Contents

Preface xv

Author xix

Acronyms etc. xxi

Nomenclature xxiii

Chapter 1 Crystal structures and mechanisms 1

1.1 Allotropes of iron 1
1.2 The illousary omega phase 5
1.3 Amorphous iron 6
1.4 Mechanisms of transformation 6
1.5 Crystallographic similarities 8
1.6 Iron-carbon phase diagram 9
1.7 Classification scheme 11
1.7.1 Thermodynamic Classification 13

Chapter 2 Thermodynamics 17

2.1 Introduction 17
2.2 Definitions 17
2.2.1 Internal energy and enthalpy 17
2.2.2 Entropy, free energy 18
2.2.3 Configurational entropy 18
2.2.4 Relationship between Clausius and Boltzmann entropies 19
2.3 Maxwell relations 20
2.4 Thermodynamic functions of iron 20
2.4.1 Relation between C_P and C_V 22
2.4.2 Debye Temperatures 22
2.5 Electronic heat capacity 23
2.6 Magnetic specific heat of iron 24
2.6.1 Diamagnetism 25
2.6.2 Paramagnetism 25
2.6.3 Ferromagnetism, antiferromagnetism and ferrimagnetism 26
2.6.4 Heat capacity due to magnetisation 27
2.6.5 Magnetic heat capacity of ferrite 28
2.6.6 Magnetic heat capacity of austenite 30
2.6.7 Invar effect and associated phenomena 35
2.6.8 Magnetic heat capacity of ε-Iron and superconductivity 38
2.6.9 Trigonal and tetragonal iron 39
2.7 Heat capacity of liquid iron 44
2.8 Free energy functions of iron 44
2.8.1 Liquid iron 45

2.9 Effect of pressure 47
2.9.1 Liquid iron 47
2.9.2 Ferrite and austenite 48
2.9.3 Hexagonal close-packed iron 49
2.10 Mechanical mixtures and solutions 49
2.10.1 Alloying by deformation 49
2.11 Chemical potential 51
2.12 Equilibrium between solutions 52
2.13 Activity 53
2.14 Ideal solution 54
2.15 Regular solutions 55
2.16 Quasichemical solution 57
2.17 quasichemical model for carbon in austenite 61
2.17.1 Dilute solution, $\omega_\gamma \rightarrow 0$ limit 66
2.17.2 Infinite repulsion limit 66
2.17.3 Zeroth-order quasichemical model 67
2.17.4 Reference state for carbon 67
2.17.5 Carbon-carbon interaction energy in austenite 67
2.17.6 Carbon-carbon interaction energy in ferrite 70
2.18 Zener ordering 71
2.19 Computer calculation of phase diagrams 72
2.19.1 Stoichiometric phases: regular solution model 73
2.19.2 Interstitial solution 74
2.19.3 Generalised regular solution model 77
2.19.4 Magnetic effects 78
2.19.5 Magnetisation 84
2.20 Order parameter 84
2.20.1 Short-range order 86
2.21 Superlattices 87
2.21.1 Ordered crystals 87
2.22 Thermodynamics of irreversible processes 88
2.22.1 Reversibility 89
2.22.2 Linear laws 90
2.22.3 Multiple irreversible processes 91
2.22.4 Onsager reciprocal relations 92

Chapter 3 Diffusion 103

3.1 Introduction 103
3.2 Fick's law and diffusion coefficients 103
3.2.1 Reaction rate expression 107
3.3 Diffusion of carbon in ferrite 107
3.3.1 Interstitial sites in ferrite 107
3.3.2 Dual-site occupancy 110
3.4 Diffusion of carbon in martensite 112
3.5 Interactions between carbon atoms 114
3.5.1 Repulsion between carbon atoms 114
3.5.2 Clustering of interstitial atoms 115
3.5.3 Association of carbon with defects 117
3.6 Diffusion of carbon in austenite 119
3.6.1 Dependence of diffusivity on composition 119

