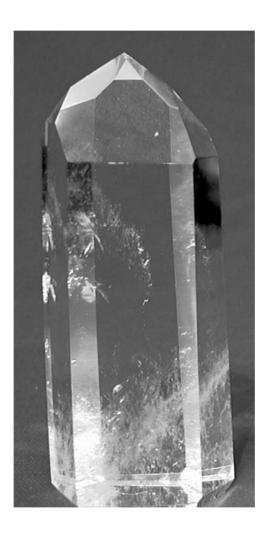
STRUCTURE OF CERAMICS AND GLASSES



Quartz is the second most common mineral (after feldspar) in the earth's crust. The silica (SiO_2) tetrahedron is a basic molecular building block. It has a Mohs scale hardness of 7 and a density of 2.65 g/cm³. Large industrial crystals can be grown using a furnace with a controlled rate of solidification. These are cut and used in watch movements, telephone receivers, etc.

2.1. ATOMIC BONDING AND ARRANGEMENT

When (neutral) atoms such as sodium (metal) and chlorine (nonmetal) are ionized, the sodium loses an electron and the chlorine gains an electron:

$$Na \Leftrightarrow Na^+ + e^-, \quad e^- + Cl \Leftrightarrow Cl^-.$$
 (2.1)

Thus, the sodium and chlorine are able to make up an "ionic compound" by the strong attraction of the positive and negative ions. The negatively charged ions are much larger than the positively charged ones (see Table 2.1) due to the gain and loss of valence electrons. The radius of an ion varies according to the coordination number (CN): the higher the CN, the larger the radius. For example, an oxygen ion (O²⁻) has a radius of 1.28, 1.40, and 1.44 Å for CNs of 4, 6, and 8, respectively.

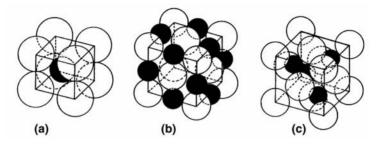


Figure 2.1. AX structures of ceramics: (a) CsCl; (b) NaCl; (c) ZnS. The dark spheres represent positive ions (A^+) and the circled ones represent negative ions (X^-) .

Ceramics can be classified according to their structural compounds, of which $A_m X_n$ is an example (A represents a metal and X a nonmetal element; and m and n are integers). The simplest case of this system is the AX structure (m = n = 1), of which there are three types (Fig. 2.1). CsCl has a *simple cubic* structure, as shown in Figure 2.1a. One must not confuse this with the *body-centered cubic* (bcc) structure, which would have the *same* ion or atom occupying the center (body) of the unit cell. CsBr and CsI have the same CsCl structure. The NaCl has a *face-centered cubic* (fcc) structure, where the positive (Na[†]) and negative (Cl[¬]) ions are surrounded by 6 opposite ions (CN = 6). This is called a *rock salt structure*; MgO, CaO, SrO, BaO, CdO, MnO, FeO, CoO, and NiO belong to the same group.

The difference between these structures is due to the relative size of the ions (minimum radius ratio). If the positive and negative ions are about the same size $(r_A/R_X > 0.732)$, the structure becomes a simple cubic (CsCl) structure. The face-centered cubic structure arises if the relative size of the ions is quite different since the positive ions can be fitted in the tetragonal or octagonal spaces created among larger negative ions. These are summarized in Table 2.2. The aluminum and chromium oxide have an A_2X_3 type structure. The O^2 ions form a hexagonal close-packed (hcp) structure, while the positive ions (Al^{3+}, Cr^{3+}) fill in 2/3 of the octahedral sites, leaving a third of them vacant.

