

## Contents

<b>Foreword</b>	<i>V</i>
<b>Preface</b>	<i>XVII</i>
<b>List of Contributors</b>	<i>XXI</i>

### Part One Thermodynamics 1

<b>1</b>	<b>Phase Formation in Multicomponent Monotectic Al-based Alloys</b>	<b>3</b>
	<i>Joachim Gröbner, Djordje Mirković, and Rainer Schmid-Fetzer</i>	
1.1	Introduction	3
1.2	Experimental Methods	4
1.3	Systematic Classification of Ternary Monotectic Phase Diagrams	4
1.4	Selected Ternary Monotectic Alloy Systems	6
1.4.1	Al–Bi–Zn: Type 2a Monotectic System	6
1.4.2	Al–Bi–Sn: Type 1b Monotectic System	6
1.4.3	Al–Sn–Cu: Type 3a Monotectic System	8
1.4.4	Al–Bi–Cu: Type 2b Monotectic System	9
1.4.5	Bi–Cu–Sn: Type 3a Monotectic System	11
1.5	Quaternary Monotectic Al–Bi–Cu–Sn System	11
1.6	Conclusion	15
<b>2</b>	<b>Liquid-liquid Interfacial Tension in Multicomponent Immiscible Al-based Alloys</b>	<b>19</b>
	<i>Walter Hoyer and Ivan G. Kaban</i>	
2.1	Introduction	19
2.2	Measurement Technique	21
2.3	Experimental Details	24
2.4	Results	25
2.5	Discussion	30
2.5.1	Composition Dependences of the l–l Interfacial Tension	30
2.5.2	Adsorption at the l–l Interface	32
2.5.3	Temperature Dependence of the l–l Interfacial Tension	34

VIII | Contents

2.5.4	Wetting Phenomena	34
2.6	Summary	36
<b>3</b>	<b>Monotectic Growth Morphologies and Their Transitions</b>	<b>39</b>
	<i>Lorenz Ratke, Anja Müller, Martin Seifert, and Galina Kasperovich</i>	
3.1	Introduction	39
3.2	Experimental Procedures	40
3.2.1	Alloys	40
3.2.2	ARTEMIS Facility	41
3.2.3	Evaluation Procedures	42
3.3	Experimental Results	42
3.3.1	Microstructures	42
3.3.2	Jackson–Hunt Plot	45
3.3.3	Stability Diagrams	46
3.4	Discussion	47
3.4.1	Fibrous Monotectic Growth	47
3.4.2	Transition from Fibers to String of Pearls	48
3.4.3	Origin of Irregular Drops	50
3.5	Outlook	53
<b>4</b>	<b>Thermal Expansion and Surface Tension of Multicomponent Alloys</b>	<b>55</b>
	<i>Jürgen Brillo and Ivan Egry</i>	
4.1	Introduction	55
4.1.1	General	55
4.1.2	Density and Thermal Expansion	56
4.1.3	Surface Tension	57
4.2	Experimental	58
4.2.1	Levitation	58
4.2.2	Density and Thermal Expansion	59
4.2.3	Surface Tension	59
4.3	Results	60
4.3.1	Density	60
4.3.2	Surface Tension	64
4.4	Conclusion and Summary	69
<b>5</b>	<b>Measurement of the Solid-Liquid Interface Energy in Ternary Alloy Systems</b>	<b>73</b>
	<i>Annemarie Bulla, Emir Subasic, Ralf Berger, Andreas Bührig-Polaczek, and Andreas Ludwig</i>	
5.1	Introduction	73
5.2	Experimental Procedure	74
5.2.1	The Radial Heat Flow Apparatus	74
5.2.2	Equilibration of the Sample	75
5.2.3	Quenching	75
5.3	Evaluation of the Local Curvature of the Grain Boundary Grooves	75