3.6.2 Dependence of diffusivity on C-C interactions 121
3.6.3 Dilatation effects 123
3.6.4 Ågren's method 125
3.7 Diffusion of nitrogen in ferrite 126
3.8 Diffusion of nitrogen in austenite 127
3.9 Diffusion of C and N in cementite and Hägg carbide 127
3.10 Migration of point defects 129
3.10.1 Iron interstitials 129
3.10.2 Iron defects in austenite 130
3.10.3 Vacancies 131
3.11 Migration of hydrogen and deuterium 132
3.11.1 Diffusion in ferrite 132
3.11.2 Diffusion of hydrogen in austenite 133
3.11.3 Hydrogen-vacancy interactions 134
3.12 Self-diffusion in iron 134
3.12.1 The isotope effect 138
3.13 Magnetism and interstitial diffusion in ferrite 139
3.14 Substitutional solutes 140
3.15 Grain boundary diffusion 142
3.16 Phenomenological treatment of binary diffusion 143
3.17 Diffusion in multicomponent systems 144
3.17.1 Diffusion in ternary Fe-X-C alloys 145
3.18 Diffusion in liquid iron 148
3.19 Stress-induced migration 149
3.20 Electromigration 150
3.21 Thermomigration 153
3.22 Electropulsing 154

Chapter 4 Ferrite by reconstructive transformation 165

4.1 Introduction 165
4.2 Interfaces 167
4.2.1 Coherency 167
4.2.2 Glissile semi-coherent interfaces 168
4.2.3 Sessile semi-coherent interfaces 169
4.2.4 Incoherent interfaces 170
4.3 Crystallography 170
4.3.1 Orientation relationships 170
4.3.2 The γ/α interface 174
4.4 Nucleation of allotriomorphic and idiomorphic ferrite 174
4.4.1 Heterogeneous nucleation from vapour 178
4.4.2 Heterogeneous nucleation on inclusions 180
4.5 Interface motion: rate-controlling processes 184
4.6 Diffusion-controlled growth 187
4.6.1 Growth in Fe-C Alloys 187
4.6.2 Lengthening of ferrite allotriomorphs 190
4.6.3 Soft impingement 191
4.6.4 Phase fields 192
4.6.5 Ferrite growth in Fe-X-C alloys: local equilibrium 194
4.6.6 Interface-composition contours 200
4.6.7 Interface-velocity (IV) contours 201

4.6.8 Tie-line shifting due to soft impingement 202
4.6.9 Invalidity of the NP-LE concept 204
4.7 Breakdown of local equilibrium 207
4.7.1 Paraequilibrium 207
4.7.2 Solute and solvent trapping 210
4.8 Interface-controlled growth 215
4.8.1 Pure iron 215
4.8.2 Iron alloys 217
4.9 Growth with mixed control 217
4.10 Step mechanism of interfacial motion 220
4.10.1 Boundary topology, ledge nucleation 220
4.10.2 Motion of isolated ledge 223
4.10.3 Multiledge interactions 227
4.10.4 Ledge motion in finite medium 228
4.10.5 Relative kinetics of stepped and continuous growth 229
4.11 Solute drag: grain boundaries 231
4.11.1 Solute drag and diffusion coefficients 234
4.11.2 Interaction free energy 234
4.12 Solute drag: interphase boundaries 235
4.12.1 Segregation to α/γ interfaces 235
4.13 Massive ferrite 236
4.14 Interphase precipitation 239
4.14.1 Interphase precipitation: theory 240

Chapter 5 Martensite 255

5.1 Diffusionless transformations 255
5.2 Other characteristics of martensite 257
5.2.1 Habit plane 260
5.2.2 Orientation relationships 260
5.2.3 Structure of the interface 263
5.2.4 Shape deformation 268
5.2.5 Microstructure 268
5.2.6 Summary 270
5.2.7 Crystallographic theory 271
5.3 Quantitative theory 272
5.3.1 fcc to bcc martensitic transformation 272
5.4 ε-martensite 278
5.4.1 Crystallography: fcc to hcp transformation 278
5.4.2 $\alpha \rightarrow \varepsilon$ transformation 281
5.5 Martensite-start temperature 282
5.5.1 Effect of austenite grain size on M_S 285
5.6 Thermodynamics 287
5.6.1 Thermoelastic equilibrium 289
5.7 Martensite: nucleation mechanism 291
5.7.1 fcc to hcp transformation 291
5.7.2 Role of thermal activation 294
5.7.3 fcc to bcc transformation 295
5.7.4 Nucleation at large driving forces 297
5.8 Overall transformation kinetics 300
5.8.1 Partitioning of austenite 301