Group I			Group II			Group IV			Group VI		
Element	Atomic radius	Ionic radius	Element	Atomic radius	Ionic radius	Element	Atomic radius	Ionic radius	Element	Atomic radius	Ionic radius
Li ⁺ Na ⁺ K ⁺	1.52 1.86 2.27	0.68 0.95 1.33	Be ²⁺ Mg ²⁺ Ca ²⁺	1.11 1.60 1.97	0.31 0.65 0.99	O^{2-} S^{2-} Se^{2-}	0.74 1.02 1.16	1.40 1.84 1.98	F⁻ Cl⁻ Br⁻	0.71 0.99 1.14	1.36 1.81 1.95

Table 2.1. Atomic and Ionic Radii of Some Elements (units in Å)

Table 2.2. Selected A.X. Structures

Prototype compound	Lattice of A (or X)	CN of A (or X) sites	Available sites filled	$Minimum r_{A}/R_{X}$	Other compounds
CsCl	Simple cubic	8	All	0.732	CsI
NaCl	fcc	6	All	0.414	MgP, MnS, LiF
ZnS	fcc	4	1/2	0.225	β-SiC, CdS, AlP
Al_2O_3	hcp	6	2/3	0.414	Cr_2O_3 , Fe_2O_3

Cubic zirconia (ZrO_2) has an fcc packing of the Zr^{4+} ions and O^{2-} ions occupying the octahedral sites. Due to charge balance, two O^{2-} ions will balance one Zr^{4+} ion; therefore, half the available tetrahedral sites in the unit cell will be occupied by O^{2-} ions. Similarly, the MgO can be said to have O^{2-} ions occupying all available octahedral sites in the unit cell structure. There are one octahedral and two tetrahedral sites per atom in face-centered cubic and hexagonal close-packed structures, which represent the most close-packed structure (see Fig. 2.2). The unit cell structure of cubic zirconia and alumina are shown in Figure 2.3. Aluminum ions (AI^{3+}) occupy 2/3 of the available octahedral sites of the hcp structure due to the valence electron balance with oxygen ion (O^{2-}) , as mentioned. The Fe $_2O_3$, Cr_2O_3 , Ti_2O_3 , V_2O_3 , and Ga_2O_3 belong to the same group.

Some ceramics have *covalent bonds* as their primary chemical bonding force, e.g., diamond and silica. The diamond structure is shown in Figure 2.4a, where one can see a tetrahedron of carbons. Also, one can discern the fcc structure, in which the carbon atoms occupy half the tetrahedral sites available. Silicon carbide (SiC) has a similar structure, in which the Si atoms occupy half the tetrahedral sites available, as shown in Figure 2.4b. Silica structure can be understood similarly as having the SiO₄ *tetrahedron* on each Si site, as shown in Figure 2.4c. These structures are not close-packed structures since the CNs are not 12 but 4; therefore, their densities are low. However, the SiC is a very hard ceramic and is used as an abrasive, similar to diamond.

Silicate glasses are based on the silica (SiO₂) tetrahedron, which can be linked together into a two- or three-dimensional network structure, as shown in Figure 2.5.

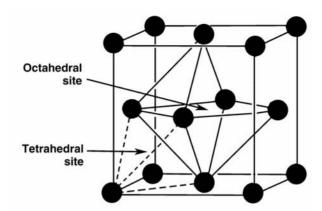


Figure 2.2. Unit cell representation of close packing of fcc. There are 4 octahedral and 8 tetrahedral sites in the unit cell. The hcp structure has a close packed structure, with the same number of octahedral and tetrahedral sites in the unit cell.

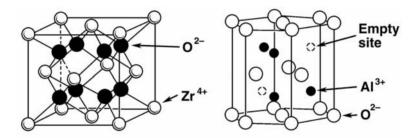


Figure 2.3. Unit cell representation of (a) cubic zirconia and (b) alumina.

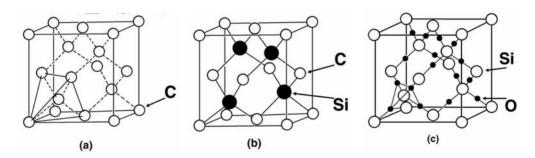


Figure 2.4. Unit cell representation of covalently bonded ceramics: (a) diamond, (b) SiC, and (c) cubic silica.

