Contents

Foreword XIII List of Contributors XV Introduction XIX

1 Estimation of Thermodynamic Data of Metallic Nanoparticles Based on Bulk Values 1

Dieter Vollath and Franz Dieter Fischer

- 1.1 Introduction 1
- 1.2 Thermodynamic Background 2
- 1.3 Size-Dependent Materials Data of Nanoparticles 4
- 1.4 Comparison of Experimental and Calculated Melting Temperatures 8
- 1.5 Comparison with Data for the Entropy of Melting 16
- 1.6 Discussion of the Results 17
- 1.7 Conclusions 19
- 1.A Appendix: Zeros and Extrema of the Free Enthalpy of Melting *G*_{m-nano} 20 References 21

2 Numerical Simulation of Individual Metallic Nanoparticles 25

- D.S. Wen and P.X. Song
- 2.1 Introduction 25
- 2.2 Molecular Dynamics Simulation 27
- 2.2.1 Motion of Atoms 27
- 2.2.2 Temperature and Potential Energy 28
- 2.2.3 Ensembles 29
- 2.2.4 Energy Minimization 30
- 2.2.5 Force Field 30
- 2.2.6 Potential Truncation and Neighbor List 31
- 2.2.7 Simulation Program and Platform 32
- 2.3 Size-Dependent Properties 33
- 2.3.1 Introduction 33
- 2.3.2 Simulation Setting 34



۷

3

- 2.3.3 Size-Dependent Melting Phenomenon 35
- 2.4 Sintering Study of Two Nanoparticles 38
- 2.4.1 Introduction 38
- 2.4.2 Simulation Setting 40
- 2.4.3 Sintering Process Characterization 40
- 2.5 Oxidation of Nanoparticles in the Presence of Oxygen 45
- 2.5.1 Introduction 45
- 2.5.2 Simulation Setting 47
- 2.5.3 Characterization of the Oxidation Process 48
- 2.6 Heating and Cooling of a Core-Shell Structured Particle 54
- 2.6.1 Simulation Method 54
- 2.6.2 Heating Simulation 56
- 2.6.2.1 Solidification Simulation 59
- 2.7 Chapter Summary 61

References 63

Electroexplosive Nanometals 67

- Olga Nazarenko, Alexander Gromov, Alexander Il'in, Julia Pautova, and Dmitry Tikhonov
- 3.1 Introduction 67
- 3.2 Electrical Explosion of Wires Technology for Nanometals Production 67
- 3.2.1 The Physics of the Process of Electrical Explosion of Wires 68
- 3.2.2 Nonequilibrium State of EEW Products Nanometals 70
- 3.2.3 The Equipment Design for *nMe* Production by Electrical Explosion of Wires Method 71
- 3.2.4 Comparative Characteristics of the Technology of Electrical Explosion of Wires 73
- 3.2.5 The Methods for the Regulation of the Properties of Nanometals Produced by Electrical Explosion of Wires 74
- 3.3 Conclusion 75 Acknowledgments 75 References 76

4 Metal Nanopowders Production 79

- M. Lerner, A. Vorozhtsov, Sh. Guseinov, and P. Storozhenko
- 4.1 Introduction 79
- 4.2 EEW Method of Nanopowder Production 81
- 4.2.1 Electrical Explosion of Wires Phenomenon 81
- 4.2.2 Nanopowder Production Equipment 84
- 4.3 Recondensation NP-Producing Methods: Plasma-Based Technology 85
- 4.3.1 Fundamentals of Plasma-Chemical NP Production 89
- 4.3.2 Vortex-Stabilized Plasma Reactor 90
- 4.3.3 Starting Material Metering Device (Dispenser) 92

4.3.4	Disperse Material Trapping Devices (Cyclone Collectors and Filters) 93
4.3.5	NP Encapsulation Unit 94
4.4	Characteristics of Al Nanopowders 95
4.5	Nanopowder Chemical Passivation 97
4.6	Microencapsulation of Al Nanoparticles 99
4.7	The Process of Producing Nanopowders of Aluminum by
	Plasma-Based Technology 102
4.7.1	Production of Aluminum Nanopowder 102
4.7.2	Some Properties of Produced Nanopowders of Aluminum, Boron,
	Aluminum Boride, and Silicon 103
	References 104
5	Characterization of Metallic Nanoparticle Agglomerates 107 Alfred P. Weber
5.1	Introduction 107
5.2	Description of the Structure of Nanoparticle Agglomerates 108
5.3	Experimental Techniques to Characterize the Agglomerate
	Structure 112
5.3.1	TEM and 3-D TEM Tomography 113
5.3.2	Scattering Techniques 115
5.3.3	Direct Determination of Agglomerate Mass and Size 117
5.4	Mechanical Stability 120
5.5	Thermal Stability 124
5.6	Rate-Limiting Steps: Gas Transport versus Reaction Velocity 126
5.7	Conclusions 127
	Acknowledgments 128
	References 128
6	Passivation of Metal Nanopowders 133
	Alexander Gromov, Alexander Il'in, Ulrich Teipel, and Julia Pautova
6.1	Introduction 133
6.2	Theoretical and Experimental Background 136
6.2.1	Chemical and Physical Processes in Aluminum Nanoparticles during
	Their Passivation by Slow Oxidation under Atmosphere
	(Ar + Air) 136
6.2.2	Chemical Mechanism of Aluminum Nanopowder Passivation by Slow
	Air Oxidation 140
6.3	Characteristics of the Passivated Particles 143
6.3.1	Characteristics of Aluminum Nanopowders, Passivated by Gaseous
	and Solid Reagents (Samples No 1-6, Table 6.7) 148
6.3.2	Characteristics of Aluminum Nanopowders, Passivated by Gaseous
	and Solid Reagents (Samples No 7–11, Table 6.7) 149
6.4	Conclusion 150

