Mass transport in solids and fluids

David S. Wilkinson
Department of Materials Science and Engineering, McMaster University

Cover photograph: Transmission electron micrograph images of an Al–4 wt% Cu alloy during *in-situ* annealing within the electron microscope at 320 °C. These two micrographs, taken 15 minutes apart, show the progressive dissolution of platelike particles of $CuAl_2$. The field of each micrograph is about 4 μm wide. (Courtesy of Prof. G. C. Weatherly, McMaster University.)

CAMBRIDGE
UNIVERSITY PRESS

Contents

Preface *xiii*
Principal symbols *xv*

Part A: Overview *1*
1 Introduction to mass transport mechanisms *3*
1.1 Mass transport processes *3*
1.2 Statement of Fick's First Law *4*
1.3 Mechanisms of diffusion *6*
1.4 Diffusion in solids *7*
1.4.1 Interstitial diffusion *8*
1.4.2 Vacancy diffusion *11*
1.4.3 Diffusion in alloys *13*
1.4.4 Diffusion in compounds *14*
1.5 Diffusion in liquids *14*
1.6 Diffusion in gases *15*
1.7 Diffusion data *17*
1.8 Mass transport by convection *19*
1.9 Further reading *20*
1.10 Problems to chapter 1 *20*

Part B: Solid-state diffusion in dilute alloys *23*
2 Steady-state diffusion *25*
2.1 Fick's First Law *26*
2.2 Applications to steady-state problems *26*
2.2.1 Measurement of the diffusion coefficient *26*
2.2.2 Permeability of gases through a solid *29*
2.2.3 Diffusion in parallel through a composite solid *35*

2.3 Growth of surface layers – pseudo steady state *39*
2.3.1 Growth of oxide films *39*
2.3.2 Slip casting *43*
2.4 Further reading *44*
2.5 Problems to chapter 2 *44*

3 Transient diffusion problems *47*
3.1 Fick's Second Law *47*
3.2 Solutions to Fick's Second Law *50*
3.2.1 Introduction *50*
3.2.2 Approaches to solving transient diffusion problems *51*
3.3 Solutions to Fick's Second Law at short time (far from equilibrium) *54*
3.3.1 Plane initial source *54*
3.3.2 Diffusion from a distributed source *60*
3.3.3 Diffusion from a surface at fixed concentration *64*
3.3.4 Diffusion between two solids with different initial solute concentration *68*
3.4 The nominal diffusion distance *68*
3.5 Solution methods for Fick's Second Law at longer time (near equilibrium) *72*
3.5.1 Diffusion in a slab from a plane initial source *72*
3.5.2 Use of image sources *73*
3.5.3 General solutions to Fick's Second Law *77*
3.6 Standard solutions to long-time transient diffusion problems *80*
3.6.1 Uniform initial concentration C_i and fixed surface concentration C_s *80*
3.6.2 Uniform initial concentration C_i with fixed surface flux J^* *85*
3.6.3 Uniform initial concentration but different boundary conditions *86*
3.6.4 Diffusion through a hollow cylinder or sphere *88*
3.6.5 Other solutions *89*
3.7 Further reading *90*
3.8 Problems to chapter 3 *90*

4 Applications to problems in materials engineering *96*
4.1 Introduction *96*
4.2 Boundary conditions *97*

5 Applications involving gas–solid reactions *99*
5.1 Introduction *99*

5.2 Simple gas–solid reactions *100*
5.3 Reactions involving gas mixtures *104*
5.4 Semiconductor doping *105*
5.5 Gas/solid interfaces without local equilibrium *107*
5.6 Further reading *109*
5.7 Problems to chapter 5 *109*

6 Heat treatment of binary alloys *114*
6.1 Introduction *114*
6.2 Changing temperature within a two-phase field *115*
6.2.1 Solution valid at short time *117*
6.2.2 Solution valid at long time *117*
6.3 Particle dissolution *120*
6.3.1 Dissolution of plates *120*
6.3.2 Dissolution of spherical particles *123*
6.4 Growth of second-phase particles by solute rejection *125*
6.4.1 Planar growth *125*
6.4.2 Precipitation of spherical particles *130*
6.5 Cooperative growth processes *132*
6.6 Further reading *136*
6.7 Problems to chapter 6 *136*

Part C: Mass transport in concentrated alloys and fluids *147*
7 Diffusion in concentrated alloys and fluids *149*
7.1 Concept of counter diffusion *150*
7.2 Kirkendall effect in solids *153*
7.2.1 Interdiffusion coefficient *153*
7.2.2 Diffusion couples *157*
7.3 Solid-state diffusion couples involving immiscible phases *159*
7.3.1 Simple diffusion couples for immiscible solids with no intermediate phases *159*
7.3.2 Couples with intermediate phases *162*
7.4 Diffusion in quiescent fluids *166*
7.4.1 Simple evaporation *167*
7.4.2 Evaporation involving reactions at a front *169*
7.4.3 Particle condensation during evaporation *171*
7.5 Near-surface internal precipitation in alloys *173*
7.6 Further reading *176*
7.7 Problems to chapter 7 *176*

8 Mass transport in the presence of convection *183*
8.1 Transient diffusion in fluids *183*

8.2 Mass transport at a flowing interface *185*
8.3 Mass transfer coefficient *187*
8.3.1 Mass transfer to spheres *188*
8.3.2 Mass transfer coefficient for other geometries *190*
8.4 Models for mass transfer *191*
8.4.1 Stagnant film model *191*
8.4.2 Higbie penetration model *192*
8.4.3 Application to modelling evaporation from molten metal *194*
8.5 Quiescent systems containing internal reactions *195*
8.6 Further reading *197*
8.7 Problems to chapter 8 *197*

9 Advanced topics *202*
9.1 Overall mass balance *202*
9.2 Multi-phase resistances *206*
9.3 Topochemical reaction kinetics *209*
9.3.1 Reduction of oxide pellets *209*
9.3.2 Gas diffusivity in porous solids *212*
9.4 Further reading *214*
9.5 Problems to chapter 9 *214*

Part D: Alternative driving forces for diffusion *221*
10 General driving force for diffusion *223*
10.1 Theory *223*
10.2 Diffusion due to an electrical field *226*
10.3 Diffusion due to mechanical stress *227*
10.3.1 Vacancy diffusion due to local forces *227*
10.3.2 Application to diffusion creep *230*
10.4 Diffusion due to surface curvature *231*
10.5 Diffusion due to an activity gradient *232*
10.5.1 Application to 'uphill' diffusion *233*
10.6 Further reading *234*
10.7 Problems to chapter 10 *234*

Appendices *236*
A Mathematical methods for the solution of Fick's Second Law *236*
A.1 Separation of variables method *236*
A.2 Laplace transform method *240*

B Selected diffusion data *242*
B.1 Self-diffusivity of the elements *242*

B.2 Solute diffusivity in compounds *242*
B.3 Solute diffusivity in alloys *243*

C Selected binary and pseudo-binary phase diagrams *244*

D Solving problems by developing conceptual models *258*
D.1 Introduction *258*
D.2 General method (to be adapted for particular cases) *259*
D.3 Example *261*
D.4 Problems on modelling *264*

E Useful fundamental constants and conversions *267*

Index *268*