

Materials Science

AN INTERMEDIATE TEXT

William F. Hosford



CAMBRIDGE

Materials Science

AN INTERMEDIATE TEXT

WILLIAM F. HOSFORD

University of Michigan



CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town,
Singapore, São Paulo, Delhi, Tokyo, Mexico City

Cambridge University Press
32 Avenue of the Americas, New York, NY 10013-2473, USA

www.cambridge.org

Information on this title: www.cambridge.org/9780521356251

© William F. Hosford 2007

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without the written
permission of Cambridge University Press.

First published 2007

Reprinted 2008

First paperback edition 2011

A catalog record for this publication is available from the British Library

Library of Congress Cataloging in Publication data

Hosford, William F.

Materials science : an intermediate text / William F. Hosford.

p. cm.

Includes bibliographical references and index.

ISBN-13: 978-0-521-86705-4 (hardback)

ISBN-10: 0-521-86705-3 (hardback)

1. Materials science – Textbooks. I. Title.

TA403.H63 2006

620.1'1 – dc22 2006011097

ISBN 978-0-521-86705-4 Hardback

ISBN 978-0-521-35625-1 Paperback

Cambridge University Press has no responsibility for the persistence or
accuracy of URLs for external or third-party internet websites referred to in
this publication, and does not guarantee that any content on such websites is,
or will remain, accurate or appropriate.

MATERIALS SCIENCE

This text is intended for a second-level course in materials science and engineering. Chapters encompass crystal symmetry including quasi-crystals and fractals, phase diagrams, diffusion including treatment of diffusion in two-phase systems, solidification, solid-state phase transformations, amorphous materials, and bonding in greater detail than is usual in introductory materials science courses. Additional subject material includes stereographic projection, the Miller–Bravais index system for hexagonal crystals, microstructural analysis, the free energy basis for phase diagrams, surfaces, sintering, order–disorder reaction, liquid crystals, molecular morphology, magnetic materials, porous materials, and shape memory and superelastic materials. The final chapter includes useful hints in making engineering calculations. Each chapter has problems, references, and notes of interest.

William F. Hosford is a Professor Emeritus of Materials Science and Engineering at the University of Michigan. Professor Hosford is the author of a number of books including the leading selling *Metal Forming: Mechanics and Metallurgy*, 2/e (with R. M. Caddell), *Mechanics of Crystals and Textured Polycrystals*, *Physical Metallurgy*, and *Mechanical Behavior of Materials*.

Preface

This text is written for a second-level materials science course. It assumes that the students have had a previous course covering crystal structures, phase diagrams, diffusion, Miller indices, polymers, ceramics, metals, and other basic topics. Many of those topics are discussed in further depth, and new topics and concepts are introduced. The coverage and order of chapters are admittedly somewhat arbitrary. However, each chapter is more or less self-contained so those using this text may omit certain topics or change the order of presentation.

The chapters on microstructural analysis, crystal symmetry, Miller–Bravais indices for hexagonal crystals, and stereographic projection cover material that is not usually covered in introductory materials science courses. The treatment of crystal defects and phase diagrams is in greater depth than the treatments in introductory texts. The relation of phase diagrams to free energy will be entirely new to most students. Although diffusion is covered in most introductory texts, the coverage here is deeper. It includes the Kirkendall effect, Darken's equation, and diffusion in the presence of two phases.

The topics of surfaces and sintering will be new to most students. The short chapter on bonding and the chapters on amorphous materials and liquid crystals introduce new concepts. These are followed by treatment of molecular morphology. The final chapters are on magnetic materials, porous and novel materials, and the shape memory.

This text may also be useful to graduate students in materials science and engineering who have not had a course covering these materials.

The author wishes to thank David Martin for help with liquid crystals.

Contents

Preface	page xiii
1 Microstructural Analysis	1
Grain size	1
Relation of grain boundary area per volume to grain size	3
Relation of intersections per area and line length	4
Volume fraction of phases	4
Alloy composition from volume fraction of two or more phases	4
Microstructural relationships	5
Three-dimensional relations	6
Kelvin tetrakaidecahedron	6
Notes of interest	8
References	8
Problems	9
2 Symmetry	11
Crystal systems	11
Space lattices	11
Quasicrystals	14
Fractals	17
Note of interest	18
References	19
Problems	19
3 Miller–Bravais Indices for Hexagonal Crystals	21
Planar indices	21
Direction indices	22
Three-digit system	23
Note of interest	24
References	24
Problems	24