When the Si-4O tetrahedron forms a three-dimensional network and is arranged in a coordinated manner, it takes on a crystalline structure, as shown in Figure 2.6a, but it can be distorted, resulting in amorphous silica glass, as shown in Figure 2.6b. The silica glass has a very high glass transition temperature $(T_{\rm g})$; therefore, network-

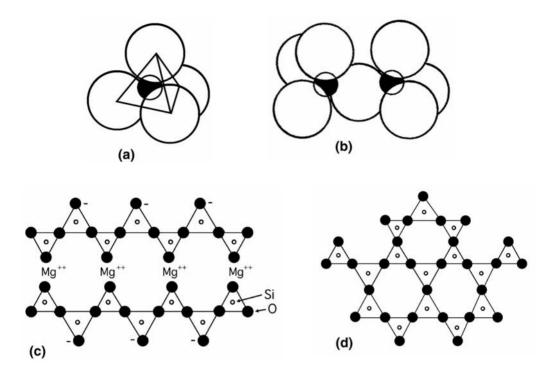


Figure 2.5. Silicate structures: (a) SiO₄ tetrahedron; (b) two SiO₄ tetrahedra with a bridging oxygen; (c) chain silicates with metal ion (Mg²⁺) links; (d) a silicate sheet.

modifying chemicals such as Na_2O and CaO are added to lower T_g , as shown in Figure 2.6c, thus lowering the cost of processing the glass.

Similar to metals, two or more ceramics can be melted and solidified to make alloys (solid solutions) (see Fig. 2.7). The SiO_2 and Al_2O_3 will form an intermediate compound, *mullite* ($3Al_2O_3 \cdot SiO_2$). The high-temperature form of pure SiO_2 is called *cristobalite* and the low temperature form *tridymite*. Other oxides can be solid solutionized to obtain higher-density and more fracture-resistant ceramic compounds. The same *phase rule* can be applied to ceramic materials as those applied to metals.

Example 2.1

Calculate the densities of diamond and NaCl.

Answer:

a. Diamond has a crystalline structure (Fig. 2.4a) in which 8 carbon atoms per unit cell exist and the unit cell volume is a³.

Density:

$$\frac{\text{mass}}{\text{unit cell}} = \left(\frac{8 \text{ atoms}}{\text{unit cell}}\right) \left(\frac{12 \text{ g}}{\text{mole}}\right) \left(\frac{\text{mole}}{6 \times 10^{23} \text{ atoms}}\right) = 1.59 \times 10^{-22} \text{ g/unit cell,}$$

$$\frac{\text{volume}}{\text{unit cell}} = a^3 = \left(\frac{4 \text{ atoms} \times 0.154 \text{ nm}}{\sqrt{3}}\right)^3 = 4.5 \times 10^{-23} \text{ cm}^3/\text{unit cell,}$$

$$\text{Density} = \frac{1.59 \times 10^{-22} \text{ g/unit cell}}{4.5 \times 10^{-23} \text{ cm}^3/\text{unit cell}} = \frac{3.53 \text{ g/cm}^3}{4.5 \times 10^{-23} \text{ cm}^3/\text{unit cell}}$$

which is close to the reported value of 3.51 g/cm³ (*Physics and Chemistry Handbook*, 49th ed, Cleveland: CRC Press, 1968).

b. The crystal structure of NaCl is fcc (face centered cubic), therefore the density can be calculated,

$$\begin{split} \frac{\text{mass}}{\text{unit cell}} = & \left(\frac{4(\text{Na}^+ + \text{Cl}^-)}{\text{unit cell}} \right) \! \left(\frac{58.44 \text{ g}}{\text{mole}} \right) \! \left(\frac{\text{mole}}{6 \times 10^{23} (\text{Na}^+ + \text{Cl}^-)} \right) = 3.896 \times 10^{-22} \text{ g/unit cell,} \\ & \frac{\text{volume}}{\text{unit cell}} = a^3 = \left[2(r_{\text{Na}^+} + r_{\text{Cl}^-}) \right]^3 = \left[2(0.097 + 0.181) \text{ nm} \right]^3 / \text{unit cell} \\ & = 1.72 \times 10^{-22} \text{ cm}^3 / \text{unit cell,} \end{split}$$

$$\text{Density} = \frac{3.896 \times 10^{-22} \text{ g/unit cell}}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} = \frac{2.265 \text{ g/cm}^3}{1.72 \times 10^{-23} \text{ cm}^3 / \text{unit cell}}$$

which is close to the reported value of 2.165 g/cc; $T_m = 801^{\circ}\text{C}$, $T_b = 1413^{\circ}\text{C}$, m.w. = 58.44 amu (from *Physics and Chemistry Handbook*).

