	112
Effects of Temperature	113
Effects of Irradiation	116
3.4 Lattice Defects	118
3.4.1 Point Defects	118

	Page
3.4.2 Dislocations in UO_2	133
Dislocations in {100} Glide Planes	134
Dislocations in {110} Glide Planes	135
Dislocations in {111} Planes	135
Dislocation Loops	137
3.4.3 Stacking Faults	137
Table of Conversion Factors	139