5.3.1	Preparation of the Sample	75
5.3.2	Geometrical Correction of the Groove Coordinates	76
5.3.3	Determination of the Local Undercooling	77
5.3.4	Determining the Interface Energy	78
5.4	Results and Discussion	79
5.4.1	Al–Cu System with Eutectic Composition	80
5.4.2	Al–Cu–Ag System with Invariant Eutectic Composition	81
5.4.3	Concentration Dependence of $\sigma_{SL}$	83
5.5	Summary and Conclusions	84
<b>6</b>	<b>Phase Equilibria of Nanoscale Metals and Alloys</b>	<b>87</b>
	<i>Gerhard Wilde, Peter Bunzel, Harald Rösner, and Jörg Weissmüller</i>	
6.1	Introduction	87
6.2	Phase Stability and Phase Transformations in Nanoscale Systems	88
6.2.1	Single-Phase Material: External Interfaces	88
6.2.2	Binary Nanoalloys: Internal Heterophase Interfaces	97
6.3	Summary	105
	<b>Part Two Microscopic and Macroscopic Dynamics</b>	<b>109</b>
<b>7</b>	<b>Melt Structure and Atomic Diffusion in Multicomponent Metallic Melts</b>	<b>111</b>
	<i>Dirk Holland-Moritz, Oliver Heinen, Suresh Mavila Chathoth, Anja Ines Pommrich, Sebastian Stüber, Thomas Voigtmann, and Andreas Meyer</i>	
7.1	Introduction	111
7.2	Experimental Details	113
7.2.1	Quasi elastic Neutron Scattering	113
7.2.2	Elastic Neutron Scattering	115
7.3	Results and Discussion	115
7.3.1	Atomic Dynamics in Liquid Ni	115
7.3.2	Atomic Dynamics in Ni–P-based Glass-forming Alloy Melts	118
7.3.3	Atomic Dynamics in Zr–Ti–Ni–Cu–Be and $Zr_{64}Ni_{36}$ Alloy Melts	119
7.3.4	The Short-Range Order of Liquid $Zr_{64}Ni_{36}$	120
7.3.5	Analysis Within Mode Coupling Theory	124
7.4	Conclusions	125
<b>8</b>	<b>Diffusion in Multicomponent Metallic Melts Near the Melting Temperature</b>	<b>131</b>
	<i>Axel Griesche, Michael-Peter Macht, and Günter Froberg</i>	
8.1	Introduction	131
8.2	Experimental Diffusion Techniques	132
8.2.1	Long-Capillary Method	132
8.2.2	Long-Capillary Method Combined with X-ray Radiography	134
8.3	Influence of Thermodynamic Forces on Diffusion	135

x | Contents

- 8.3.1 Systems with Mixing Tendency: Al–Ni 136
- 8.3.2 Systems with Demixing Tendency: Pd–Cu–Ni–P 137
  
- 9 Phase Behavior and Microscopic Transport Processes in Binary Metallic Alloys: Computer Simulation Studies 141**  
*Subir K. Das, Ali Kerrache, Jürgen Horbach, and Kurt Binder*
- 9.1 Introduction 141
- 9.2 Transport Coefficients 143
- 9.3 A Symmetric LJ Mixture with a Liquid–Liquid Demixing Transition 144
- 9.4 Structure, Transport, and Crystallization in Al–Ni Alloys 148
- 9.5 Summary 154
  
- 10 Molecular Dynamics Modeling of Atomic Processes During Crystal Growth in Metallic Alloy Melts 157**  
*Helmar Teichler and Mohamed Guerdane*
- 10.1 Introduction 157
- 10.2 Entropy and Free Enthalpy of Zr-rich  $\text{Ni}_x\text{Zr}_{1-x}$  Melts from MD Simulations and Their Application to the Thermodynamics of Crystallization 158
  - 10.2.1 Survey 158
  - 10.2.2 Results and Their Meaning 158
    - 10.2.2.1 The Method that Works 158
    - 10.2.2.2 Free Enthalpy Results for Zr-rich  $\text{Ni}_x\text{Zr}_{1-x}$  Melts 159
    - 10.2.2.3 Zr-rich Part of the (x, T) Phase Diagram 161
- 10.3 Bridging the Gap between Phase Field Modeling and Molecular Dynamics Simulations. Dynamics of the Planar  $[\text{Ni}_x\text{Zr}_{1-x}]_{\text{liquid}} - \text{Zr}_{\text{crystal}}$  Crystallization Front 162
  - 10.3.1 Survey 162
  - 10.3.2 Results and Their Meaning 162
    - 10.3.2.1 MD-Generated Input Parameter for PF Modeling 162
    - 10.3.2.2 Comparison of MD and PF Results for the Concentration Profiles and Propagation of the Crystallization Front 163
- 10.4 Entropy and Free Enthalpy in Ternary  $\text{Al}_y\text{Ni}_{0.4-y}\text{Zr}_{0.6}$  Alloy Melts 165
  - 10.4.1 Survey 165
  - 10.4.2 Results and Their Meaning 166
    - 10.4.2.1 The Method: Test of Its Numerical Reliability 166
    - 10.4.2.2 Results for the Entropy Change in the  $\text{Al}_y\text{Ni}_{0.4-y}\text{Zr}_{0.6}$  Melt Series at 1700 K 167
- 10.5 Concluding Remarks 169
  
