Composites and Powder Metallurgy
Ch 12 “Properties of Ceramics”

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Introduction

- Most ceramics are compounds between metallic and nonmetallic elements
  - the interatomic bonds are either totally ionic, or predominantly ionic but having some covalent character.
- The term *ceramic* comes from the Greek word *keramikos,* which means “burnt stuff”
  - indicating that desirable properties of these materials are normally achieved through a high-temperature heat treatment process called firing.

Introduction

- Up until the past 60 or so years, the most important materials in this class were termed the “traditional ceramics”
    - those for which the primary raw material is clay: china, porcelain, bricks, tiles, and, in addition, glasses and high-temperature ceramics.
- Of late, significant progress has been made in understanding the fundamental character of these materials and of the phenomena that occur in them that are responsible for their unique properties.
    - Consequently, a new generation of these materials has evolved, and the term *ceramic* has taken on a much broader meaning.
- To one degree or another, these new materials have a rather dramatic effect on our lives; electronic, computer, communication, aerospace, and a host of other industries rely on their use.

Ceramic Phase Diagrams

The Al_2O_3–Cr_2O_3 System

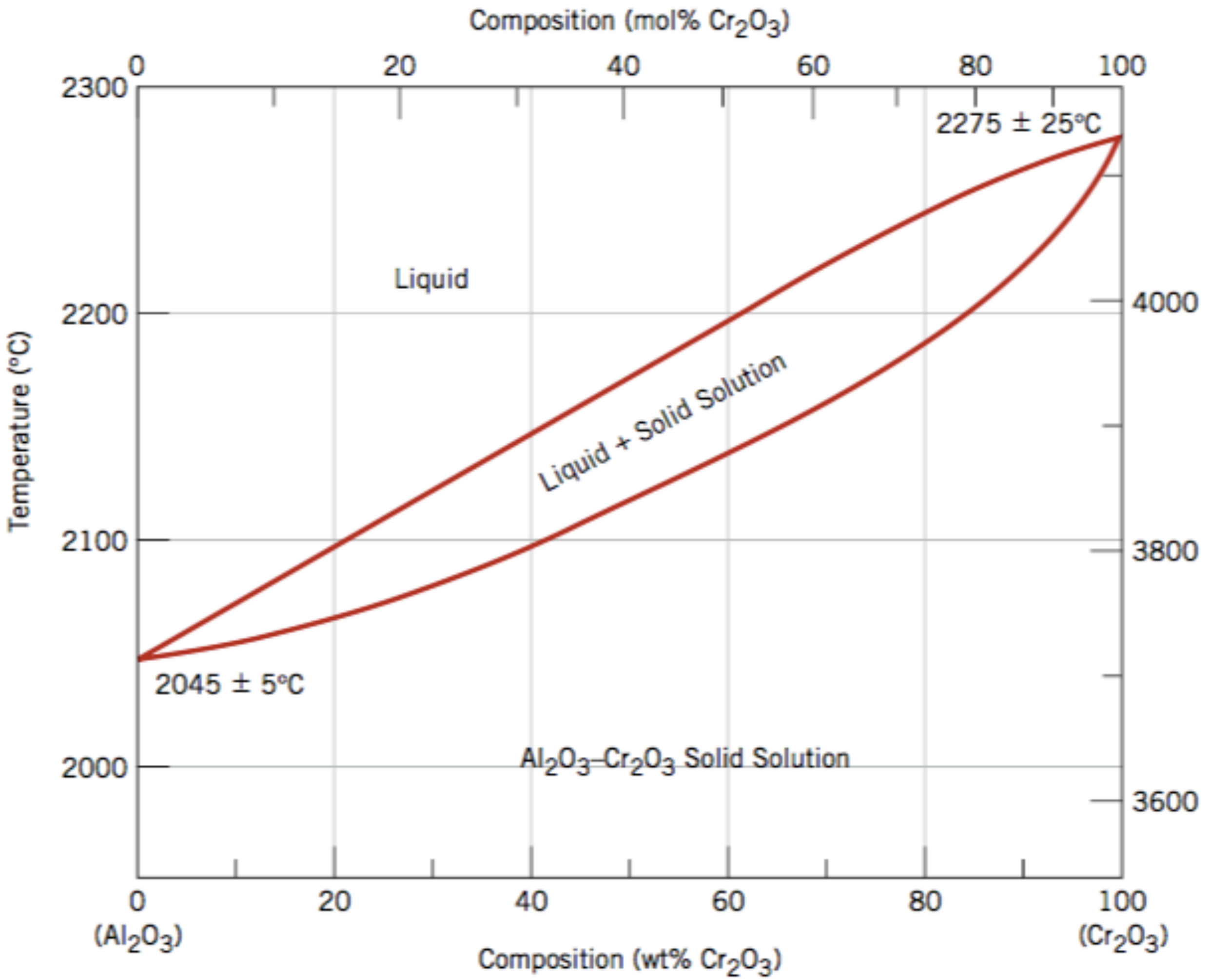


Figure 12.22 The aluminum oxide–chromium oxide phase diagram. (Adapted from E. N. Bunting, "Phase Equilibria in the System Cr_2O_3–Al_2O_3," *Bur. Standards J. Research*, **6,** 1931, p. 948.)