	Acknowledgments 150 References 150
7	Safety Aspects of Metal Nanopowders 153 M. Lerner, A. Vorozhtsov, and N. Eisenreich
7.1	Introduction 153
7.2	Some Basic Phenomena of Oxidation of Nanometal Particles in Air 154
7.3	Determination of Fire Hazards of Nanopowders 155
7.4	Sensitivity against Electrostatic Discharge 158
7.5	Ranking of Nanopowders According to Hazard Classification 159
7.6	Demands for Packing 160
	References 161
8	Reaction of Aluminum Powders with Liquid Water and Steam 163 Larichev Mikhail Nikolaevich
8.1	Introduction 163
8.2	Experimental Technique for Studying Reaction Al Powders with Liquid and Gaseous Water 166
8.2.1	Oxidation of Aluminum Powder with Distilled Water 168
8.3	Oxidation of Aluminum Powder in Water Vapor Flow 174
8.4	Nanopowders Passivated with Coatings on the Base of Aluminum Carbide 175
8.5	Study of Al Powder/H ₂ O Slurry Samples Heated Linear in "Open System" by STA 183
8.6	Ultrasound (US) and Chemical Activation of Metal Aluminum Oxidation in Liquid Water 184
8.7	Conclusion 194
	Acknowledgments 195
	References 195
9	Nanosized Cobalt Catalysts for Hydrogen Storage Systems Based on
	Ammonia Borane and Sodium Borohydride 199
9.1	Valentina I. Simagina, Oksana V. Komova, and Olga V. Netskina Introduction 199
9.1 9.1.1	Experimental 200
9.1.1 9.1.2	Study of the Activity of Nanosized Cobalt Boride Catalysts Forming in
J.1.2	the Reaction Medium of Sodium Borohydride and Ammonia Borane 202
9.2	A Study of Nanosized Cobalt Borides by Physicochemical
0.2.1	Methods 204 A Study of the Crystallization of Amerphane Coholt Porides Ferming
9.2.1	A Study of the Crystallization of Amorphous Cobalt Borides Forming
9.2.2	in the Medium of Sodium Borohydride and Ammonia Borane 208 The Effect of the Reaction Medium on the State of Cobalt Boride Catalysts 214

9.3	Conclusions 223 Acknowledgments 224 References 224
10	Reactive and Metastable Nanomaterials Prepared by Mechanical Milling 227 Edward L. Dreizin and Mirko Schoenitz
10.1	Introduction 227
10.2	Mechanical Milling Equipment 228
10.3	Process Parameters 229
10.4 [,]	Material Characterization 232
10.5	Ignition and Combustion Experiments 233
10.6	Starting Materials 235
10.7	Mechanically Alloyed and Metal-Metal Composite Powders 236
10.7.1	Preparation and Characterization 236
10.7.2	Thermal Analysis 242
10.7.3	Heated Filament Ignition 245
10.7.4	Constant Volume Explosion 249
10.7.5	Lifted Laminar Flame (LLF) Experiments 250
10.8	Reactive Nanocomposite Powders 254
10.8.1	Preparation and Characterization 256
10.8.2	Thermally Activated Reactions and their Mechanisms 257
10.8.3	Ignition 263
10.8.4	Particle Combustion Dynamics 267
10. 8 .5	Constant Volume Explosion 268
10.8.6	Consolidated Samples: Mechanical and Reactive Properties 271
10.9	Conclusions 273
	References 274
11	Characterizing Metal Particle Combustion In Situ: Non-equilibrium Diagnostics 279 Michelle Pantoya, Keerti Kappagantula, and Cory Farley
11.1	Introduction 279
11.2	Ignition and Combustion of Solid Materials 281
11.2.1	Ignition 281
11.2.2	Propagation 282
11.2.3	Flame Speeds 286
11.3	Aluminum Reaction Mechanisms 287
11.4	The Flame Tube 289
11.5	Flame Temperature 292
11.5.1	Background 292
11.5.2	Radiometer Setup 294
11.5.3	Infrared Setup 295
11.5.4	Linking Radiometer and IR Data for a Spatial Distribution of
	Temperature 295