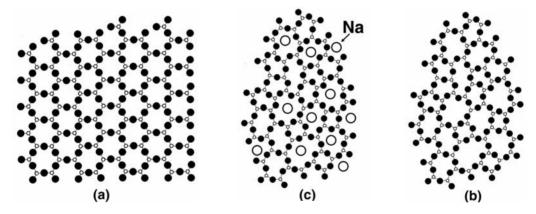


Figure 2.6. Glass structures: (a) coordinated network structure of crystalline silica; (b) uncoordinated random network structure of amorphous glass of silica; (c) network-modified glass structure lowering its T_{ν} considerably.

Example 2.2

Give descriptions or steps to make 99.99% pure alumina from 99% pure alumina by using the phase diagram in Figure 2.7.

Answer:

Purification of any materials can be accomplished by using the phase separation phenomenon since each phase will contain a different amount of the original composition. The following steps can therefore yield a purer material:

- 1. Heat the 99% alumina above the liquidus line (>2,050°C)
- 2. Cool below the liquidus line
- 3. Throw away the liquid
- 4. Reheat the remaining solid above the liquidus line
- 5. Cool below the liquidus line
- 6. Throw away the liquid

These steps can be repeated until the desirable purity is attained. The material is then cooled to room temperature.

Similar results can be obtained if one uses a "zone melting and solidification" process in which cylindrical solids are melted and solidified in one direction slowly (to achieve thermal equilibrium). Finally, the "impure liquid" will be accumulated. The process can be repeated as many times as is necessary to reach the desired purity.

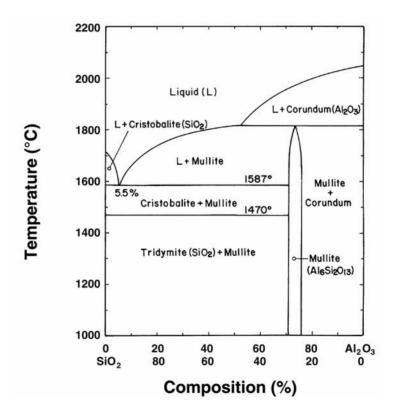


Figure 2.7. Phase diagram of SiO₂–Al₂O₃. Modified with permission from [1]. Copyright © 1976, Wiley.

2.2. CHARACTERIZATION OF MICROSTRUCTURE

The physical properties of ceramics depend on their microstructure, which can be characterized in terms of the number and types of phases present, the relative amount of each, and the size, shape, and orientation of each phase. Microstructures can usually be studied by thin sectioning (15–30 µm) on a diamond or silicon carbide-dressed wafer saw and polishing by a graded series of sandpaper. The final polishing involves using alumina or diamond paste on a wheel. The thin sections can be observed under a plain or polarized light microscope. A reflected light microscope can be used if the specimen is mounted on a polymer resin and only one side is polished. Optical microscopy can magnify an object up to 1,500 times due to the large wavelength of light ($\lambda \sim 10^{-6}$ m), but scanning and transmission electron microscopy (SEM and TEM) can theoretically magnify an object more than 1,000,000 times ($\lambda \sim 10^{-12}$ m). In addition, elemental analysis can be made with an SEM electron microprobe and electron diffraction can be undertaken using TEM, which give a better understanding of microstructure.

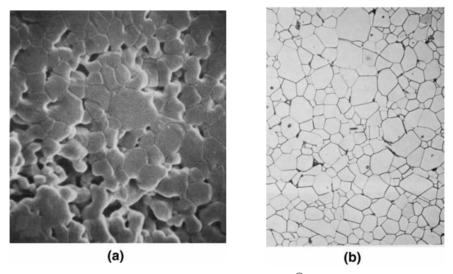


Figure 2.8. SEM (a) and optical microscopic pictures of Lucalox[®] alumina. Note the large pores in the SEM image $(5,000\times)$ and the very small pores in optical microscopic picture $(500\times)$. Reprinted with permission from [1]. Copyright © 1976, Wiley.