4 Stereographic Projection	26
Projection	26
Standard cubic projection	27
Locating the hkl pole in the standard stereographic projection of a cubic crystal	28
Standard hexagonal projection	30
Spherical trigonometry	31
Note of interest	31
References	31
Problems	31
5 Crystal Defects	33
Vacancies in pure metals	33
Point defects in ionic crystals	34
Dislocations	36
Burgers vectors	37
Energy of dislocations	38
Stress fields around dislocations	38
Partial dislocations	39
Notes of interest	40
References	41
Problems	41
6 Phase Diagrams	43
The Gibbs phase rule	43
Invariant reactions	44
Ternary phase diagrams	44
Notes of interest	49
References	49
Problems	50
7 Free Energy Basis for Phase Diagrams	52
Gibbs free energy	52
Enthalpy of mixing	52
Entropy of mixing	53
Solid solubility	55
Relation of phase diagrams to free energy curves	55
Pressure effects	57
Metastability	57
Extrapolations of solubility limits	60
Notes of interest	61
References	62
Problems	62

8	Ordering of Solid Solutions	64
	Long-range order	64
	Effect of long-range order on properties	67
	Short-range order	67
	Note of interest	67
	References	68
	Problems	68
9	Diffusion	69
	Fick's first law	69
	Fick's second law	70
	Solutions of Fick's second law and the error function	70
	Mechanisms of diffusion	73
	Kirkendall effect	74
	Temperature dependence	75
	Special diffusion paths	76
	Darken's equation	77
	Diffusion in systems with more than one phase	78
	Note of interest	81
	References	82
	Problems	82
10	Freezing	85
	Liquids	85
	Homogeneous nucleation	85
	Heterogeneous nucleation	88
	Growth	89
	Grain structure of castings	90
	Segregation during freezing	91
	Zone refining	93
	Steady state	95
	Dendritic growth	95
	Gas solubility and gas porosity	98
	Growth of single crystals	98
	Eutectic solidification	98
	Peritectic freezing	100
	Notes of interest	101
	References	101
	Problems	102
11	Phase Transformations	104
	Nucleation in the solid state	104
	Eutectoid transformations	106

Avrami kinetics	108
Growth of precipitates	111
Transition precipitates	113
Precipitation-free zones	113
Ostwald ripening	113
Martensitic transformations	114
Spinodal decomposition	116
Note of interest	118
References	119
Problems	119
12 Surfaces	121
Relation of surface energy to bonding	121
Orientation-dependence of surface energy	122
Surfaces of amorphous materials	125
Grain boundaries	125
Segregation to surfaces	127
Direct measurements of surface energy	128
Measurements of relative surface energies	129
Wetting of grain boundaries	130
Relative magnitudes of energies	131
Note of interest	131
References	131
Problems	131
13 Bonding	133
Ionic binding energy	133
Melting points	134
Elastic moduli	134
Covalent bonding	136
Geometric considerations	136
Ionic radii	139
Structures of compounds	140
Note of interest	142
References	143
Problems	143
14 Sintering	144
Mechanisms	144
Early stage of sintering	146
Intermediate stage of sintering	147
Final stage of sintering	147
Loss of surface area	147
Particle-size effect	148

Activated sintering	150
Liquid-phase sintering	150
Hot isostatic pressing	151
Note of interest	151
References	151
Problems	151
15 Amorphous Materials	153
Glass transition	153
Glass transition in polymers	154
Molecular length	154
Hard sphere model	155
Voronoi cells	157
Silicate glasses	157
Chemical composition	158
Bridging versus nonbridging oxygen ions	158
Glass viscosity	159
Thermal shock	160
Thermal expansion	161
Vycor	161
Devitrification	162
Delayed fracture	163
Other inorganic glasses	163
Metal glasses	164
Note of interest	166
References	167
Problems	167
16 Liquid Crystals	168
Types of liquid crystals	168
Orientational order parameter	169
Disclinations	170
Lyotropic liquid crystals	171
Temperature and concentration effects	171
Phase changes	172
Optical response	173
Liquid crystal displays	174
Note of interest	174
References	175
Problems	175
17 Molecular Morphology	176
Silicates	176
Molybdenum disulfide	178

