

Contents

Part I Fundamentals

1 Introduction.....	3
References.....	7
2 Field Ion Microscopy.....	9
2.1 Principles.....	9
2.1.1 Theory of Field Ionisation	10
2.1.2 “Seeing” Atoms: Field Ion Microscopy	11
2.1.3 Spatial Resolution of FIM	16
2.2 Instrumentation and Techniques for FIM.....	18
2.2.1 FIM Instrumentation	18
2.2.2 eFIM or Digital FIM.....	19
2.2.3 Tomographic FIM Techniques.....	20
2.3 Interpretation of FIM Images	21
2.3.1 Interpretation of the Image in a Pure Material	21
2.3.2 Interpretation of the Image for Alloys.....	22
2.3.3 Selected Applications of the FIM.....	23
2.3.4 Summary	27
References.....	27
3 From Field Desorption Microscopy to Atom Probe	
Tomography.....	29
3.1 Principles.....	29
3.1.1 Theory of Field Evaporation.....	29
3.1.2 “Analysing” Atoms one-by-one: Atom	
Probe Tomography.....	39

3.2	Instrumentation and Techniques for APT.....	43
3.2.1	Experimental Setup	43
3.2.2	Field Desorption Microscopy	47
3.2.3	HV-Pulsing Techniques.....	50
3.2.4	Laser-Pulsing Techniques.....	52
3.2.5	Energy-Compensation Techniques	62
	References.....	64

Part II Practical Aspects

4	Specimen Preparation.....	71
4.1	Introduction.....	71
4.1.1	Sampling Issues in Microscopy for Materials Science and Engineering.....	72
4.1.2	Specimen Requirements	73
4.2	Polishing Methods.....	74
4.2.1	The Electropolishing Process	74
4.2.2	Chemical Polishing	79
4.2.3	Safety Considerations	79
4.2.4	Advantages and Limitations	81
4.3	Broad Ion-Beam Techniques.....	81
4.4	Focused Ion-Beam Techniques	82
4.4.1	Cut-Away Methods	83
4.4.2	Lift-out Methods	88
4.4.3	The Final Stages of FIB Preparation	96
4.4.4	Understanding and Minimising Ion-Beam Damage and Other Artefacts.....	96
4.5	Deposition Methods for Preparing Coatings and Films	101
4.6	Methods for Preparing Organic Materials	101
4.6.1	Polymer Microtips	101
4.6.2	Self-assembled Monolayers.....	102
4.6.3	Cryo-Preparation	103
4.7	Other Methods.....	104
4.7.1	Dipping.....	104
4.7.2	Direct Growth of Suitable Structures.....	104
4.8	Issues Associated with Specimen Geometry.....	104
4.8.1	Influence of Specimen Geometry on Data Quality.....	104
4.9	A Guide to Selecting an Optimal Method for Specimen Preparation	106
	References.....	107

5	Experimental Protocols in Field Ion Microscopy	111
5.1	Step-by-Step Procedures for FIM	111
5.2	Operational Space of the Field Ion Microscope	114
5.2.1	Imaging-Gas	114
5.2.2	Temperature	115
5.2.3	The “Best Image Field”	116
5.2.4	Other Parameters	117
5.3	Summary	119
	References	119
6	Experimental Protocols in Atom Probe Tomography	121
6.1	Specimen Alignment	121
6.2	Aspects of Mass Spectrometry	123
6.2.1	Detection of the Ions	123
6.2.2	Mass Spectra	124
6.2.3	Formation of the Mass Spectrum	125
6.2.4	Mass Resolution	127
6.2.5	Common Artefacts	129
6.2.6	Elemental Identification	132
6.2.7	Measurement of the Composition	135
6.2.8	Detectability	136
6.3	Operational Space	136
6.3.1	Flight Path	137
6.3.2	Pulse Fraction and Base Temperature	137
6.3.3	Selecting the Pulsing Mode	139
6.3.4	Pulsing Rate	140
6.3.5	Detection Rate	141
6.4	Specimen Failure	142
6.5	Assessment of Data Quality	144
6.5.1	Field Desorption map	145
6.5.2	Mass Spectrum	146
6.5.3	Multiple Events	150
6.6	Discussion	151
	References	153
7	Tomographic Reconstruction	157
7.1	Projection of the Ions	157
7.1.1	Estimation of the Electric Field	158
7.1.2	Field Distribution	159
7.1.3	Ion Trajectories	160
7.1.4	Point-Projection Model	162
7.1.5	Radial Projection with Angular Compression	163
7.1.6	Which Is the Best Model of Ion Trajectories?	164