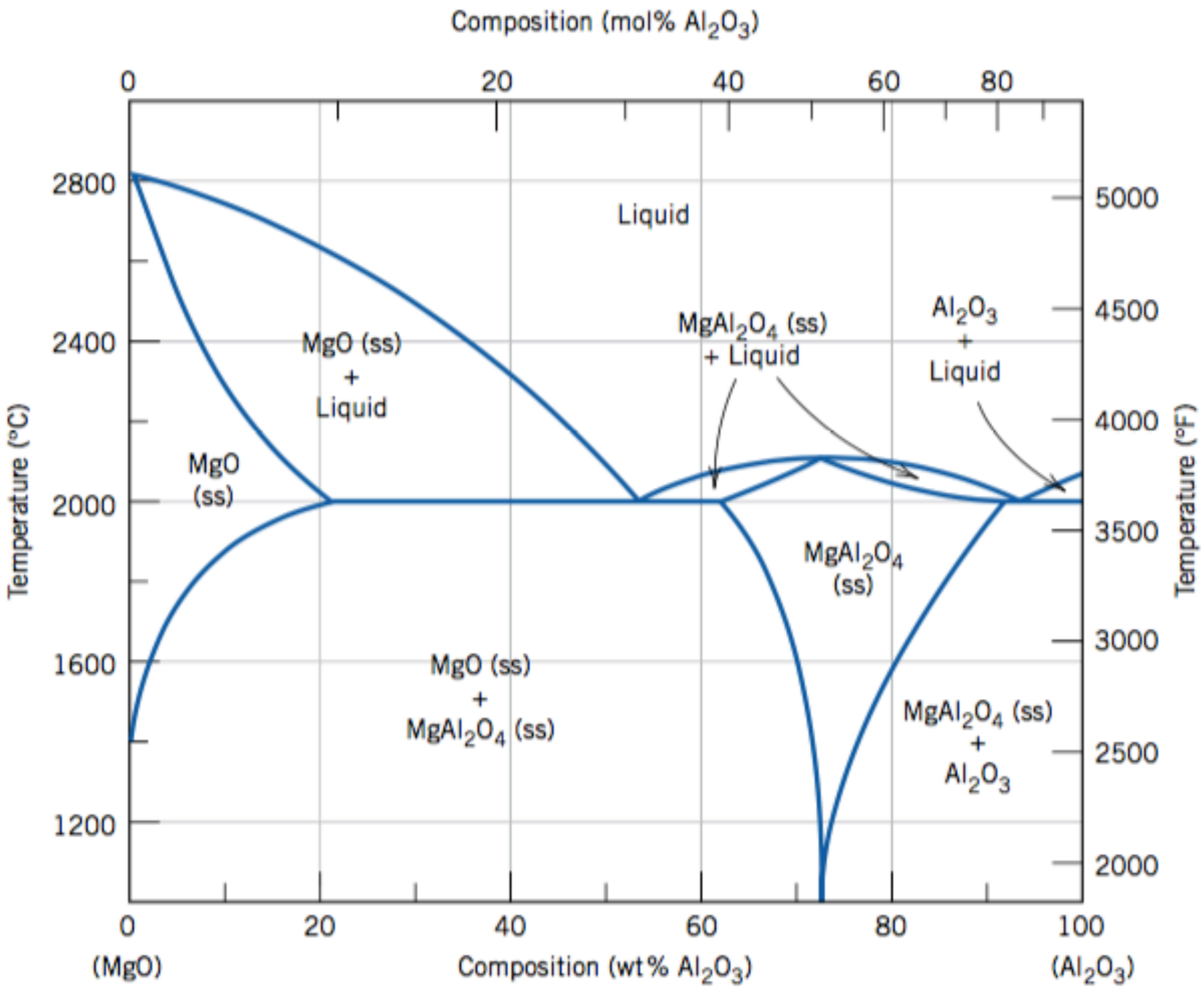
Ceramic Phase Diagrams

The Al_2O_3–Cr_2O_3 System

- This diagram has the same form as the isomorphous copper–nickel phase diagram
  - consisting of single liquid-phase and single solid-phase regions separated by a two-phase solid–liquid region having the shape of a blade.
- The solid solution is a substitutional one in which Al_3 substitutes for Cr_3 and vice versa.
  - It exists for all compositions below the melting point of Al_2O_3 because both aluminum and chromium ions have the same charge as well as similar radii (0.053 and 0.062 nm, respectively).
- Furthermore, both Al_2O_3 and Cr_2O_3 have the same crystal structure.

Ceramic Phase Diagrams
The Al_2O_3–MgO System

Figure 12.23 The magnesium oxide–aluminum oxide phase diagram; ss denotes solid solution.
(Adapted from B. Hallstedt, "Thermodynamic Assessment of the System MgO–Al_2O_3," *J. Am. Ceram. Soc.*, **75**[6], 1502 (1992). Reprinted by permission of the American Ceramic Society.)