5.8.2 Athermal transformation 304
5.8.3 Isothermal martensite 305
5.8.4 Bursts of transformation 308
5.9 Stress AND strain effects 310
5.9.1 Transformation texture 312
5.9.2 Mechanical stabilisation 314
5.10 Tetragonality of martensite 316

Chapter 6 Bainite 329

6.1 Microstructure 329
6.2 More about the mechanism 332
6.2.1 Stage 1: vestiges 334
6.2.2 Stage 2a: carbon partitioning 335
6.2.3 Stage 2b: precipitation from ferrite 336
6.2.4 Stage 3: termination 337
6.3 Kinetics 340

Chapter 7 Widmanstätten ferrite 349

7.1 Introduction 349
7.2 Crystallography 351
7.3 Accommodation of shape deformation 354
7.3.1 Interfacial structure 356
7.3.2 Mechanical stabilisation 356
7.4 Transformation-start temperature 357
7.5 Mechanism of nucleation 359
7.6 Rationalisation of shear transformations 361
7.7 Nucleation rate 363
7.8 Capillarity 364
7.9 Growth of Widmanstätten ferrite 365
7.9.1 Interface-controlled growth 370
7.9.2 Groups of plates 370
7.10 Plate thickening 372
7.11 Growth from allotriomorphic ferrite 374

Chapter 8 Cementite 381

8.1 Crystal structure of cementite 383
8.1.1 Types of interstitial sites 384
8.2 Carbon content of cementite 385
8.3 Magnetic properties 387
8.4 Thermal properties 389
8.5 Surface energy 390
8.6 Elastic properties of single crystalline cementite 391
8.7 Elastic properties of polycrystalline cementite 393
8.8 Substitutional solutes 394
8.8.1 Precipitates inside cementite 397
8.9 Thermodynamic properties 398
8.9.1 Heat capacity 398
8.9.2 Equilibrium between cementite and matrix dislocations 399
8.9.3 Graphitisation and synthesis 399

8.10 Cementite precipitation in metallic glass 400
8.11 Carbon nanotubes – role of cementite 401
8.12 Displacive mechanism of cementite precipitation 402
8.13 α/θ orientation relations in pearlite 406
8.14 Pitsch γ/θ orientation relationship 407

Chapter 9 Other Fe-C carbides 419

9.1 Generic considerations 419
9.1.1 Observations of χ, η, ε and θ carbides in tempered Fe-C 420
9.2 χ-carbide 422
9.3 η-carbide 425
9.4 ε-carbide 427
9.4.1 Elastic moduli of ε-carbide 433

Chapter 10 Nitrides 445

10.1 γ'-nitride 446
10.2 ε-nitrides 448
10.3 ζ-Fe_2N 450
10.4 α''-$Fe_{16}N_2$ 451
10.5 Z-phase 453
10.6 Nb(CN), CrN, TiN, Cr_2N, AlN 454

Chapter 11 Substitutionally alloyed precipitates 463

11.1 TiC, NbC 463
11.2 Vanadium carbide 467
11.3 $M_{23}C_6$ 469
11.4 M_6C 471
11.5 M_7C_3 473
11.6 Mo_2C 475
11.7 κ-carbide 478
11.8 Laves phase 480
11.9 Other intermetallic compounds 481
11.9.1 NiAl 482
11.9.2 σ-phase 482
11.9.3 μ-phase 484
11.9.4 Iron-zinc compounds 485
11.10 Competitive precipitation and dissolution 487

Chapter 12 Pearlite 497

12.1 Shape 497
12.2 Nucleation 500
12.3 Growth 503
12.4 Fe-C-X: growth with local equilibrium 508
12.4.1 Local equilibrium? 510
12.5 Forced velocity pearlite 512
12.6 Pearlite not containing cementite 512
12.7 Divorced eutectoid transformation 513

Chapter 13 Aspects of kinetic theory 519

13.1 Grain growth 519
13.2 Recrystallisation 521
13.2.1 Phenomenological treatment of recrystallisation 524
13.2.2 Thermomechanical processing: limits to grain refinement 525
13.3 Overall transformation kinetics 526
13.3.1 Isothermal transformation 526
13.4 Simultaneous transformations 528
13.4.1 Basis of microstructural models 529
13.4.2 Allotriomorphic ferrite 529
13.4.3 Widmanstätten ferrite and pearlite 532
13.5 Time-temperature-transformation diagrams 535
13.5.1 Continuous cooling transformation diagrams 537
Author index 544
Subject index 568