

Contents

Preface	viii
<i>Chapter 1 (A.V. Ruban, H.L. Skriver and J. Nørskov)</i>	
Local equilibrium properties of metallic surface alloys	
1. Introduction	1
2. Surface energy	2
2.1 Monoatomic solids	2
2.2 Alloys	5
3. Stable surface alloy configurations	7
4. Generic classes of surface alloying	8
4.1 Mixing energy	9
4.2 Segregation energy	10
5. General trends for the surface mixing energies in transition metal alloys	11
6. General trends for the surface segregation energies in transition metal alloys	13
7. Island formation: multilayer versus monolayer growth	15
8. Bulk-type ordered surface alloys	19
9. Alternative ordered structures on the surface	23
Acknowledgement	27
References	28
<i>Chapter 2 (G. Bozzolo and J.E. Garces)</i>	
Atomistic modelling of surface alloys	
1. Introduction	30
2. The BFS method	36
2.1 Calculation of the BFS strain energy	39
2.2 Calculation of the BFS chemical energy	44
2.3 The BFS reference state in surface alloys vs. epitaxial growth	45
3. BFS modelling of surface alloys	47
3.1 Computational procedure	48
3.2 Au/Ni(110)	51
3.3 Pd/Ni(110)	60
3.4 Pd/Cu(100)	62
3.5 Pd/Cu(110)	68
3.6 Cu/Pd(110)	68
3.7 Pt/Cu(100)	68
3.8 Au/Cu(100) and Au/Cu(110)	72
3.9 Cu/Ni(110)	78
3.10 (Cu, Au)/Ni(110)	79
4. Conclusions	82
Acknowledgements	83
References	83

Chapter 3 (M. Polak and L. Rubinovich)

Alloy surface segregation and ordering phenomena: recent progress	
1. Overview	86
2. Segregation in multi-element alloys	90
3. Surface segregation in ordered alloys	96
3.1 Prediction of order/segregation interplay by means of a simple model	97
3.1.1 Equiatomic binary alloys	97
3.1.2 Non-equiatomic binary alloys	99
3.2 Case studies	101
3.2.1 Compositional variations in Cu ₃ Au(100) and Cu ₃ Pd(100)	101
3.2.2 Surface order in Pt ₃ Sn(111) and Co ₃ Pt(111)	104
3.2.3 Segregation characteristics of aluminide surfaces	105
4. Segregation in a bi-phase binary alloy	109
5. Summary	113
References	115

Chapter 4 (M. Schmid and P. Varga)

Segregation and surface chemical ordering – an experimental view on the atomic scale	
1. Introduction	118
2. Chemical discrimination on bimetallic surfaces with atomic resolution by STM	120
2.1 True topographic effect	121
2.2 Difference in local electronic density of states	123
2.3 Tip-surface interaction	125
3. Segregation on alloys – surface and subsurface composition	127
3.1 Segregation	127
3.2 Preferential sputtering and segregation in the altered layer	128
4. Chemical ordering of alloy surfaces	130
4.1 Bulk chemical order	130
4.2 Fundamentals of surface chemical order	131
4.3 Chemical order of close-packed alloy surfaces	134
4.4 fcc(100) surfaces	140
4.5 Site-specific segregation	141
5. Implications for adsorption on alloys	144
5.1 Chemical affinity	144
5.2 The ensemble effect	145
5.3 The ligand effect	147
6. Conclusions	148
Acknowledgement	149
References	149

Chapter 5 (G.L. Kellogg)**Surface alloying and de-alloying of Pb on single-crystal Cu surfaces**

1. Introduction	152
2. Experimental and theoretical techniques	154
2.1 Experimental	154
2.2 Theoretical	157
3. Atomic structure, surface alloying and de-alloying	158
3.1 Pb on Cu(111)	158
3.2 Pb on Cu(100)	165
3.3 Pb on Cu(110)	172
3.4 Pb on stepped surfaces of Cu	175
3.5 Summary of Pb surface alloy and overlayer structures on single-crystal surfaces of Cu	178
4. Concluding remarks	178
Acknowledgements	180
References	180

Chapter 6 (S. Speller and U. Bardi)**Surface alloys and alloy surfaces: the platinum-tin system**

1. Introduction	184
2. Methods	185
3. The platinum-tin system	190
3.1 Low index surfaces of the Pt ₃ Sn alloy	191
3.1.1 Pt ₃ Sn(111)	191
3.1.2 Pt ₃ Sn(001)	197
3.1.3 Pt ₃ Sn(110)	202
3.2 Surface alloys obtained depositing tin on platinum surfaces	207
3.2.1 Sn-Pt(111)	207
3.2.2 Sn-Pt(100)	209
4. Discussion	210
4.1 Surface atomic structure of the bulk Pt ₃ Sn alloys	212
4.2 Defects and disorder on Pt ₃ Sn alloy surfaces	215
4.3 Multilayer and single layer surface alloys	217
5. Conclusion	219
Appendix: Notes on nomenclature	220
References	221

