

# Contents

<i>Foreword</i>	<i>page</i> xv	
<i>by G. B. Olson</i>		
<i>Preface</i>	xvii	
<i>Acknowledgments</i>	xix	
<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Definition of a Few Terms Used in Computational Design of Materials	2
1.2	The Past and Present Development of Computational Design of Engineering Materials	3
1.3	The Structure of the Book	7
	References	9
<b>2</b>	<b>Fundamentals of Atomistic Simulation Methods</b>	<b>12</b>
2.1	Density Functional Theory	13
2.1.1	The Many-Body Schrödinger Equation	13
2.1.2	The Hartree Approximation	15
2.1.3	Kohn–Sham Equation	15
2.1.4	Pseudopotential Method	20
2.2	Molecular Dynamics	22
2.2.1	The Basic Mechanical Quantities in MD	22
2.2.2	Periodic Boundary Conditions	26
2.2.3	Time Integration Algorithm	28
2.2.4	Ensemble	29
2.2.5	Procedure of MD Simulation	30
2.2.6	Ab Initio Molecular Dynamics	31
2.3	Some Quantities Obtained from First-Principles Calculations	33
2.3.1	Lattice Parameter	33
2.3.2	Thermodynamic Properties above 0 K	35
2.3.3	Elastic Properties	36
2.3.4	Defect Properties	39
2.4	A Case Study: Design of an Ultra-lightweight Mg–Li Alloys Using First-Principles Calculations	41
	References	44

<b>3</b>	<b>Fundamentals of Mesoscale Simulation Methods</b>	46	<b>3.6</b>	<b>A Case Study: Polymers</b>
3.1	Mesoscale Simulation	47		References
3.2	Phase-Field Method	48	<b>4</b>	<b>Fundamentals of Phase-Field Modeling</b>
3.2.1	History of the Phase-Field Method	48	4.1	Crystallization
3.2.2	Principles of the Phase-Field Method	50	4.2	Basic Concepts
3.2.2.1	Diffuse Interface	50	4.2.1	Order Parameter
3.2.2.2	Order Parameter	51	4.2.2	Free-Energy Functional
3.2.2.3	Free-Energy Functional	51	4.2.3	Dynamic Equations
3.2.2.4	Dynamic Equations	52	4.2.4	Anisotropy
3.2.2.5	Anisotropy	53		
3.2.3	Phase-Field Model for Solidification of a Pure Substance	54	<b>4.2.5</b>	Mechanisms
3.2.4	Phase-Field Model for Alloy Solidification	55	4.3	4.3.1
3.2.4.1	WBM Model	55	4.3.2	KKS Model
3.2.4.2	KKS Model	56	4.4	Multiphase-Field Model
3.2.5	Multiphase-Field Model	58	4.5	Phase-Field Crystal Model
3.2.6	Phase-Field Crystal Model	60	4.6	Microscopic Phase-Field Models
3.2.7	Microscopic Phase-Field Models	63		Applications of the Phase-Field Method
3.2.8	Applications of the Phase-Field Method	65		
3.3	Cellular Automaton Method	66	<b>5</b>	<b>Fundamentals of Cellular Automaton Modeling</b>
3.3.1	Historical Background	67	5.1	Introduction
3.3.2	Principles of the Cellular Automaton Method	67	5.2	Overview
3.3.3	Classical Cellular Automaton Model	68	5.3	5.3.1
3.3.3.1	Nucleation Model	69	5.3.2	5.3.3
3.3.3.2	Grain Growth Model	69	5.3.4	5.3.5
3.3.4	Modified Cellular Automation Model	71	5.4	5.4.1
3.3.4.1	Growth Kinetics and Orientation	71	5.4.2	5.4.3
3.3.4.2	Solute Redistribution	72	5.4.4	5.4.5
3.3.4.3	Thermal Transport	72	5.5	5.5.1
3.3.4.4	Interface Curvature	72	5.6	5.6.1
3.3.5	Discussion Regarding Grid Anisotropy	73		
3.3.6	Applications of the Cellular Automation Method	74		
3.4	Other Mesoscale Simulation Methods	74		
3.4.1	Front-Tracking Method	75		
3.4.2	Level-Set Method	76		
3.4.3	Comparisons among Different Mesoscale Simulation Methods	77		
3.5	Integration of the Phase-Field Method with Other Simulation Approaches	79		
3.5.1	PF Modeling with Atomic Simulations	79		
3.5.2	PF Modeling with Crystal Plasticity	82		
3.5.3	PF Modeling with Macro Transport Equations	84		
3.5.4	PF Modeling with CALPHAD	86		
3.5.5	PF Modeling with Machine Learning	87		