Carbon: graphite	179
Diamond	179
Carbon fibers	180
Fullerenes	180
Nanotubes	181
Zeolites	182
Notes of interest	183
References	183
Problems	183
18 Magnetic Behavior of Materials	184
Ferromagnetism	184
Exchange energy	185
Magnetostatic energy	187
Magnetocrystalline energy	188
Magnetostriuctive energy	189
Physical units	189
The B - H curve	190
Curie temperature	191
Bloch walls	191
Magnetic oxides	192
Soft versus hard magnetic materials	194
Soft magnetic materials	194
Hard magnetic materials	197
Square-loop materials	199
Notes of interest	200
References	201
Problems	201
19 Porous and Novel Materials	202
Applications of porous materials	202
Fabrication of porous foams	202
Morphology of foams	203
Relative density of foams	203
Structural mechanical properties	204
Honeycombs	204
Novel structures	205
Notes of interest	205
Reference	206
Problems	206
20 Shape Memory and Superelasticity	208
Shape memory alloys	208
Superelasticity	209

Applications	212
Shape memory in polymers	212
Note of interest	213
References	213
Problems	213
21 Calculations	214
Estimates	214
Sketches	215
Units	217
Available data	219
Algebra before numbers	220
Ratios	220
Percentage changes	221
Finding slopes of graphs	221
Log-log and semilog plots	222
Graphical differentiation and integration	224
Iterative and graphical solutions	226
Interpolation and extrapolation	228
Analyzing extreme cases (bounding)	228
Significant figures	229
Logarithms and exponents	230
The Greek alphabet	231
Problems	231
Index	235

1 Microstructural Analysis

Many properties of materials depend on the grain size and the shape of grains. Analysis of microstructures involves interpreting two-dimensional cuts through three-dimensional bodies. Of interest are the size and aspect ratios of grains, and the relations between grain size and the amount of grain boundary area per volume. Also of interest is the relation between the number of faces, edges, and corners of grains.

Grain size

There are two commonly used ways of characterizing the grain size of a crystalline solid. One is the ASTM grain size number, N , defined by

$$n = 2^{N-1} \quad \text{or} \quad N = 1 + \ln(n)/\ln 2, \quad (1.1)$$

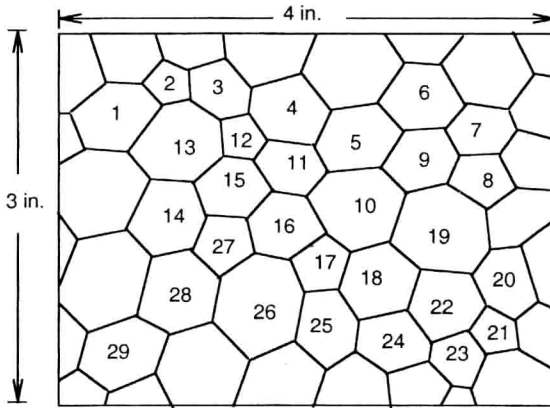
where n is the number of grains per square inch observed at a magnification of 100X. Large values of N indicate a fine grain size. With an increase of the grain diameter by a factor of $\sqrt{2}$, the value of n is cut in half and N is decreased by 1.

EXAMPLE 1.1. Figure 1.1 is a micrograph taken at 200X. What is the ASTM grain size number?

SOLUTION: There are 29 grains entirely within the micrograph. Counting each grain on an edge as one half, there are $22/2 = 11$ edge grains. Counting each corner grain as one quarter, there is 1 corner grain. The total number of grains is 41. The 12 square inches at 200X would be 3 square inches at 100X, so $n = 41/3 = 13.7$. From Equation (1.1),

$$N = \ln(n)/\ln(2) + 1 = 4.78 \text{ or } 5.$$

The average linear intercept diameter is the other common way to characterize grain sizes. The system is to lay down random lines on the microstructure and count the number of intersections per length of line. The average intercept diameter is then $\bar{\ell} = L/N$, where L is the total length of line and N is the number

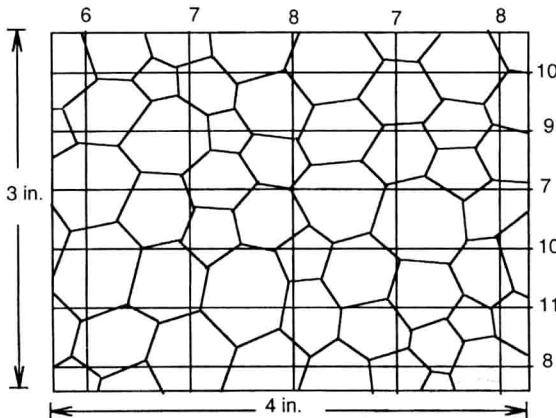


1.1. Counting grains in a microstructure at 200X.

of intercepts. Alternatively, a rectangular grid of lines may be laid down on an equiaxed microstructure.