7.2	Reconstruction.....	165
7.2.1	Fundamentals of the Reconstruction Protocol.....	166
7.2.2	Bas et al. Protocol.....	169
7.2.3	Geiser et al. Protocol.....	171
7.2.4	Gault et al. Protocol.....	172
7.2.5	Reflectron-Fitted Instruments.....	172
7.2.6	Summary and Discussion.....	173
7.3	Calibration of the Reconstruction.....	174
7.3.1	Techniques for Calibrating the Reconstruction Parameters.....	174
7.3.2	Importance of Calibrating the Reconstruction.....	179
7.3.3	Limitations of the Current Procedures.....	181
7.4	Common Artefacts and Potential Corrections.....	185
7.4.1	Trajectory Aberrations and Local Magnification Effects.....	185
7.4.2	Surface Migration.....	188
7.4.3	Chromatic Aberrations.....	190
7.4.4	Impact of These Artefact on Atom Probe Data.....	190
7.4.5	Correction of the Reconstruction.....	190
7.5	Perspectives on the Reconstruction in Atom Probe Tomography.....	194
7.5.1	Advancing the Reconstruction by Correlative Microscopy.....	195
7.5.2	Improving Reconstructions with Simulations.....	197
7.5.3	Alternative Ways to Reconstruct Atom Probe Data.....	197
7.6	Spatial Resolution in APT.....	198
7.6.1	Introduction.....	198
7.6.2	Means of Investigation.....	198
7.6.3	Definition of the Spatial Resolution.....	199
7.6.4	Depth Resolution.....	199
7.6.5	Lateral Resolution.....	201
7.6.6	Optimisation of the Spatial Resolution.....	202
7.7	Lattice Rectification.....	204
	References.....	205

Part III Applying Atom Probe Techniques for Materials Science

8	Analysis Techniques for Atom Probe Tomography.....	213
8.1	Characterising the Mass Spectrum.....	213
8.1.1	Noise Reduction.....	214
8.1.2	Quantifying Peak Contributions from Isotopic Natural Abundances.....	219
8.1.3	Spatially Dependent Identification of Mass Peaks.....	221
8.1.4	Analyses of Multi-hit Detector Events.....	222

8.2	Characterising the Chemical Distribution	225
8.2.1	Quality of Atom Probe Data	226
8.2.2	Random Comparators	228
8.3	Grid-Based Counting Statistics	230
8.3.1	Voxelisation	230
8.3.2	Density	232
8.3.3	Concentration Analyses	232
8.3.4	Smoothing by Delocalisation	233
8.3.5	Visualisation Techniques Based on Isoconcentration and Isodensity	233
8.3.6	One-Dimensional Profiles	235
8.3.7	Grid-Based Frequency Distribution Analyses	242
8.4	Techniques for Describing Atomic Architecture	253
8.4.1	Nearest Neighbour Distributions	253
8.4.2	Cluster Identification Algorithms	260
8.4.3	Influence of Detection Efficiency on Nanostructural Analyses	274
8.5	Radial-Distributions	280
8.5.1	Radial-Distribution and Pair Correlation Functions	280
8.5.2	Solute Short-Range Order Parameters	284
8.6	Structural Analyses	286
8.6.1	Fourier Transforms for APT	287
8.6.2	Spatial Distribution Maps	288
8.6.3	Hough Transform	292
	References	294
9	Atom Probe Microscopy and Materials Science	299
9.1	Phase Composition	301
9.2	Crystal Defects	301
9.3	Solute-Atom Clustering and Short Range Order	302
9.4	Precipitation Reactions	303
9.5	Long-Range Order	304
9.6	Spinodal Decomposition	304
9.7	Interfaces	305
9.8	Amorphous Materials	306
9.9	Atom Probe Crystallography	306
	References	309

Appendices	313
A. Appendix: χ^2 Distribution	313
References	318
B. Appendix: Polishing Chemicals and Conditions	319
References	321
C. Appendix: File Formats Used in APT	322
POS	322
EPOS	323
RNG	324
RRNG	325
ATO	325
ENV	326
PoSAP	328
Cameca Root Files: RRAW, RHIT, ROOT	328
D. Appendix: Image Hump Model Predictions	330
E. Appendix: Essential Crystallography for APT	332
Bravais Lattices	332
Notation	332
Structure Factor (F) Rules for bcc, fcc, hcp	332
Interplanar Spacings (d_{hkl})	333
Interplanar Angles (ϕ)	335
F. Appendix: Stereographic Projections and Commonly Observed Desorption Maps	338
Stereographic Projection for the Most Commonly Found Structures and Orientations	339
References	351
G. Appendix: Periodic Tables	352
H. Appendix: Kingham CURVES	356
References	356
I. Appendix: List of Elements and Associated Mass to Charge Ratios	363
J. Appendix: Possible Element Identity of Peaks as a Function of their Location in the Mass Spectrum	370
Index	387