Ceramic Phase Diagrams
The Al_2O_3–MgO System

- There exists an intermediate phase (a compound) called spinel, which has the chemical formula $MgAl_2O_4$ (or MgO–Al_2O_3).
  - Composition: 50 mol% Al_2O_3–50 mol% MgO (72 wt% Al_2O_3–28 wt% MgO).
  - There is a range of compositions over which spinel is a stable compound.
  - Thus, spinel is nonstoichiometric for other than the 50 mol% Al2O3–50 mol% MgO composition.
  - Furthermore, there is limited solubility of Al_2O_3 in MgO below about 1400 C at the left-hand extreme of Figure 12.23, which is due primarily to the differences in charge and radii of the Mg^{2+} and Al^{3+} ions (0.072 vs. 0.053 nm).
- For the same reasons, MgO is virtually insoluble in Al_2O_3, as evidenced by a lack of a terminal solid solution on the right-hand side of the phase diagram. Also, two eutectics are found, one on either side of the spinel phase field, and stoichiometric spinel melts congruently at about 2100 C.

Ceramic Phase Diagrams

The Al_2O_3–MgO System

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Ceramic Phase Diagrams

The Al_2O_3–SiO_2 System

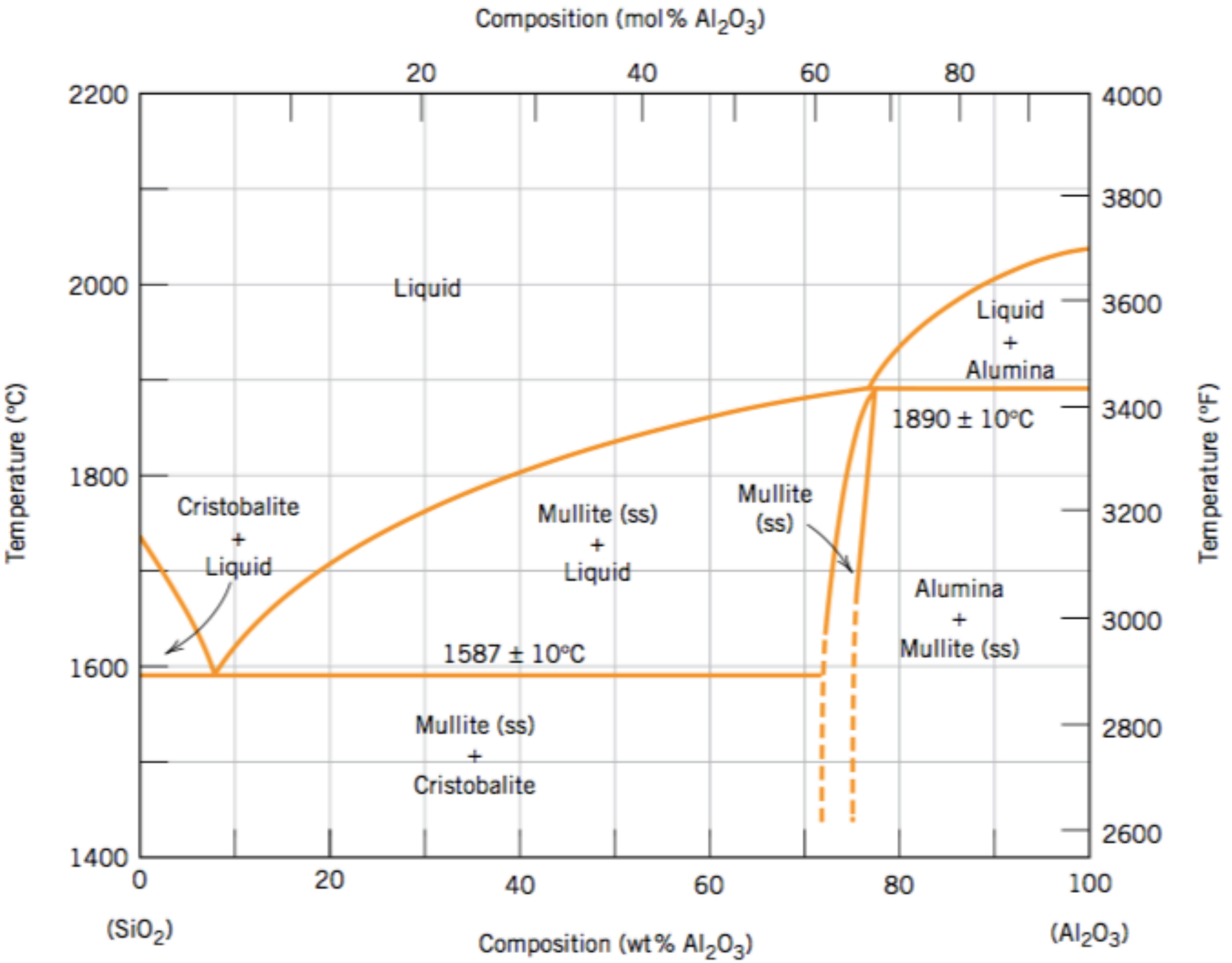


Figure 12.25 The silica–alumina phase diagram; ss denotes solid solution. (Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina–Silica Phase Diagram in the Mullite Region," *J. Am. Ceram. Soc.*, **70**[10], 758 (1987). Reprinted by permission of the American Ceramic Society.)