- 11 Computational Optimization of Multicomponent Bernal’s Liquids 171**  
*Helmut Hermann, Antje Elsner, and Valentin Kokotin*
- 11.1 Introduction 171
- 11.2 Methods 172

- 11.2.1 Force Biased Algorithm 172
- 11.2.2 The Nelder–Mead Algorithm 173
- 11.2.3 Voronoi Tessellation 174
- 11.3 Results and Discussion 175
- 11.3.1 Monoatomic Liquids 175
- 11.3.2 Multicomponent Liquids 177
- 11.4 Conclusion 180

## 12 Solidification Experiments in Single-Component and Binary Colloidal Melts 185

*Thomas Palberg, Nina Lorenz, Hans Joachim Schöpe, Patrick Wette, Ina Klassen, Dirk Holland-Moritz, and Dieter M. Herlach*

- 12.1 Introduction 185
- 12.2 Experimental Procedure 186
- 12.2.1 Tunable Interactions in Charged Colloidal Suspensions 186
- 12.2.2 Instrumentation for Time-Resolved Static Light Scattering 190
- 12.3 Results 193
- 12.3.1 The Full Phase Diagram of Charge Variable Systems 193
- 12.3.2 Shapes of Phase Diagrams of Charged Sphere Mixtures 196
- 12.3.3 Growth of Binary Colloidal Crystals 199
- 12.3.4 Quantitative Determination of Nucleation Kinetics and Extraction of Key Parameters 203
- 12.3.5 Investigations on the Structure of Undercooled Melts 206
- 12.4 Conclusions 208

## Part Three Nd–Fe based Alloys 213

### 13 Phase-Field Simulations of Nd–Fe–B: Nucleation and Growth Kinetics During Peritectic Growth 215

*Ricardo Siquieri and Heike Emmerich*

- 13.1 Introduction 215
- 13.2 Phase-Field Model with Hydrodynamic Convection 217
- 13.3 Investigating Heterogeneous Nucleation in Peritectic Materials via the Phase-Field Method 220
- 13.4 Conclusion 223

### 14 Investigations of Phase Selection in Undercooled Melts of Nd–Fe–B Alloys Using Synchrotron Radiation 227

*Thomas Volkmann, Jörn Strohmeier, and Dieter M. Herlach*

- 14.1 Introduction 227
- 14.2 Description of the Investigations 228
- 14.3 Experimental Results and Discussion 231
- 14.4 Analysis Within Models of Nucleation and Dendrite Growth 236
- 14.5 Summary and Conclusion 240

