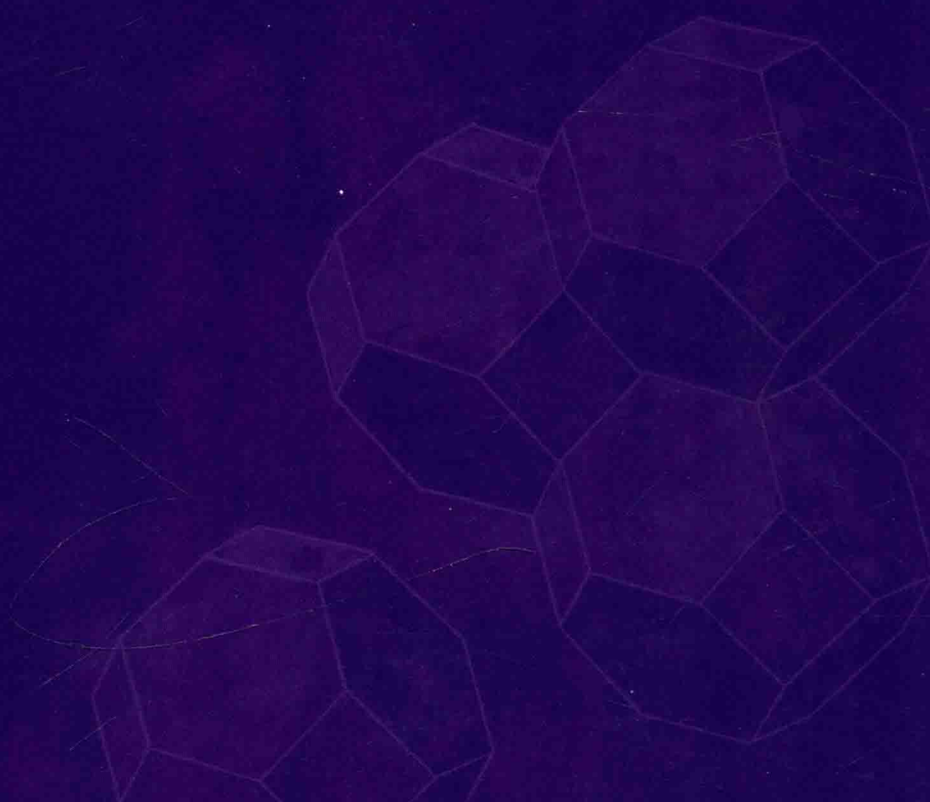
Materials Science

AN INTERMEDIATE TEXT

William F. Hosford



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MATERIALS SCIENCE

This text is intended for a second-level course in materials science and engineering. Chapters encompass crystal symmetry including quasicrystals 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

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

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

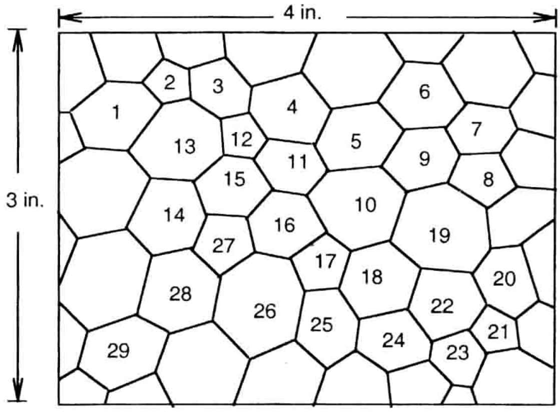
where n is the number of grains per square inch observed at a magnification of 100X. Large values of N indicate a fine grain size. With an increase of the grain diameter by a factor of $\sqrt{2}$, the value of n is cut in half and N is decreased by 1.

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

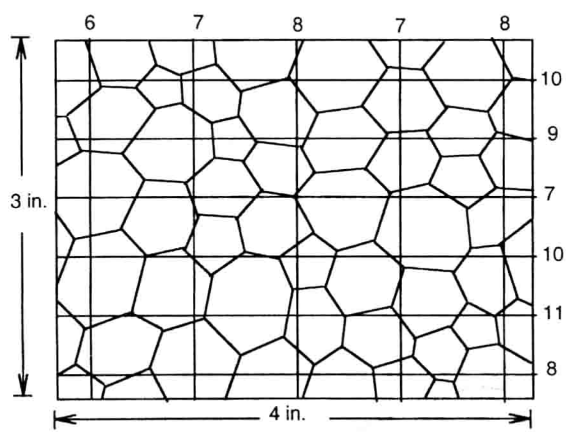


1.1. Counting grains in a microstructure at 200X.

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.