Ceramic Phase Diagrams

The Al_2O_3–SiO_2 System

- Commercially, the silica–alumina system is an important one because the principal constituents of many ceramic refractories are these two materials.

  - The polymorphic form of silica that is stable at these temperatures is termed *cristobalite*.

  - Silica and alumina are not mutually soluble in one another, which is evidenced by the absence of terminal solid solutions at both extremes of the phase diagram.

  - Also, it may be noted that the intermediate compound mullite, $3Al_2O_3$–$2SiO_2$, exists, which is represented as a narrow phase field.

Mechanical Properties

- Prior to the Bronze Age, human tools and vessels were primarily made of stone (a ceramic).
    - Between 3000 and 4000 years ago, metals came into widespread use because of their toughness that is derived from their ductility.
    - For most of that history, ceramic materials were somewhat limited in applicability because of their brittle nature.
    - Their principal drawback has been a disposition to catastrophic fracture in a brittle manner with very little energy absorption.
    - Although many new composites and other multiphase ceramics with useful toughness are being developed, the bulk of ceramic materials currently in use are brittle.

Mechanical Properties
Brittle Fracture of Ceramics

- The brittle fracture process consists of the formation and propagation of cracks through the cross section of material in a direction perpendicular to the applied load.

  - The measured fracture strengths of most ceramic materials are substantially lower than predicted by theory from interatomic bonding forces.

  - This may be explained by very small flaws in the material that serve as stress raisers—points at which the magnitude of an applied tensile stress is amplified and no mechanism such as plastic deformation exists to slow down or divert such cracks.

Mechanical Properties
Brittle Fracture of Ceramics

- For single-phase (i.e., monolithic) ceramics, the degree of stress amplification depends on crack length and tip radius of curvature, being greatest for long and pointed flaws.

- These stress raisers may be minute surface or interior cracks (microcracks), internal pores, inclusions, and grain corners, which are virtually impossible to eliminate or control.

- For example, even moisture and contaminants in the atmosphere can introduce surface cracks in freshly drawn glass fibers, thus deleteriously affecting the strength.

- A stress concentration at a flaw tip can cause a crack to form that may propagate until the eventual failure.

Mechanical Properties
Brittle Fracture of Ceramics

- The measure of a ceramic material’s ability to resist fracture when a crack is present is specified in terms of fracture toughness.

- The plane strain fracture toughness K_{IC} is defined according to the expression:

$$K_{IC} = Y\sigma(\pi a)^{0.5}$$

where Y is a dimensionless parameter that depends on both specimen and crack geometries, σ is the applied stress, and a is the length of a surface crack or half of the length of an internal crack.

Crack propagation will not occur as long as the right-hand side of the equation is less than the plane strain fracture toughness of the material.

Mechanical Properties
Brittle Fracture of Ceramics

- *Static failure*: Under some circumstances, fracture of ceramic materials will occur by the slow propagation of cracks, when stresses are static in nature, and the right-hand side of the equation is less than K_{Ic}.
    - This type of fracture is especially sensitive to environmental conditions, specifically when moisture is present in the atmosphere. With regard to mechanism, a stress–corrosion process probably occurs at the crack tips.
    - That is, the combination of an applied tensile stress and atmospheric moisture at crack tips causes ionic bonds to rupture; this leads to a sharpening and lengthening of the cracks until, ultimately, one crack grows to a size capable of rapid propagation
    - Silicate glasses are especially susceptible to this type of fracture.

Mechanical Properties
Brittle Fracture of Ceramics

- There is usually considerable variation and scatter in the fracture strength for many specimens of a specific brittle ceramic material.
  - A distribution of fracture strengths for a silicon nitride material is shown in Figure 12.26.
  - This phenomenon may be explained by the dependence of fracture strength on the probability of the existence of a flaw that is capable of initiating a crack.
  - This probability varies from specimen to specimen of the same material and depends on fabrication technique and any subsequent treatment.
  - Specimen size or volume also influences fracture strength; the larger the specimen, the greater this flaw existence probability, and the lower the fracture strength.