EXAMPLE 1.2. Find the average intercept diameter for the micrograph in Figure 1.1.

SOLUTION: In Figure 1.2, $6 \times 4 + 5 \times 3 = 39$ inches of line are superimposed on the microstructure. This corresponds to $(39 \text{ in.} / 200)(25.4 \text{ mm/in.}) = 4.95 \text{ mm}$. There are 91 intercepts so $\bar{\ell} = .495 / 91 = 0.054 \text{ mm} = 54 \mu\text{m}$.

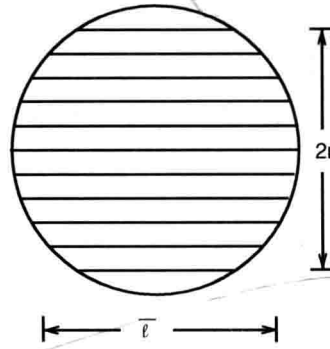


1.2. Finding the linear intercept grain size of a microstructure at 200X.

For random microstructures, $\bar{\ell}$ and the ASTM grain size are related. An approximate relationship can be found by assuming that the grains can be approximated by circles of radius, r . The area of a circular grain, πr^2 , can be expressed as the average linear intercept, $\bar{\ell}$, times its width, $2r$, as shown in Figure 1.3, so $\bar{\ell} \cdot 2r = \pi r^2$. Therefore,

$$r = (2/\pi)\bar{\ell} \quad \text{or} \quad \bar{\ell} = (\pi/2)r. \quad (1.2)$$

1.3. The area of a circle, πr^2 , equals the average intercept times twice the radius, $2\bar{\ell}r$, so $\bar{\ell} = (\pi/2)r$.



Thus, the area per grain is $A = 2r\bar{\ell} = (4/\pi)\bar{\ell}^2$. The number of grains per area is $(\pi/4)/\bar{\ell}^2$. From the definition of n , the number of grains per area is also $n[(25.4 \text{ mm/in.})/(100 \text{ in.})]^2$. Substituting $n = 2^{N-1} = 2^N/2$ and equating,

$$(\pi/4)/\bar{\ell}^2 = (2^N/2)(0.254)^2. \quad (1.3)$$

Solving for $\bar{\ell}$,

$$\bar{\ell} = 4.93/2^{N/2}. \quad (1.4)$$

Often grains are not equiaxed. They may be elongated in the direction of prior working. Restriction of grain growth by second-phase particles may prevent formation of equiaxed grains by recrystallization. In these cases, the linear intercept grain size should be determined from randomly oriented lines or an average of two perpendicular sets of lines. The degree of shape anisotropy can be characterized by an aspect ratio, α , defined as the ratio of average intercept in the direction of elongation to that at 90° :

$$\alpha = \bar{\ell}_{||}/\bar{\ell}_{\perp}. \quad (1.5)$$

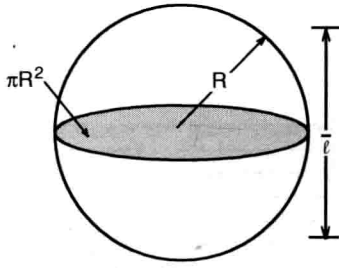
Relation of grain boundary area per volume to grain size

The grain boundary area per volume is related to the linear intercept. Assuming that grain shapes can be approximated by spheres, the grain boundary surface per grain is $2\pi R^2$, where R is the radius of the sphere. (The reason that it is not $4\pi R^2$ is that each grain boundary is shared by two neighboring grains.) The volume per spherical grain is $(4/3)\pi R^3$, so the grain boundary area/volume, S_v , is given by

$$S_v = (2\pi R^2)/[(4/3)\pi R^3] = 3/(2R). \quad (1.6)$$

To relate the spherical radius, R , to the linear intercept, $\bar{\ell}$, consider the circle through its center, which has an area of πR^2 (Figure 1.4). The volume equals the product of this area, πR^2 , and the average length of line, $\bar{\ell}$, perpendicular to it, $v = \bar{\ell}\pi R^2$. Therefore, $(4/3)\pi R^3 = \pi R^2\bar{\ell}$ or $R = (3/4)\bar{\ell}$. Substituting into $S_v = 3/(2R)$,