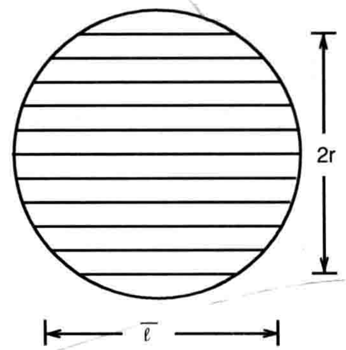
SOLUTION: In Figure 1.2, $6 \times 4 + 5 \times 3 = 39$ inches of line are superimposed on the microstructure. This corresponds to (39 in. /200)(25.4 mm/in.) = 4.95 mm. There are 91 intercepts so $\bar{\ell} = .495/91 = 0.054\,\text{mm} = 54\,\mu\text{m}$.



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,

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



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,

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

Solving for $\bar{\ell}$,

$$\bar{\ell} = 4.93/2^{N/2}. \tag{1.4}$$

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°:

$$\alpha = \bar{\ell}_{||}/\bar{\ell}_{\perp}. \tag{1.5}$$

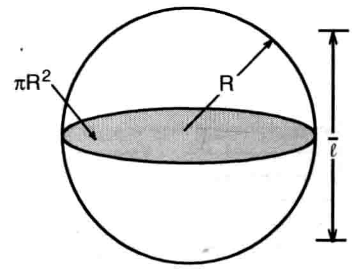
Relation of grain boundary area per volume to grain size

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

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

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 $S_v = 3/(2R)$,

$$S_v = 2/\bar{\ell}. \tag{1.7}$$

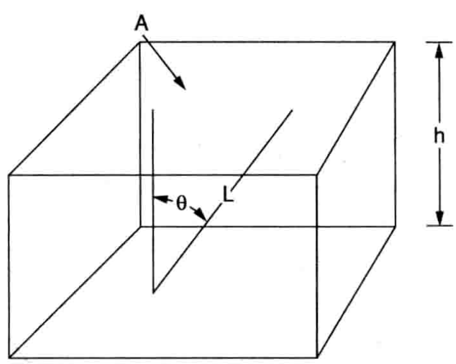


1.4. The volume of a sphere $= \bar{\ell}\pi R^2$.

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 $dn = ndf$, where $df = \sin\theta d\theta$. For randomly oriented lines, $N_A/L_V = \int^{2\pi} \cos\theta \sin\theta d\theta = 1/2$. Therefore,

$$N_A = L_V/2. \tag{1.8}$$



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

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

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

$$\%\mathrm{B} = 100 W_B/(W_A + W_B + \cdots). \quad (1.10)$$

Microstructural relationships

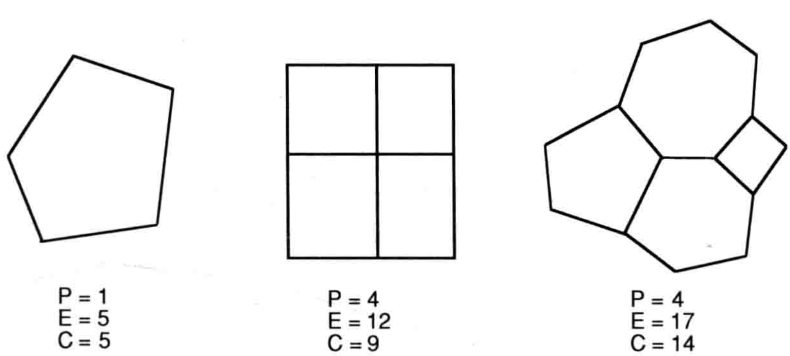
Microstructures consist of three-dimensional networks of cells or grains that fill space. Each cell is a polyhedron with faces, edges, and corners. Their shapes are strongly influenced by surface tension. However, before examining the nature of three-dimensional microstructures, the characteristics of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