Mechanical Properties
Brittle Fracture of Ceramics

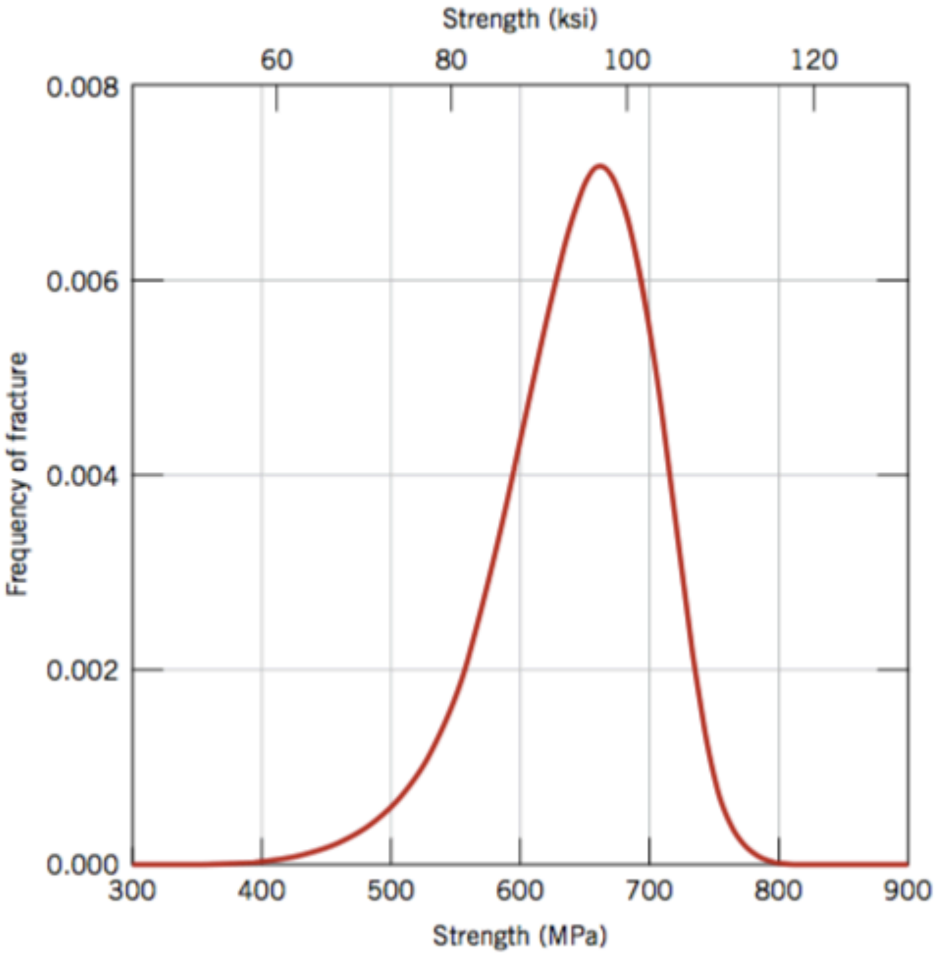


Figure 12.26 The frequency distribution of observed fracture strengths for a silicon nitride material.

For compressive stresses, there is no stress amplification associated with any existent flaws. For this reason, brittle ceramics display much higher strengths in compression than in tension (on the order of a factor of 10), and they are generally used when load conditions are compressive.

Also, the fracture strength of a brittle ceramic may be enhanced dramatically by imposing residual compressive stresses at its surface. One way this may be accomplished is by thermal tempering.

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

- It is sometimes necessary to acquire information regarding the cause of a ceramic fracture so that measures may be taken to reduce the likelihood of future incidents

  - A failure analysis normally focuses on determination of the location, type, and source of the crack-initiating flaw.

  - A fractographic study is normally a part of such an analysis, which involves examining the path of crack propagation, as well as microscopic features of the fracture surface.

  - It is often possible to conduct an investigation of this type using simple and inexpensive equipment—for example, a magnifying glass and/or a low-power stereo binocular optical microscope in conjunction with a light source.

  - When higher magnifications are required, the scanning electron microscope is used.

