Contents

1. Introduction 1

1–0. General 1
1–1. Equilibrium between Solid and Liquid 1
1–2. Melting Point 2
1–3. Equilibrium of Alloys 4

Equilibrium Diagrams 4
Congruent Melting 6
Eutectics 6
Peritectics 7
Monotectics 10

1–4. Gas–Metal Equilibrium 11
1–5. Ternary and Multicomponent Alloys 12
1–6. The Phase Rule 14
1–7. The Distribution Coefficient 15
1–8. Thermodynamic Criteria for Equilibrium 17

2. Solidification as an Atomic Process 20

2–1. Solids and Liquids 20

The Nature of Crystalline Solids 20
Nature of Liquids 22
The Differences Between Crystals and Liquids 24
Quasi-chemical Approach 25

2–2. The Solid-Liquid Interface 26

Microtopography of the Interface 28

2–3. Equilibrium between a Pure Metal and Its Melt 35
2–4. The Process of Crystal Growth 43

Kinetics of Crystal Growth 44

2–5. Solid-Liquid Equilibrium in Alloys 46
2–6. Origin of Defects 51

Vacancies 52
Dislocations 56
Lineage Structures 59

3. Nucleation 62

3–1. Metastability of Supercooled Liquids 62
3–2. Equilibrium Conditions for a Curved Interface 63

Stability of a Curved Interface; Atomic Considerations 63
Thermodynamic Treatment of Equilibrium across a Curved Interface 64

3–3. Calculation of Critical Radius 65
3–4. The Process of Nucleation 68

Theory of Nucleation Rate 69
Nucleation Temperature 70
Comparison between Experiment and Theory 71
Size of the Critical Nucleus 74

3–5. Homogeneous Nucleation in Alloys 76
3–6. Heterogeneous Nucleation 77
3–7. The Nucleation of Melting 84
3–8. Dynamically Stimulated Nucleation 86
3–9. Summary of Present Status of Nucleation Theory 89

4. Microscopic Heat Flow Considerations 91

4–1. Qualitative Observations 91
4–2. Removal of Latent Heat 95
4–3. Extraction of Latent Heat by Conduction into the Crystal 96

Effect of Surfaces and of Grain Boundaries 97

4–4. Conduction of Latent Heat into the Liquid 99

"Ribbon" Crystals 101
"Feather" Growth 102

4–5. Dendritic Growth 103

Total Amount Solidified 104
Speed of Growth 104

Direction of Dendritic Growth 116
Spacing of Dendrite Arms 120

4–6. Solidification at Very High Supercooling 122

5. Redistribution of Solute during Solidification 126

5–1. General Considerations 126
5–2. The Distribution Coefficient 126
5–3. Rejection of Solute 128

Equilibrium Maintained at All Times 129
Mixing in the Liquid by Diffusion Only: No Diffusion in the Solid 131
Influence of Fluid Motion: Convection 138
Complete or Partial Mixing of Liquid: No Diffusion in Solid 139
Solidus Temperature of an Alloy 142

5–4. Zone Refining 143
5–5. Constitutional Supercooling 150

Instability Due to Constitutional Supercooling 152

5–6. Cellular Substructure 154

Origin of the Cellular Substructure 154
Quantitative Studies of Cell Formation 157
Geometry of Cells 160

5–7. Cellular Dendrites 164
5–8. Free Dendritic Growth in Alloys 169

Spacing of Dendrite Arms 170

5–9. Nucleation of Crystals ahead of the Existing Interface 171
5–10. Types of Segregation 171

Normal Segregation 171
Grain Boundary Segregation 172
Cellular Segregation 173
Dendritic Segregation 175
Inverse Segregation 178
Coring and Intercrystalline Segregation 183
Gravity Segregation 183

6. Polyphase Solidification 186

6–1. Evolution of a Gas During Solidification 186

Gas–Metal Equilibrium 186
Bubble Formation 187
Formation of Compounds by Dissolved Gases 194

6–2. Eutectics 194

Microstructure of Eutectics 196
Pure Binary Eutectics 197
Solidification of Lamellar Eutectics 198
Shape of the Interface 200
Lamellar Growth: Theoretical 201
Lamellar Growth: Experimental 204
Degenerate Eutectic Structures 206
Modification of Eutectics 207
Discontinuous Eutectics 211
Noneutectic Compositions 215
Structure of Eutectic Liquids 216
Gravity Segregation of Eutectics 218
Divorced Eutectic 218
Ternary Eutectics 219
Cast Iron 219

6–3. Peritectic Solidification 224
6–4. Solidification in the Presence of a Solid Phase 227

Suspended Particles 227
Solidification of a Liquid in a Porous Solid 229

7. Macroscopic Heat Flow and Fluid Flow 232

7–1. General Considerations 232
7–2. Fluid Flow 232

Viscosity of Liquid Metals 233
Fluidity 234

7–3. Heat Flow 235

Rate of Solidification 237
Continuous Casting 242
Dip Forming 247

7–4. Thermal Stresses in a Solidifying Body 250

8. The Structure of Cast Metals 253

8–1. General Considerations 253
8–2. The Macrostructure of Cast Metals 255

Description of Cast Structures 255
Experimental Observations 257
Solidification in a Mold 259
Structure of Continuous Castings 276
Effect of Vibration on Structure 278
Welding, Brazing and Soldering as Casting Processes 281

8–3. Segregation 282
8–4. The Significance of Small-Scale Experiments 284
8–5. Change of Volume on Freezing 285

Pipe Formation 286
Unidirectional Shrinkage 287
Cavity Formation 287
Control of Unsoundness 287
Porosity 288
Surface Porosity 289

8–6. Blowholes 289
8–7. Surface Topography Resulting from Solidification 290

Surface Tension Effects 291
Cold Shut 292
Trapped Gas 292
Surface Dendrites 292
Exudation and Surface Porosity 294
Topography of the Free Surface 294
Changes of Topography after Solidification 294
Metal Coating by Hot Dipping 295
Tinplate 295

Appendix. The Production of Single Crystals from the Melt 298

A–1. General Considerations 298
A–2. Control of Orientation 299
A–3. Control of Shape 300
A–4. Control of Composition 302

Contamination 302

Evaporation 303
Uniformity of Composition: Short Range 303
Uniformity of Composition: Long Range 303
Peritectic Compound 305

A–5. Control of Perfection 305

Vacancies 305
Dislocations 306
Lineage 306
"Stray Crystals" 307

A–6. Bicrystals 308

Index 311