The most important property of brittle materials such as ceramics and glasses is their *porosity*. Porosity has a tremendous influence on the physical properties of brittle materials since it greatly increases and intensifies stress. In addition, it is difficult to avoid formation of pores during processing of materials. The nonyielding nature of brittle materials is the main reason for the increased stress. The microstructure of polycrystalline alumina is shown in Figure 2.8.

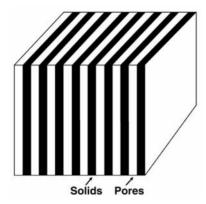


Figure 2.9. Representation of two phase materials in slabs. Reprinted with permission from [1]. Copyright © 1976, Wiley.

If we idealize the pores, as shown in Figure 2.9, where there is a series of pores and solid slabs, then electrical or thermal conductivity can be expressed in the parallel direction according to the Voigt model as

$$K_{t} = v_{s}K_{s} + v_{p}K_{p}, \qquad (2.2)$$

and in series according to the Reuss model as

$$\frac{1}{K_{1}} = \frac{v_{s}}{K_{s}} + \frac{v_{p}}{v_{p}}.$$
 (2.3)

Equations (2.2) and (2.3) are plotted in Figure 2.10.

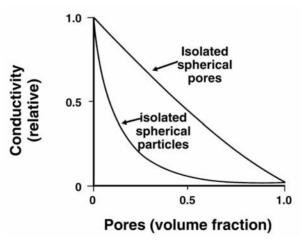


Figure 2.10. Thermal conductivity of Voigt and Reuss models, representing an isolated spherical pore and a matrix, respectively. Reprinted with permission from [1]. Copyright © 1976, Wiley.

The strength of ceramics and other materials — e.g., some ductile materials such as metals and some polymers like polymethylmethacrylate (PMMA) — depends on porosity as follows:

$$\sigma = \sigma_0 e^{-np}, \qquad (2.4)$$

where σ_0 is the pore free strength, p is the volume fraction of porosity, and n is an integer ($n = 4 \sim 7$). Figure 2.11 depicts strength versus porosity plotted for two different materials: plaster of Paris and stainless steel.

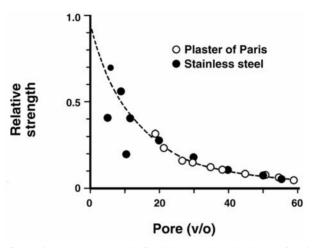


Figure 2.11. Plot of porosity versus strength of stainless steel and plaster of Paris. Reprinted with permission from [1]. Copyright © 1976, Wiley.

Pores connected to the surface are termed *open pores*; all others are *closed pores*. Total porosity includes open and closed pores, while *apparent porosity* includes only open pores. Open pores can be nearly eliminated if porosity decreases below 5%.

The fraction of porosity, f_p , is related to the density of a material as

$$f_{P} = \frac{\rho_{t} - \rho_{b}}{\rho_{c}} = 1 - \frac{\rho_{b}}{\rho_{c}},$$
 (2.5)

where ρ_i is the true density, and ρ_b is the bulk density, which is the total weight per unit volume, including pores.

Example 2.3

Calculate the relative conductivity of a material with 1 and 50% porosity for isolated particles using Eqs. (2.2) and (2.3).

Answer:

From Eq. (2.3), for 1% porosity, $K_t = 0.99K_s + 0.01K_p$, and assume that $K_s = 10K_p$; therefore, $K_r = 0.991K_s$. For 50%, porosity $K_t = 0.5K_s + 0.5K_p$; thus, $K_r = 0.55K_s$.

From Eq. (2.4), for 1% porosity, $K_t^{-1} = 0.99 K_s^{-1} + 0.01 K_p^{-1}$; therefore, $\underline{K}_t = 0.917 K_s$. For 50% porosity, $K_t^{-1} = 0.5 K_s^{-1} + 0.5 K_p^{-1}$, and thus, $\underline{K}_t = 0.182 K_s$.