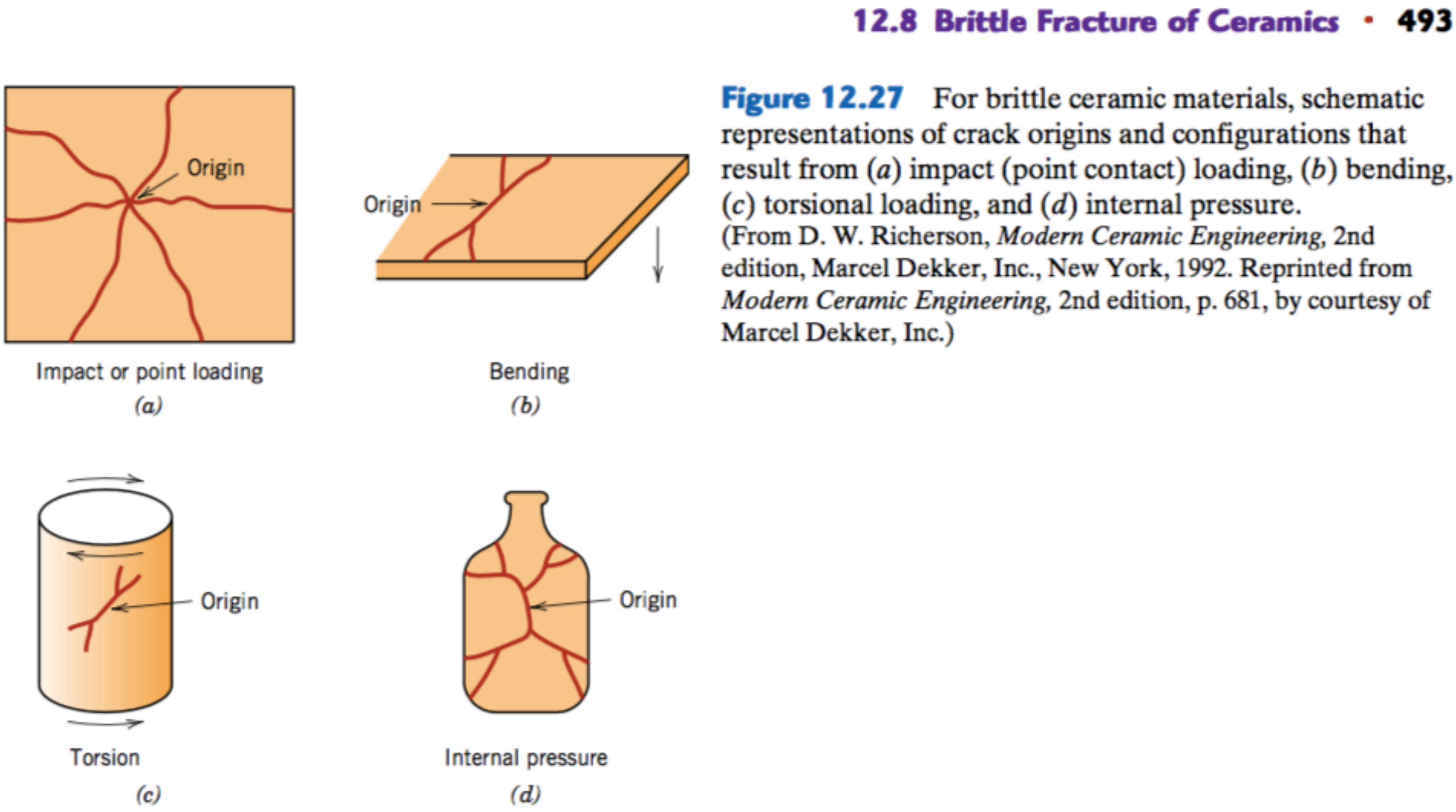
Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

- After nucleation and during propagation, a crack accelerates until a critical velocity is achieved;
    - For glass, this critical value is approximately one-half of the speed of sound.
    - Upon reaching this critical velocity, a crack may branch (or bifurcate), a process that may be successively repeated until a family of cracks is produced.
    - The site of nucleation can often be traced back to the point where a set of cracks converges. Furthermore, the rate of crack acceleration increases with increasing stress level; correspondingly the degree of branching also increases with rising stress.

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*



12.8 Brittle Fracture of Ceramics • **493**

Figure 12.27 For brittle ceramic materials, schematic representations of crack origins and configurations that result from (*a*) impact (point contact) loading, (*b*) bending, (*c*) torsional loading, and (*d*) internal pressure. (From D. W. Richerson, *Modern Ceramic Engineering*, 2nd edition, Marcel Dekker, Inc., New York, 1992. Reprinted from *Modern Ceramic Engineering*, 2nd edition, p. 681, by courtesy of Marcel Dekker, Inc.)

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

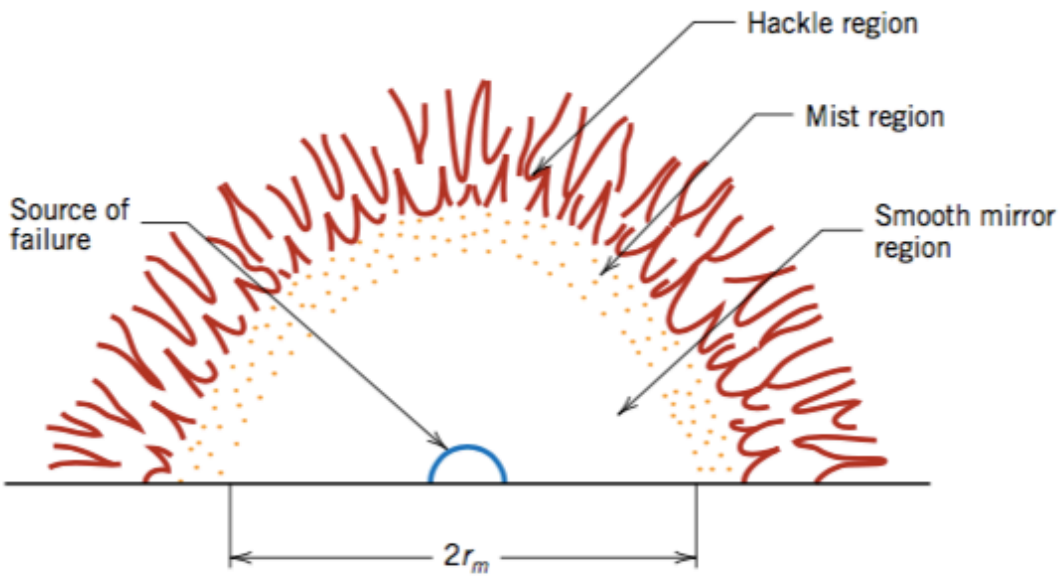


Figure 12.28 Schematic diagram that shows typical features observed on the fracture surface of a brittle ceramic.
(Adapted from J. J. Mecholsky, R. W. Rice, and S. W. Freiman, "Prediction of Fracture Energy and Flaw Size in Glasses from Measurements of Mirror Size," *J. Am. Ceram. Soc.*, **57**[10] 440 (1974). Reprinted with permission of The American Ceramic Society, *www.ceramics.org*. Copyright 1974. All rights reserved.)