- 15 Effect of Varying Melt Convection on Microstructure Evolution of Nd–Fe–B and Ti–Al Peritectic Alloys 245**  
*Regina Hermann, Gunter Gerbeth, Kaushik Biswas, Octavian Filip, Victor Shatrov, and Janis Priede*
- 15.1 Introduction 245
- 15.2 Methods Developed 246
- 15.2.1 Forced Rotation Technique 246
- 15.2.1.1 Experimental 246
- 15.2.1.2 Numerical Simulation 247
- 15.2.2 Floating Zone Facility with Additional Magnetic Field 248
- 15.2.2.1 Experimental 248
- 15.2.2.2 Numerical Simulation 250
- 15.3 Sample Preparation 251
- 15.4 Results and Discussion 252
- 15.4.1 Nd–Fe–B Alloys 252
- 15.4.2 Ti–Al Alloys 256
- 15.5 Conclusion 258
- 16 Nanosized Magnetization Density Profiles in Hard Magnetic Nd–Fe–Co–Al Glasses 263**  
*Olivier Perroud, Albrecht Wiedenmann, Mihai Stoica, and Jürgen Eckert*
- 16.1 Introduction 263
- 16.2 SANS with polarized neutrons in unsaturated magnetic systems 265
- 16.3 Experimental Procedure 267
- 16.3.1 Sample Preparation 267
- 16.3.2 SANS POL Measurements 267
- 16.4 Results and Discussion 268
- 16.4.1 Microstructure 268
- 16.4.2 Magnetic Behavior 268
- 16.5 Conclusion 275
- 17 Microstructure and Magnetic Properties of Rapidly Quenched (Nd<sub>100-x</sub>Ga<sub>x</sub>)<sub>80</sub>Fe<sub>20</sub> (x = 0, 5, 10, and 15 at%) alloys 277**  
*Mihai Stoica, Golden Kumar, Mahesh Emmi, Olivier Perroud, Albrecht Wiedenmann, Annett Gebert, Shanker Ram, Ludwig Schultz, and Jürgen Eckert*
- 17.1 Introduction 277
- 17.2 Sample Preparation and Experimental Investigations 279
- 17.3 Binary Nd<sub>80</sub>Fe<sub>20</sub> Rapidly Quenched Alloys 280
- 17.3.1 Structure and Cooling Rate 280
- 17.3.2 The Metastable A1 “Phase” 283
- 17.3.3 Magnetic Properties 287
- 17.4 Ternary (Nd<sub>100-x</sub>Ga<sub>x</sub>)<sub>80</sub>Fe<sub>20</sub> (x = 5, 10, and 15) Rapidly Quenched Alloys 288
- 17.4.1 XRD Studies 288

- 17.4.2 Tuning the Metastable Hard Magnetic A1 Zones 290  
 17.5 Conclusions 292

#### Part Four Solidification und Simulation 297

### 18 Solidification of Binary Alloys with Compositional Stresses— A Phase-Field Approach 299

*Bo Liu and Klaus Kassner*

- 18.1 Introduction 299  
 18.2 Equations of Motion 301  
 18.3 Neutral Curves 304  
 18.4 Phase-Field Model 305  
 18.5 Simulation Results 306  
 18.6 Conclusions 308

### 19 Elastic Effects on Phase Transitions in Multi-component Alloys 311

*Efim A. Brener, Clemens Gugenberger, Heiner Müller-Krumbhaar, Denis Pilipenko, Robert Spatschek, and Dmitrii E. Temkin*

- 19.1 Melting of Alloys in Eutectic and Peritectic Systems 312  
 19.1.1 Isothermal Melting in Eutectic System 313  
 19.1.2 Isothermal Melting in Peritectic Systems 315  
 19.2 Combined Motion of Melting and Solidification Fronts 316  
 19.3 Continuum Theory of Fast Crack Propagation 319  
 19.4 Summary 323

### 20 Modeling of Nonisothermal Multi-component, Multi-phase Systems with Convection 325

*Harald Garcke and Robert Haas*

- 20.1 Introduction 325  
 20.2 Phase-field Models for Multicomponent, Multiphase Systems 326  
 20.3 Multiphase Ginzburg–Landau Energies 327  
 20.3.1 Some Examples of Ginzburg–Landau Energies 329  
 20.4 Convective Phase-Field Models 330  
 20.4.1 Conservation Laws and Entropy Inequality 330  
 20.4.2 Exploitation of the Entropy Principle 332  
 20.4.2.1 Example 336  
 20.5 Mathematical Analysis 337

### 21 Phase-field Modeling of Solidification in Multi-component and Multi-phase Alloys 339

*Denis Danilov and Britta Nestler*

- 21.1 Introduction 339  
 21.2 Phase-field Model for Multicomponent and Multiphase Systems 339  
 21.3 Modeling of Dendritic Growth 341