46	3.6 A Case Study: Phase-Field Design of High-Energy-Density	
47	Polymer Nanocomposites	89
48	References	90
49	<b>Fundamentals of Crystal Plasticity Finite Element Method</b> 95	
50	4.1 Crystal Plasticity and Its General Features	95
51	4.2 Basic Concepts and Equations of Continuum Mechanics	96
52	4.2.1 Definition of a Few Basic Terms in Continuum Mechanics	96
53	4.2.2 Three Coordinate Systems and the Deformation Gradient	97
54	4.2.3 Isochoric/Volumetric Split of the Deformation Gradient	98
55	4.2.4 Polar Decomposition	99
56	4.2.5 Eulerian and Lagrangian Finite Strain Tensors	99
57	4.3 Mechanical Constitutive Laws of Crystal Plasticity	100
58	4.3.1 Dislocation-Based Constitutive Models	101
59	4.3.2 Constitutive Models for Displacive Transformation	102
60	4.4 Brief Introduction to the Finite Element Method	103
61	4.5 Software and Procedure for the Crystal Plasticity Finite	
62	Element Simulation	105
63	4.5.1 Brief Introduction to Several FEM Software Packages	105
64	4.5.2 Procedure for the Crystal Plasticity Finite Element Method	107
65	4.6 A Case Study: Plastic Deformation-Induced Surface Roughening	
66	in Al Polycrystals	108
67	References	111
68	<b>Fundamentals of Computational Thermodynamics and the CALPHAD Method</b> 113	
69	5.1 Introduction	114
70	5.2 Overview of the CALPHAD Method	115
71	5.2.1 Origins and Development of the CALPHAD Method	115
72	5.2.2 Principles of the CALPHAD Method	116
73	5.2.3 Overview of Commercial and Open-Source	
74	CALPHAD-Based Software	122
75	5.3 Thermodynamic Modeling of Gibbs Energy	123
76	5.3.1 Phases with Fixed Composition	123
77	5.3.1.1 Pure Elements	123
78	5.3.1.2 Magnetic Contribution	125
79	5.3.1.3 Pressure Contribution	127
80	5.3.1.4 Stoichiometric Compounds	129
81	5.3.2 Solution Phases	133
82	5.3.2.1 Substitutional Solution	133
83	5.3.2.2 Gas Phase	138
84	5.3.2.3 Associate Solution	140
85	5.3.2.4 Quasichemical Model	143
86	5.3.2.5 Comparison of Models for Ordered Liquid Solutions	145
87	5.3.2.6 Sublattice Model for Solid Solution Phases	146

5.4	Establishment of Thermodynamic CALPHAD Databases	155	6.3	Interfa
5.5	Alloy Design Applications Using Solely Thermodynamic CALPHAD Databases	159	6.4	Viscos
5.5.1	Overview	159	6.5	Volum
5.5.2	Applications Based on Equilibrium Calculations	160	6.6	Therm
5.5.2.1	Stable Phase Diagram Calculations	162	6.7	Some
5.5.2.2	Metastable Phase Diagram Calculations	166	6.8	Estab
5.5.2.3	Property Diagram Calculations	168	6.9	A Ca
5.5.3	Applications Based on Scheil Simulations	170		Al A
5.6	Alloy Design Applications Using Extended CALPHAD-Type Databases	178		References
5.6.1	Overview	178	<b>7</b>	<b>Case Stud</b>
5.6.2	Simulation of Solidification	179	7.1	Brie
5.6.3	Simulation of Heat Treatment	181	7.2	Ultra
5.7	A Case Study: CALPHAD Design of Al Alloys with High Resistance to Hot Tearing	184	7.2.	7.2.
	References	189		
<b>6</b>	<b>Fundamentals of Thermophysical Properties</b>	<b>198</b>	7.2	7.2
6.1	Definition of Thermophysical Properties	199		
6.2	Diffusion Coefficient	200	7.2	7.2
6.2.1	Fick's Laws of Diffusion and Various Diffusion Coefficients	200		
6.2.2	Atomic Mechanism of Diffusion	204	7.2	7.2
6.2.2.1	Interstitial Mechanism	205		
6.2.2.2	Direct Exchange and Ring Mechanisms	205	7.3	AlS
6.2.2.3	Vacancy Mechanism	205		
6.2.2.4	Indirect Interstitial Mechanism	205	7.3	7.3
6.2.2.5	Diffusion in Ordered Phase	206		
6.2.3	Interdiffusion in Binary, Ternary, and Multicomponent Systems	207		
6.2.3.1	Interdiffusion in Binary Systems	207	7.	7.
6.2.3.2	Interdiffusion in Ternary Systems	210		
6.2.3.3	Interdiffusion in Multicomponent Systems	217		
6.2.4	Diffusion in Phases with Narrow Homogeneity Ranges	219		
6.2.4.1	Wagner's Approach	219		
6.2.4.2	Du and Schuster Approach	220		
6.2.5	Short-Circuit Diffusion	223		
6.2.5.1	A-Type Kinetic Regime	224	<b>8</b>	<b>Case S</b>
6.2.5.2	B-Type Kinetic Regime	225	8.1	Int
6.2.5.3	C-Type Kinetic Regime	226	8.2	Al
6.2.6	Computational Methods for Calculations of Diffusivity	227	8.3	M
6.2.6.1	Atomistic Description of Diffusion	227		
6.2.6.2	MD Simulation	232		
6.2.6.3	Semi-Empirical Methods	233		
6.2.6.4	Diffusion Simulations Using DICTRA Software	236		