11.6	Conclusions 297 Acknowledgments 297 References 297
12	Characterization and Combustion of Aluminum Nanopowders in Energetic Systems 301
	Luigi T. De Luca, Luciano Galfetti, Filippo Maggi, Giovanni Colombo, Christian Paravan, Alice Reina, Stefano Dossi, Marco Fassina, and Andrea Sossi
12.1	Fuels in Energetic Systems: Introduction and Literature Survey 301
12.1.1	An Overall Introduction to Energetic Systems 302
12.1.2	Experimental Investigations on Micro and Nano Energetic Additives 304
12.1.3	Theoretical/Numerical Investigations on Energetic Additives 305
12.1.4	Thermites 308
12.1.4.1	Nanocomposite Thermites 308
12.1.5	Explosives 311
12.1.6	A Short Historical Survey of SPLab Contributions 315
12.1.7	Concluding Remarks on Energetic Additives 319
12.2	Thermochemical Performance of Energetic Additives 319
12.2.1	Ideal Performance Analysis of Metal Fuels .319
12.2.2	Solid Propellant Optimal Formulations 320
12.2.3	Hybrid Rocket Performance Analysis 322
12.2.4 [·]	Oxidizing Species in Hybrid Rocket Nozzles 324
12.2.5	Active Aluminum Content and Performance Detriment 325
12.2.6	Two-Phase Losses 326
12.2.7	Concluding Remarks on Theoretical Performance 329
12.3	Nanosized Powder Characterization 330
12.3.1	Introduction 330
12.3.2	Facilities Used for Nanosized Powder Analyses 331
12.3.3	Tested nAl Powders: Production, Coating, and Properties 331
12.3.3.1	Production of nAl Particles 331
12.3.3.2	Coating of nAl Particles 332
12.3.3.3	Morphology and Internal Structure of nAl Particles 333
12.3.3.4	BET Area and Aluminum Content of nAl Particles 333
12.3.4	DSC/TGA Slow Heating Rate Reactivity 337
12.3.4.1	Nonisothermal Oxidation of 50 nm Powder 338
12.3.4.2	Nonisothermal Oxidation of 100 nm Powder 339
12.3.4.3	Passivation/Coating Efficiency 339
12.3.5	High Heating Rate Reactivity 341
12.3.5.1	nAl Powder Ignition Experimental Setup 341
12.3.5.2	nAl Powder Ignition Representative Results 342
12.3.6	CCP Collection by Strand Burner 344
12.3.6.1	Condensed Combustion Product Analysis 344
12.3.7	Concluding Remarks on Powder Characterization 350

.

X

Contents XI

- 12.4 Mechanical and Rheological Behavior with Nanopowders 350
- 12.4.1 Solid Propellants and Fuels: Mechanical and Rheological Behavior 350
- 12.4.2 Viscoelastic Behavior 352
- 12.4.3 Additive Dispersion 354
- 12.4.4 Rheology of Suspensions 355
- 12.4.5 Aging Effects 359
- 12.4.6 Experimental Results: Data Processing and Discussions 360
- 12.4.7 Tested Formulations 361
- 12.4.8 Uniaxial Tensile Stress-Strain Tests 362
- 12.4.9 Dynamic Mechanical Analysis 364
- 12.4.10 Rheological Tests 365
- 12.4.11 Concluding Remarks 367
- 12.5 Combustion of Nanopowders in Solid Propellants and Fuels 367
- 12.5.1 Solid Rocket Propellants 368
- 12.5.1.1 Particle Clustering Phenomena 368
- 12.5.1.2 Propellant Volume Microstructure 369
- 12.5.1.3 Steady Combustion Mechanisms of AP/HTPB-Based Composite Propellants 370
- 12.5.1.4 Transient Combustion Mechanisms 374
- 12.5.1.5 Concluding Remarks 379
- 12.5.2 Solid Rocket Fuels for Hybrid Propulsion 380
- 12.5.2.1 Tested Ingredients and Solid Fuel Formulations 380
- 12.5.2.2 Experimental Setup 381
- 12.5.2.3 Time-Resolved Regression Rate 383
- 12.5.2.4 Ballistic Characterization: Analyses of the Results 386
- 12.5.2.5 Concluding Remarks on Solid Fuel Burning 394
- 12.5.3 Chapter Summary 395 Nomenclature 396 References 400

Index 411