The crack surface that formed during the initial acceleration stage of propagation is flat and smooth and is appropriately termed the *mirror* region.

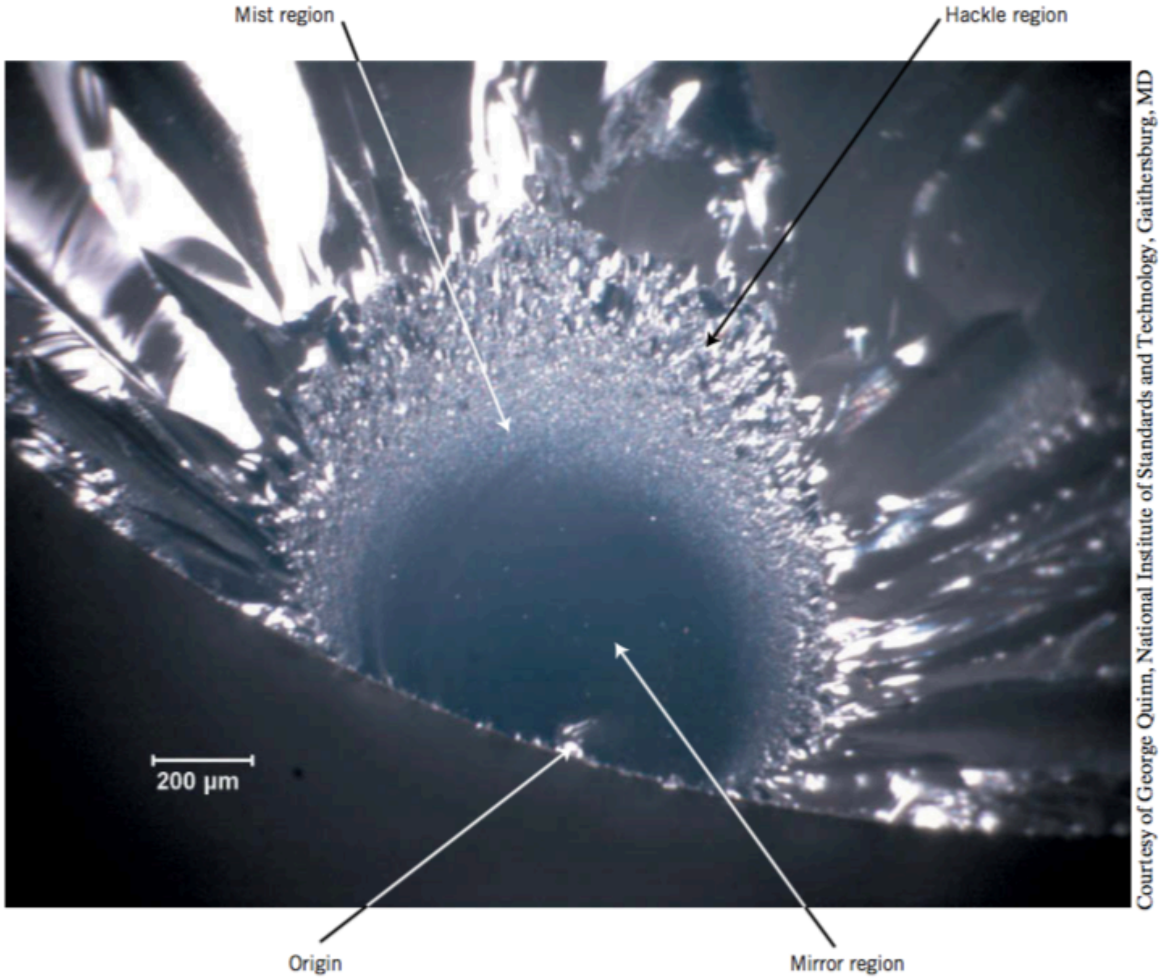
For glass fractures, this mirror region is extremely flat and highly reflective; for polycrystalline ceramics, the flat mirror surfaces are rougher and have a granular texture.

The outer perimeter of the mirror region is roughly circular, with the crack origin at its center.

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

Upon reaching its critical velocity, the crack begins to branch—that is, the crack surface changes propagation direction. At this time there is a roughening of the crack interface on a microscopic scale and the formation of two more surface features—mist and hackle.



Courtesy of George Quinn, National Institute of Standards and Technology, Gaithersburg, MD

Figure 12.29 Photomicrograph of the fracture surface of a 6-mm-diameter fused silica rod that was fractured in four-point bending. Features typical of this kind of fracture are noted—the origin as well as the mirror, mist, and hackle regions. 60×.

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

- The *mist* is a faint annular region just outside the mirror; it is often not discernible for polycrystalline ceramic pieces.