155	6.3 Interfacial Energy	239
159	6.4 Viscosity	243
159	6.5 Volume	245
159	6.6 Thermal Conductivity	247
160	6.7 Some Other Thermophysical Properties	251
162	6.8 Establishment of Thermophysical Property Databases	252
166	6.9 A Case Study: Precipitation and Age Hardening in an AA6005 Al Alloy	253
168	References	257
178		
178	<b>7 Case Studies on Steel Design</b>	264
179	7.1 Brief Introduction about Steel	264
181	7.2 Ultrahigh-Strength and Corrosion-Resistant Ferrium S53 Steel	268
184	7.2.1 Strategy for the Systems Design of Ferrium S53	269
189	7.2.2 Design of Strength, Toughness, and Fatigue Resistance	269
198	7.2.2.1 Martensitic Transformation Behavior	271
199	7.2.2.2 Precipitation of Coherent M <sub>2</sub> C Carbides	273
200	7.2.2.3 Solidification Microsegregation and Castability	275
200	7.2.3 Design of Resistance to General Corrosion and Stress Corrosion Cracking	277
200	7.2.4 Hydrogen Embrittlement	279
204	7.2.5 Prototype and Applications of Ferrium S53	279
205	7.3 AISI H13 Hot-Work Tool Steel	281
205	7.3.1 Simulations of Microstructure Evolution, Yield Stress, Flow Curve, and Creep	282
205	7.3.1.1 Simulation of Microstructure	282
206	7.3.1.2 Simulation of Yield Stress	284
207	7.3.1.3 Simulation of the Flow Curve	285
207	7.3.1.4 Simulation of Creep	286
210	7.3.2 Simulation of Heat Transfer, Phase Transformation, and Stress Relaxation	287
217	7.3.2.1 Simulation of Heat Transfer	287
219	7.3.2.2 Simulation of Phase Transformations	288
219	7.3.2.3 Simulation of Stress Relaxation	289
220	References	291
223		
224	<b>8 Case Studies on Light Alloy Design</b>	295
225	8.1 Introduction	295
226	8.2 Aluminum Alloys	296
227	8.2.1 Cast Al Alloy A356: Solidification Simulation and Microsegregation	297
227	8.2.2 Wrought Al Alloy 7xxx: Heat Treatment Simulation	
232	and Precipitation Kinetics	302
233	8.3 Magnesium Alloys	304
236		

8.3.1 Selection of Cast Mg Alloy Composition and Optimized Heat Treatment 8.3.1.1 Selected Case Studies for New Creep-Resistant Mg Alloys 8.3.1.2 Solidification Path and T6 Heat Treatment of AZ Series Alloys 8.3.1.3 Computational Design and Development of New Mg-Al-Sn-Based (AT) Cast Alloys 8.3.2 Biomedical Mg Alloy Implants 8.4 Summary 8.4.1 Alloy Design Applications Using Solely Thermodynamic CALPHAD Databases 8.4.2 Alloy Design Applications Using Extended CALPHAD-Type Databases and Kinetic Simulations References	306 306 307 310 312 318 318 318 318 319	10.4 G 1 1 References Case S 11.1 I 11.2 I
<b>9 Case Studies on Superalloy Design</b>	<b>323</b>	11.3 S
9.1 Introduction	323	
9.2 Ni-Based Single-Crystal Superalloys	325	
9.2.1 Model Description	328	
9.2.1.1 Thermodynamic Properties	328	
9.2.1.2 Density	328	
9.2.1.3 Misfit	329	
9.2.1.4 Creep-Rupture Lifetime	329	
9.2.1.5 Design Criteria	329	
9.2.2 Alloy Design Procedure	330	
9.2.2.1 Surrogate Models	331	
9.2.2.2 Optimization Algorithm	331	
9.2.2.3 Alloy Design and Experimental Validation	331	
9.3 Ni-Fe-Based Superalloys for Advanced Ultrasupercritical Units	333	
9.3.1 Model Description	334	
9.3.2 Alloy Design Procedure	335	
9.3.3 Alloy Design and Experimental Validation	338	
References	340	
<b>10 Case Studies on Cemented Carbide Design</b>	<b>342</b>	
10.1 Brief Introduction to Cemented Carbides	342	
10.2 Ultrafine Cemented Carbides	344	
10.2.1 Segregation of the (Ta,W)C Cubic Phase in Ultrafine Cemented Carbides	345	
10.2.2 Optimization of Composition, Sintering Temperature, and Inhibitors	347	
10.3 Cemented Carbides with Composite Binder Phases of Co and $\gamma'$ -Ni <sub>3</sub> Al	351	