2.3. QUANTITATIVE ANALYSIS OF SINGLE-PHASE MICROSTRUCTURE [1]

Two-dimensional structure can be studied by statistical analysis assuming a random distribution of phases, which can be expressed as

$$f_{\nu}^{\alpha} = f_{\scriptscriptstyle A}^{\alpha} = f_{\scriptscriptstyle L}^{\alpha} = f_{\scriptscriptstyle P}^{\alpha}, \tag{2.6}$$

where V, A, L, and P are subscripts that represent volume, area, linear, and point, respectively. In other words, Eq. (2.6) can be written as

$$V_{V} = A_{A} = L_{L} = P_{P},$$
 (2.7)

where V_{V} is the volume fraction, A_{A} is area fraction, etc.

The surface area per unit volume can be expressed as

$$S_{V} = -\frac{4}{\pi} L_{A} = 2P_{L}, \qquad (2.8)$$

where L_A is the length fraction of linear elements per unit area, and P_L is the number of points intersected per unit line length. One can then derive the following relationships:

$$L_{V} = 2P_{A} \tag{2.9}$$

and

$$P_{v} = \frac{1}{2} L_{v} S_{v} = 2 P_{A} P_{L}. \tag{2.10}$$

The structural constituents (e.g., plates, rods, and spheres) can be represented by the mean intercept length (\bar{L}):

$$\bar{L} = \frac{L_L}{N_L} \,, \tag{2.11}$$

where L_L is the length fraction and N_L the number of intersections per unit length of test line. The spherical particles can be related to the mean intercept length as follows:

$$\overline{L} = \frac{4}{3}r; \tag{2.12}$$

for rods,

$$\overline{L} = 2r \,; \tag{2.13}$$

and for plates,

$$\overline{L} = 2t \,, \tag{2.14}$$

where r and t are the radius of the spheres and rods and the thickness of plates, respectively.

The mean free distance between particles (\overline{l}) can be expressed as

$$\overline{l} = \frac{1 - V_{\nu}}{N_{L}},\tag{2.15}$$

and is related to the mean intercept length as

$$\overline{l} = \frac{\overline{L}(1 - V_{v})}{N_{v}}, \qquad (2.16)$$

and if the mean distance between particle centers (\bar{d}) can be written as

$$\overline{d} = \frac{1}{N_L},\tag{2.17}$$

then

$$\bar{L} = \bar{d} = \bar{l} \tag{2.18}$$

2.4. MICROSTRUCTURE DETERMINATION [2]

When a single- or multicomponent material solidifies from a liquid, it forms either a single-crystal or polycrystalline solid that is composed of many grains. Each grain is a single crystal; if only one phase is present, all grains have the same crystal structure. However, grains may have different orientations and sizes. The size of grains can vary considerably: from submicrometers to several millimeters.

The most important grain features of a single-phase microstructure are size, shape, and orientation, as shown in Figure 2.12. All three of these factors influence the properties of solids. Grain size is often expressed as an average "diameter" within a two-dimensional section. This indicates the order of magnitude but leaves much to be desired, since (a) the grains are not spherical, and (b) a two-dimensional section does not represent the full "diameter" of each grain. Improved measurement techniques (e.g., SEM) are needed to compensate for these deficiencies.

A widely used grain size index is one published by the American Society for Testing and Materials (ASTM). An index n is related to the number of grains per square inch, N, at a linear magnification of $100 \times$ as

$$N = 2^{n-1} (2.19)$$

(see Table 2.3).

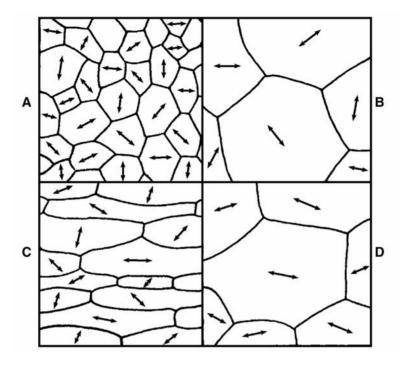


Figure 2.12. Microstructural variables of single-phase metals (from top left, clockwise: A vs. B, grain size; A vs. C, grain shape; B vs. D, preferred orientation. Reprinted with permission from [2]. Copyright © 1970, Addison-Wesley.