XIV Contents

- 21.4 Solute Trapping During Rapid Solidification 345
- 21.5 Comparison of Molecular Dynamics and Phase-field Simulations 345
- 21.6 Modeling of Eutectic Growth 346

**22 Dendrite Growth and Grain Refinement in Undercooled Melts 353**

*Peter K. Galenko and Dieter M. Herlach*

- 22.1 Introduction 353
- 22.2 Solidification of Pure (One-Component) System 354
  - 22.2.1 Diffuse Interface Model 354
  - 22.2.2 Sharp-Interface Model 356
  - 22.2.3 Results of Nominally Pure Ni 357
  - 22.2.4 Results on Congruently Melting Intermetallic Alloy Ni<sub>50</sub>Al<sub>50</sub> 359
- 22.3 Solidification of Binary Alloys with Constitutional Effects 362
  - 22.3.1 Diffuse Interface Model 362
  - 22.3.2 Sharp-Interface Model and Growth Velocities of Binary Ni–Zr Alloys 362
  - 22.3.3 Grain Refinement Through Undercooling 364
- 22.4 Solidification of a Ternary Alloy 366
  - 22.4.1 Diffuse Interface Model 366
  - 22.4.2 Sharp-Interface Model and Dendrite Growth Velocities of Ni–Zr–Al 367
- 22.5 Summary and Conclusions 369

**23 Dendritic Solidification in the Diffuse Regime and Under the Influence of Buoyancy-Driven Melt Convection 373**

*Markus Apel and Ingo Steinbach*

- 23.1 Introduction 373
- 23.2 The Multiphase-field Model 373
  - 23.2.1 Extension of the Karma corrections to Multicomponent Alloys 374
  - 23.2.2 Fluid Flow Coupling for Multicomponent Alloys 375
- 23.3 Rapid Solidification in Ni<sub>98</sub>Al<sub>1</sub>Zr<sub>1</sub> 376
- 23.4 Directional Solidification with Buoyancy-driven Interdendritic Flow 378
  - 23.4.1 Spacing Selection in Binary Alloy 379
  - 23.4.2 Buoyancy-driven Fluid Flow in a Ternary Alloy 381
- 23.5 Summary and Conclusion 383

**24 Stationary and Instationary Morphology Formation During Directional Solidification of Ternary Eutectic Alloys 387**

*Bernd Böttger, Victor T. Witusiewicz, Markus Apel, Anne Drevermann, Ulrike Hecht, and Stephan Rex*

- 24.1 Introduction 387
  - 24.1.1 About the Project 387
  - 24.1.2 General Aspects of Ternary Eutectic Systems 388
- 24.2 Investigations on the Eutectic System Ag–Cu–Zn 390

24.2.1	Thermodynamic Properties and Thermodynamic Assessment	390
24.2.2	Bridgman Experiments	391
24.3	Investigation on the Ternary Alloy System In–Bi–Sn	395
24.3.1	Measurement of Thermodynamic Properties and Thermodynamic Assessment	395
24.3.2	Micro-Bridgman Assembly	397
24.3.3	Stationary Coupled Growth	398
24.4	Transient Growth	399
24.4.1	Solidification Path During Transient Solidification	401
24.4.2	Quantitative Comparison to Simulation: Calibration of Diffusion Data	403
24.4.3	Stationary Univariant Growth: Calibration of Interfacial Energies	403
24.5	Summary and Conclusion	404
<b>25</b>	<b>Dendritic Microstructure, Decomposition, and Metastable Phase Formation in the Bulk Metallic Glass Matrix Composite</b>	
	<b>Zr<sub>56</sub>Ti<sub>14</sub>Nb<sub>5</sub>Cu<sub>7</sub>Ni<sub>6</sub>Be<sub>12</sub></b>	<b>407</b>
	<i>Susanne Schneider, Alberto Bracchi, Yue-Lin Huang, Michael Seibt, and Pappannan Thiyagarajan</i>	
25.1	Introduction	407
25.2	Experimental Procedures	409
25.3	Results and Discussion	409
25.4	Summary	418
	<b>Index</b>	<b>421</b>

