

# Phase Transformations in Multicomponent Melts

*Edited by*  
*Dieter M. Herlach*



WILEY-  
VCH

WILEY-VCH Verlag GmbH & Co. KGaA

## Contents

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

### 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

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

## 6 Phase Equilibria of Nanoscale Metals and Alloys 87

*Gerhard Wilde, Peter Bunzel, Harald Rösner, and Jörg Weissmüller*

- 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

## Part Two Microscopic and Macroscopic Dynamics 109

### 7 Melt Structure and Atomic Diffusion in Multicomponent Metallic Melts 111

*Dirk Holland-Moritz, Oliver Heinen, Suresh Mavila Chathoth, Anja Ines Pommrich, Sebastian Stüber, Thomas Voigtmann, and Andreas Meyer*

- 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

### 8 Diffusion in Multicomponent Metallic Melts Near the Melting Temperature 131

*Axel Griesche, Michael-Peter Macht, and Günter Froberg*

- 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

- 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 Volkman, 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  $(\text{Nd}_{100-x}\text{Ga}_x)_{80}\text{Fe}_{20}$  ( $x = 0, 5, 10,$  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  $\text{Nd}_{80}\text{Fe}_{20}$  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  $(\text{Nd}_{100-x}\text{Ga}_x)_{80}\text{Fe}_{20}$  ( $x = 5, 10,$  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



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
<b>22</b>	<b>Dendrite Growth and Grain Refinement in Undercooled Melts</b>	<b>353</b>
	<i>Peter K. Galenko and Dieter M. Herlach</i>	
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
<b>23</b>	<b>Dendritic Solidification in the Diffuse Regime and Under the Influence of Buoyancy-Driven Melt Convection</b>	<b>373</b>
	<i>Markus Apel and Ingo Steinbach</i>	
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
<b>24</b>	<b>Stationary and Instationary Morphology Formation During Directional Solidification of Ternary Eutectic Alloys</b>	<b>387</b>
	<i>Bernd Böttger, Victor T. Witusiewicz, Markus Apel, Anne Drevermann, Ulrike Hecht, and Stephan Rex</i>	
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>