Table 2.3. Grain Size Ranges (ASTM) $(N = 2^{n-1})$

Grain size	Grain size/in² a	Grain size/in ² at 100× (linear)		
number	Mean	Range		
n = 1	<i>N</i> = 1	_		
2	2	1.5–3		
3	4	3–6		
4	8	6–12		
5	16	12-24		
6	32	24-48		
7	64	48–96		
8	128	96–192		

If shape assumptions are made, the number of grains can be calculated from the grain boundary areas derived from Eq. (2.8). By geometric analysis,

$$N_{V} = (S_{V}/F)^{3}, (2.20)$$

where N_v is the number of grains per unit volume, and S_v is the grain boundary area per unit volume. The shape factor, F, is 3 for assumed cubic grains, but more nearly 2.7 for the equiaxed noncubic grains commonly encountered in isotropic microstructures.

Example 2.4

Calculate the grain size of the Lucalox $^{\circledR}$ shown in Figure 2.8 (500× magnification).

Answer:

The number of grains in the micrograph is about 320, and the area is $3.25" \times 2.5"$ at $500\times$. Therefore, 320/8.125 in²; hence, 39.385 grains/in² at $500\times$. At $100\times$, 985 grains/in², and from Eq. (2.19), $N = 2^{n-1}$, where N is 985. Therefore, $985 = 2^{n-1}$, and n = 11. These grains are extremely small (smaller than the wavelength of light), making the material translucent, so that it can be used as a mercury lamp housing since it can also resist high temperatures.

Example 2.5

Calculate the surface area of the grains in of the previous example. Assume the grains are cubes.

Answer:

Since there are 985 grains/in² at $100\times$, the grain distribution is $9.85\times10^6/\text{in}^2$. Thus, the number of grains is 3.13×10^3 grains/in, which yields 3.1×10^{10} grains/in³. The surface area of each grain is $6(1/3.13\times10^3)^2/\text{in}^2$; therefore, the total boundary area would be half that value, since two grains can constitute one boundary area; therefore,

Total boundary area =
$$1/2 \times 6(1/3.13 \times 10^3)^2 \text{ in}^2 \times (3.13 \times 10^3/\text{in})^3$$

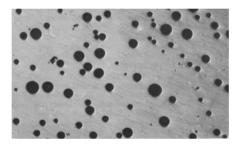
= $9.39 \times 10^3 \text{ in}^2/\text{in}^3$.

The large boundary area would make the material stronger, with a large amount of stored surface energy, which would result in deflection of cracks along the grain boundaries during crack propagation.

PROBLEMS

- 2.1. Calculate the number of atoms present per cm³ for cubic zirconia (ZrO₂), which has a density of 6.2 g/cm³.
- 2.2. Calculate the minimum radius ratios of a unit cell with CN = 6, 8.
- 2.3. Plot Eqs. (2.2) and (2.3).
- 2.4. Calculate the strength of alumina ceramics that have 1 and 5% porosity by volume. Provide your assumptions.

- 2.5. For 50%SiO₂ and 50%Al₂O₃ alloy, using the phase diagram in Figure 2.7:
 - a. What phase(s) exist at 1600°C, 1500°C, and room temperature?
 - b. What is the composition of each phase?
 - c. What is the relative amount of each phase in the fractions?
- 2.6. Calculate the exact percentage of SiO_2 and Al_2O_3 for the mullite $(Al_6Si_2O_{13})$ from the phase diagram in Figure 2.7.
- 2.7. Determine the grain size of alumina from the optical micrograph of Figure 2.8.
- 2.8. Determine the relationship between relative strength and porosity (pore volume) in Figure 2.11.
- 2.9. Use this optical microstructure of Japanese hard porcelain depicted (100×) (reprinted with permission from [1], copyright © 1976, Wiley) to answer the following questions.



- a. Calculate the mean pore diameter.
- b. Calculate the mean distance between pores.
- c. Calculate the fraction of pores.

SYMBOLS/DEFINITIONS

Roman Letters

f: fraction of a phase.

 f_{P} : fraction of porosity.

 \overline{d} : mean distance between particle centers.

 \overline{l} : mean free distance between particles.

 \overline{L} : mean intercept length.

A: area.

L: line.

N: number of intersections.

P: point.

 P_{v} : volume fraction of porosity.

r: radius of spherical particle.

S: surface area.

t: thickness of plate.

V: volume.

Greek Letters

κ: thermal conductivity.

v: volume fraction

σ: strength.