Chapter 7 (D.L. Adams and J.N. Andersen)**Alkali-aluminum surface alloys**

1. Introduction	225
1.1 Background	225
1.2 Present work	226
2. Experimental methods	228
2.1 LEED measurements	228
2.2 LEED analysis	228
2.3 The surface structures of clean Al(111), (100) and (110)	229

2.4 Core-level measurements	229
3. Adsorption on Al(111)	233
3.1 Al(111)-(2x2)-Rb and Cs phases formed at 100 K	234
3.2 Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-K, Rb and Cs phases formed at 100 K	235
3.3 Al(111)-(4x4)-Na phase formed at 100 K	235
3.4 Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Li, Na, K and Rb phases formed at 300 K	237
3.5 Al(111)-(2 $\sqrt{3}\times 2\sqrt{3}$)R30°-Cs phase formed at 300 K	240
3.6 Al(111)-(2x2)-Na phase formed at 300 K	241
3.7 Ternary surface alloys formed by coadsorption on Na and K, Rb or Cs on Al(111) at 300K	243
4. Adsorption on Al(100)	245
4.1 Al(100)-(2x2)-Na phase formed at 100 K	246
4.2 Al(100)-($\sqrt{5}\times\sqrt{5}$)R26.6°-Na phase formed at 240 K	246
4.3 Al(100)-c(2x2)-Li and Na phases formed at 300 K	247
4.4 Al(100)-c(2x2)-2Li phase formed at 400 K	248
5. Adsorption on Al(110)	253
5.1 Al(110)-c(2x2)-Li and Na phases formed at 300 K	253
5.2 Al(110)-(4x1)-3Na phase formed at 300 K	254
6. Phase transitions	257
6.1 Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-K and Rb	258
6.2 Al(100)-c(2x2)-Na	261
6.3 Al(100)-($\sqrt{5}\times\sqrt{5}$)R26.6°-Na	262
7. The role of DFT calculations	264
7.1 Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Na and K	264
7.2 Al(111)-(2x2)-Na	266
7.3 Al(100)-($\sqrt{5}\times\sqrt{5}$)R26.6°-Na	267
7.4 Al(100)-c(2x2)-Na	268
7.5 Al(100)-c(2x2)-Li	268
7.6 Al(100)-c(2x2)-2Li	269
8. Summary and conclusions	270
Acknowledgements	273
References	273

Chapter 8 (D.P. Woodruff and E. Vlieg)**The structure of surface alloy phases on metallic substrates**

1. Introduction	277
2. Case studies	278
2.1 Cu(111)/Sb and Ag(111)/Sb: interfacial stacking faults	278
2.2 Ni(111)/Pb: a case of strongly suppressed surface alloy rumpling	286
2.3 Mn and non-magnetic metals on Cu(100), Ni(100) and Pd(100): effect of local magnetic moments	288
2.4 Surface alloys formed by Sn on Cu, Ni, Pt and Rh surfaces: effect of changing substrate lattice parameter and surface orientation on rumpling amplitude	291
3. Interatomic distances in surface alloys	293
4. More complex systems	298
5. Conclusions	301
References	302

Chapter 9 (C.J. Barnes)

Surface alloy formation on Cu{100}	
1. Introduction	305
2. Cu{100}-c(2x2)-X (X=Au,Pd,Mn) surface alloys	308
2.1 Geometric and electronic structure	308
2.2 Growth mechanism of Cu{100}-c(2x2) surface alloys	315
3. Surface alloy formation upon Co, Fe and Ni adsorption	322
4. Surface alloy formation upon alkali and alkaline earth metal adsorption	326
4.1 The Cu{100}/Li surface alloy: the coverage dependent (2x1)→(3x3)→(4x4) transition	326
4.2 The Cu{100}-c(2x2)-Mg surface alloy	331
5. De-alloying transitions: adsorption of group IIIA, IVA and VA metals	333
5.1 The Cu{100}/Pb system	334
5.2 De-alloying in the Cu{100}/Bi system	339
5.3 Surface alloy formation in the Cu{100}/In and Sn systems	341
5.4 De-alloying transitions for transition metal adsorbates	343
6. Underlayer 2D alloys and overlayer to underlayer transitions	345
6.1 The Cu{100}-c(2x2)-Pd overlayer to underlayer transition	345
6.2 Cu{100}/Pt: the Cu{100}-c(2x2)-Pt underlayer alloy	347
6.3 Cu{100}/Ir: the unusual case of p(2x1) underlayer formation	349
7. Formation of ordered multilayer alloys	351
7.1 The Cu{100}-p(2x2)-1 ML Pd surface alloy	351
7.2 The Cu{100}-c(2x2)-Pt multilayer alloy	355
7.3 The Cu{100}-(4x2)-pgg-Mn structure	356
8. Conclusions	358
Acknowledgements	359
Reference	359