306	10.3.1 Optimization of Composition and Sintering Temperature	353
	10.3.2 Morphology Control of the Composite Binder Phases and WC Grains	355
306	10.4 Gradient Cemented Carbides	360
	10.4.1 Computational Design of Gradient Microstructure	361
307	10.4.2 A Microstructure-Based Hardness Model for Gradient Cemented Carbides	362
310	References	367
312		
318	<b>11 Case Studies on Hard Coating Design</b>	370
	11.1 Introduction to Cutting Tools and Hard Coatings	370
318	11.2 PVD Hard Coating	372
	11.2.1 Cathodic Arc Evaporation and Magnetron Sputtering	372
318	11.2.2 Metastable Phase Formation and TiN–AlN Phase Diagrams	375
319	11.2.3 Spinodal Decomposition	378
	11.2.4 Multilayer Hard Coating	379
323	11.3 CVD Hard Coating	383
323	11.3.1 Experimental Setup	383
325	11.3.2 Through-Process Modeling of CVD MT–Ti(C,N) Hard Coating	385
328	References	398
328		
329	<b>12 Case Studies on Energy Materials Design</b>	402
329	12.1 Case Study for Design of Hydrogen Storage Materials	403
329	12.1.1 Overview of Hydrogen Storage Materials	403
330	12.1.2 Complex Light Metal Hydride LiBH <sub>4</sub>	404
331	12.1.2.1 Overview of LiBH <sub>4</sub> Properties	404
331	12.1.2.2 Strategy for Understanding Dehydrogenation of LiBH <sub>4</sub>	406
331	12.1.2.3 Thermodynamics of LiBH <sub>4</sub>	408
333	12.1.2.4 Point Defects in LiBH <sub>4</sub> : Understand the Dehydrogenation of LiBH <sub>4</sub>	414
334	12.1.2.5 Structural Evolution and Diffusivity of LiBH <sub>4</sub>	417
335	12.2 Case Study for Design of Li–Ion Batteries	419
338	12.2.1 Overview of Li–Ion Batteries	419
340	12.2.2 Relationship among Phase Diagram, Thermodynamics, and Electrochemical Properties	421
342	12.2.3 Li–Mn–O Spinel Cathode Material	422
342	12.2.3.1 Phase Diagrams	423
344	12.2.3.2 Evaluation of Cyclability	425
345	12.2.3.3 Evaluation of Safety	428
	12.2.3.4 Evaluation of Energy Density	429
347	12.2.3.5 Optimization of the Composition Based on Comprehensive Consideration	430
351	References	431

<b>13</b>	<b>Summary and Future Development of Materials Design</b>	433
13.1	Brief Summary of This Book	434
13.2	Highlighting Computational Design of Other Engineering Materials and Processes	437
13.2.1	Highlighting the Design of Mo <sub>2</sub> BC Thin Film	438
13.2.2	Highlighting the Design of Nanocurvature-Enhanced Fabrication of Cu <sub>3</sub> Sn	438
13.2.3	Highlighting the Design of Steel Production Process	441
13.2.4	Highlighting the Design of Slag as Recycled Material	442
13.3	Future Orientations and Challenges for Computational Design of Engineering Materials	443
13.3.1	General Aspects of Computational Design of Engineering Materials, ICME, MGI, and CDMD	443
13.3.2	Advancement of Models and Approaches for More Quantitative Simulation in Materials Design	444
13.3.2.1	Heterointerface and Homointerface Thermodynamics	444
13.3.2.2	Thermodynamics under External Fields	447
13.3.2.3	More Quantitative Phase-Field Models	448
13.3.3	Databases and Materials Informatics	449
13.3.3.1	Scientific Databases	449
13.3.3.2	Materials Informatics	449
13.3.4	Enhanced Simulation Software Packages	450
13.3.5	Concurrent Design of Materials and Products	451
13.3.6	ICME and MGI as Well as Their Correlations to CDMP	453
	References	454
	<i>Appendix A Ancillary Materials</i>	457
	<i>Appendix B Notations</i>	461
	<i>Index</i>	469

Colour plates are to be found between pages 460 and 461.