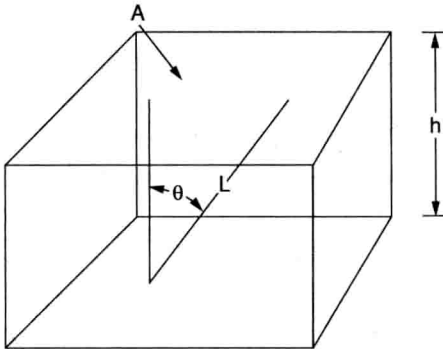
$$S_v = 2/\bar{\ell}. \quad (1.7)$$

1.4. The volume of a sphere = $\frac{4}{3}\pi R^3$.

Relation of intersections per area and line length

The number of intersections per area of dislocations with a surface is less than the total length of dislocation line per volume. Consider a single line of length L in a box of height h and area of A . The number of intersections per area, N_A , equals $1/A$ (Figure 1.5). The length per volume is $L_V = L/(hA)$ so $N_A/L_V = h/L$. Because $\cos \theta = h/L$, $N_A/L_V = \cos \theta$. For randomly oriented lines, the number oriented between θ and $\theta + d\theta$ is $dn = n df$, where $df = \sin \theta d\theta$. For randomly oriented lines, $N_A/L_V = \int_0^{\pi/2} \cos \theta \sin \theta d\theta = 1/2$. Therefore,

$$N_A = L_V/2. \quad (1.8)$$



1.5. Relation of the number of intersections per area with the length of line per volume.

Volume fraction of phases

Point counting is the easiest way of determining the volume fraction of two or more phases in a microstructure. The volume fraction of a phase equals the fraction of points in an array that lies on that phase. A line count is another way of finding the volume fraction. If a series of lines are laid on a microstructure, the volume fraction of a phase equals the fraction of the total line length that lies on that phase.

Alloy composition from volume fraction of two or more phases

The composition of an alloy can be found from the volume fractions of phases. The relative weight of component B in the α phase is $(V_\alpha)(\rho_\alpha)(C_\alpha)$, where V_α is

the volume fraction of α , ρ_α is the density of α , and C_α is the composition (%B) of the α phase. With similar expressions for the other phases, the relative weight of component B, W_B , is given by

$$W_B = (V_\alpha)(\rho_\alpha)(C_\alpha) + (V_\beta)(\rho_\beta)(C_\beta) + \dots \quad (1.9)$$

With similar expressions for the other components, the overall composition of the alloy is

$$\%B = 100W_B/(W_A + W_B + \dots). \quad (1.10)$$

Microstructural relationships

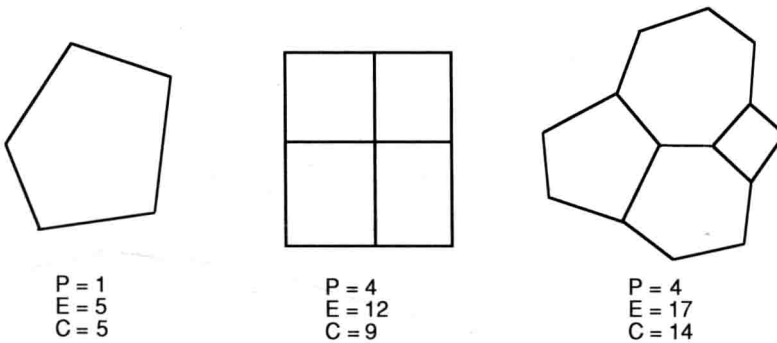
Microstructures consist of three-dimensional networks of cells or grains that fill space. Each cell is a polyhedron with faces, edges, and corners. Their shapes are strongly influenced by surface tension. However, before examining the nature of three-dimensional microstructures, the characteristics of two-dimensional networks will be treated.

A two-dimensional network of cells consists of polygons, edges (sides), and corners. The number of each is governed by the simple relation

$$P - E + C = 1, \quad (1.11)$$

where P is the number of polygons, E is the number of edges, and C is the number of corners. Figure 1.6 illustrates this relationship. If the microstructure is such that three and only three edges meet at each corner, $E = (3/2)C$, so

$$P - C/2 = 1 \quad \text{and} \quad P - E/3 = 1. \quad (1.12)$$



1.6. Three networks of cells illustrating that $P - E + C = 1$.

For large numbers of cells, the one on the right-hand side of Equations (1.9) and (1.10) becomes negligible, so $E = 3P$ and $C = 2P$. This restriction of three edges meeting at a corner also requires that the average angle at which the edges meet is 120° and that the average number of sides per polygon is six.