Chapter 10 (H. Niehus)

Surface and sub-surface alloy formation connected with ordered superstructures	
1. Introduction	364
2. Surfaces of ordered bulk alloys	366
2.1 Preparation dependent surface composition: NiAl	366
2.2 Surface properties of alloys with identical surface composition	372
2.2.1 Cu ₃ Au(110)	373
2.2.2 Cu ₃ Au(100)	375
3. Surface alloys of bulk immiscible constituents	378
3.1 Sub-surface alloy formation: iridium on Cu(100)	378
3.2 Intermixing versus phase separation: copper on Ir(100)-(5x1)	389
4. Alloy surfaces as substrates for ordered superstructures	393
4.1 Vanadium on Cu ₃ Au(100)	394
4.2 Vanadium oxide on Cu ₃ Au(100)-O	396
5. Summary	399
Acknowledgement	400
References	400

Chapter 11 (J.C. Bertolini and Y. Jugnet)

Surface structure and catalytic activity of palladium overlayers with 1,3-butadiene hydrogenation	
1. Introduction	404
2. Experimental approach	407
3. The 1,3-butadiene hydrogenation reaction	409
4. Surface and reactivity of Pd based alloy surfaces	413
4.1 General points	413
4.2 Surface composition and reactivity of Pd ₅ Ni ₉₅ and Pd ₅ Pt ₉₅ polycrystals	414
4.3 Influence of the surface orientation on reactivity	418
4.3.1 A solid solution in the whole range of composition: Pd ₈ Ni ₉₂ (111) and (110)	418
4.3.2 A system with a tendency to ordering: Pd ₅₀ Cu ₅₀ (111) and (110)	421
5. Surface and reactivity of Pd deposits	423
5.1 Pd in compression on Ni and Cu	423
5.1.1 Case thermodynamically favouring A on B: Pd on Ni	423
Pd on Ni(111)	423
Pd on Ni(110)	424
5.1.2 Case of A on B unfavourable: Pd on Cu(110)	428
5.2 Pd in tension on Au(110)	430
6. Summary and conclusion	433
Acknowledgements	434
References	435

Chapter 12 (J.A. Rodriguez)

Electronic and chemical properties of palladium in bimetallic systems: how much do we know about heteronuclear metal-metal bonding?	
1. Introduction	438
2. Photoemission studies	439
3. Thermal desorption studies	445
4. CO chemisorption studies	448
5. Models for bimetallic bonding	454
6. Theoretical studies	455
6.1 Charge redistribution in bimetallic bonding	455
6.2 Core-level and valence-band shifts	458
6.3 CO chemisorption	460
7. Conclusion	462
Acknowledgement	462
References	462

Chapter 13 (J.A. Rodriguez and J. Hrbek)**Interaction of sulphur with bimetallic surfaces: effects of structural, electronic and chemical properties**

1. Introduction	466
2. Repulsive interactions between gold and sulphur on transition metal surfaces	467
3. Interaction of sulphur with Ag/Ru(0001) and Cu/Ru(0001)	475
4. Admetal promoted sulphidation of Pt(111) and Mo(110)	482
5. Bimetallic bonding and the prevention of sulphur poisoning	488
6. Conclusion	492
Acknowledgement	492
References	492

Chapter 14 (C.J. Baddeley)**Adsorbate induced segregation at bimetallic surfaces**

1. Introduction	495
1.1 Bimetallic surface chemistry – traditional ideas	495
1.1.1 Ensemble effects	497
1.1.2 Electronic effects	499
2. Adsorbate induced segregation	500
2.1 Thermodynamic considerations	500
3. Techniques for characterising adsorbate induced segregation	505
3.1 Photoelectron spectroscopies	505
3.1.1 X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)	505
3.1.2 Photoelectron microscopy (PEEM, SPEM)	508
3.2 Ion scattering spectroscopies	508
3.2.1 Low energy ion scattering (LEIS)	509
3.2.2 Medium energy ion scattering (MEIS)	510
3.3 X-ray absorption spectroscopies	515
3.3.1 Extended X-ray absorption fine structure (EXAFS)	515
3.4 Vibrational spectroscopies	516
3.4.1 Infra-red spectroscopy	516
3.5 Other techniques	517
3.5.1 Scanning tunnelling microscopy (STM)	517
3.5.2 Low energy electron diffraction (LEED)	521
3.5.3 Nuclear magnetic resonance (NMR)	522
4. Conclusions	522
References	523
Index	527