 ρ_i : true density.

 ρ_i : bulk density.

Definitions

Apparent porosity: Ratio of the open pore space of a body to its bulk volume, expressed as

$$p = \frac{(w_s - w_f)}{V},$$

where w_s is the weight of the water-saturated specimen in (g), w_f is the weight of the original specimen (g), and v is the volume of the specimen (cm³).

Bulk density: Ratio of the weight of an abject or material to its total volume, including the pore space.

Closed pores: Pores or small bubbles entrapped in a ceramic body that are not connected to the exterior of the body, calculated as

$$p_c = \frac{w_d}{\rho_a} - \frac{w_d}{\rho_t},$$

in which p_c is the volume of sealed or closed pores, w_d is the dry weight of the specimen, ρ_a is the apparent density, and ρ_c is the true density of the specimen.

Coordination number (CN): Number of atoms or ions touching an adjacent atom or ion.

Cristobalite: A crystalline allotropic type of silica formed by inversion of quartz at 1470° C; $T_m = 1713^{\circ}$ C. It is a major component of silica refractory, and is also used in investment casting of metals. Sometimes present in siliceous ceramic bodies.

Face-centered cubic (fcc) structure: A crystal structure found in some common elemental metals. Within the cubic unit cell atoms are located at all corner and face-centered positions.

Glass transition temperature (T_g): The temperature at which, upon cooling, a noncrystalline ceramic or glass transforms from a supercooled liquid to a rigid glass-like solid.

Hexagonal close-packed structure (hcp): A crystal structure found in some metals, where the hcp unit cell is of hexagonal geometry and is generated by stacking of close-packed planes of atoms.

Mean free distance between particles (\overline{l}): Average distance between particles or pores.

- Mean free distance between particle centers (\bar{d}): Average distance between the centers of particles or pores.
- **Mean intercept length** (\overline{L}): Defined as L_t/N_t , where L_t is the length fraction and N_t is the number of intersections per unit length of the test line.
- **Minimum radius ratio** (*r/R*): Ratio between the radius of a smaller atom to be fitted into the space among larger atoms, based on geometric considerations.
- **Mullite**: With m.w. 425.9; $T_m = 1810^{\circ}\text{C}$; $T_g = 1650^{\circ}\text{C}$. Resistant to corrosion and heat; used as a refractory in high-temperature applications and as a strength-producing ingredient in stoneware and porcelain.
- **Octahedral site**: The void space among close-packed hard-sphere atoms or ions for which there are six nearest neighbors. An octahedron (double pyramid) is circumscribed by lines constructed from centers of adjacent spheres.
- **Open pores**: The pores of a solid body that may be penetrated by a liquid or gaseous substance outside the external surface of the body.
- **Phase rule**: P + V = C + E, where P is the number of phases at thermal equilibrium, V is the number of variances, C is the number of components, and E is the number of environmental variables (e.g., pressure, temperature).
- **Polymethylmethacrylate** (**PMMA**): An acrylic linear polymer having excellent resistance to the environment, including tissues, and allows excellent transmission of light. It is used for making bone cement and contact lenses.
- **Reuss model**: A mathematical model where the properties of a series of phases are represented by Eq. (2.3).
- **Simple cubic structure (CsCl)**: AX structure of ceramic crystals, where A is a metal and X nonmetal; forms a simple cubic structure resembling bcc.
- **Tetrahedron**: Geometric structure where one atom or sphere is surrounded by four nearest neighbors.
- **Tridymite**: A high-temperature polymorph of SiO₂: m.w. = 60.1; density 2.28–2.3 g/cm³; hardness (Mohs) = 7. Used in ceramic bodies to improve thermal shock resistance and minimize crazing.
- **True density**: The weight of a unit volume of a substance excluding its pore volume and interparticle voids, when measured under standard or specified conditions.
- **Voigt model**: A mathematical model where the properties of a series of phases are represented by Eq. (2.2).

REFERENCES

- 1. Kingery WD, Bowen HK, Uhlmann DR. 1976. *Introduction to ceramics*, 2nd ed, pp. 3–20. New York: Wiley.
- 2. Van Vlack LH. 1970. Materials science for engineers. Reading, MA: Addison-Wesley.