- Beyond the mist is the hackle, which has an even rougher texture.

- The hackle is composed of a set of striations or lines that radiate away from the crack source in the direction of crack propagation; they intersect near the crack initiation site and may be used to pinpoint its location.

Mechanical Properties

Brittle Fracture of Ceramics / *Fractography of Ceramics*

- Qualitative information regarding the magnitude of the fracture-producing stress is available from measurement of the mirror radius (r_m in Figure 12.28).

- This radius is a function of the acceleration rate of a newly formed crack—that is, the greater this acceleration rate, the sooner the crack reaches its critical velocity, and the smaller the mirror radius.

- Furthermore, the acceleration rate increases with stress level. Thus, as fracture stress level increases, the mirror radius decreases; experimentally it has been observed that he stress level at which fracture occurred (σ_f): $\sigma_f \propto 1/(r_m)^{0.5}$

Mechanical Properties

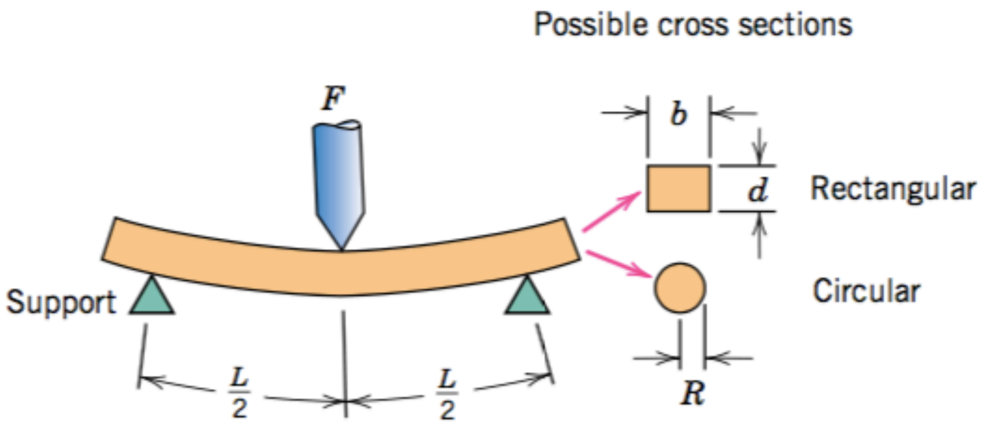
Stress - Strain Behavior / *Flexural Strength*

- The stress–strain behavior of brittle ceramics is not usually ascertained by a tensile test for three reasons.
  - First, it is difficult to prepare and test specimens having the required geometry.
  - Second, it is difficult to grip brittle materials without fracturing them.
  - Third, ceramics fail after only about 0.1% strain, which necessitates that tensile specimens be perfectly aligned to avoid the presence of bending stresses, which are not easily calculated.
- Therefore, a more suitable transverse bending test is most frequently used in which a rod specimen having either a circular or rectangular cross section is bent until fracture using a three- or four-point loading technique.

Mechanical Properties

Stress - Strain Behavior / *Flexural Strength*

Figure 12.30 A three-point loading scheme for measuring the stress–strain behavior and flexural strength of brittle ceramics, including expressions for computing stress for rectangular and circular cross sections.



$$\sigma = \text{stress} = \frac{Mc}{I}$$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

Mechanical Properties

Mechanisms of Plastic Deformation / *Crystalline Ceramics*

- For crystalline ceramics, plastic deformation occurs, as with metals, by the motion of dislocations.

- One reason for the hardness and brittleness of these materials is the difficulty of slip (or dislocation motion). For crystalline ceramic materials for which the bonding is predominantly ionic, there are very few slip systems along which dislocations may move.

    - This is a consequence of the electrically charged nature of the ions.

- For slip in some directions, ions of like charge are brought into close proximity to one another; because of electro- static repulsion, this mode of slip is very restricted, to the extent that plastic deformation in ceramics is rarely measurable at room temperature.

Mechanical Properties

Mechanisms of Plastic Deformation / *Crystalline Ceramics*

- However, for ceramics in which the bonding is highly covalent, slip is also difficult, and they are brittle for the following reasons:

- (1) the covalent bonds are relatively strong.

- (2) there are also limited numbers of slip systems.

- (3) dislocation structures are complex.

Mechanical Properties

Mechanisms of Plastic Deformation / *Noncrystalline Ceramics*

- Plastic deformation does not occur by dislocation motion for noncrystalline ceramics because there is no regular atomic structure.

- Rather, these materials deform by viscous flow, the same manner in which liquids deform; the rate of deformation is proportional to the applied stress.

- In response to an applied shear stress, atoms or ions slide past one another by the breaking and re-forming of interatomic bonds.

Mechanical Properties
Mechanisms of Plastic Deformation / *Noncrystalline Ceramics*

- The characteristic property for viscous flow, viscosity, is a measure of a noncrystalline material's resistance to deformation.

- For viscous flow in a liquid that originates from shear stresses imposed by two flat and parallel plates, the viscosity $\eta = \tau / (d\upsilon/dy)$

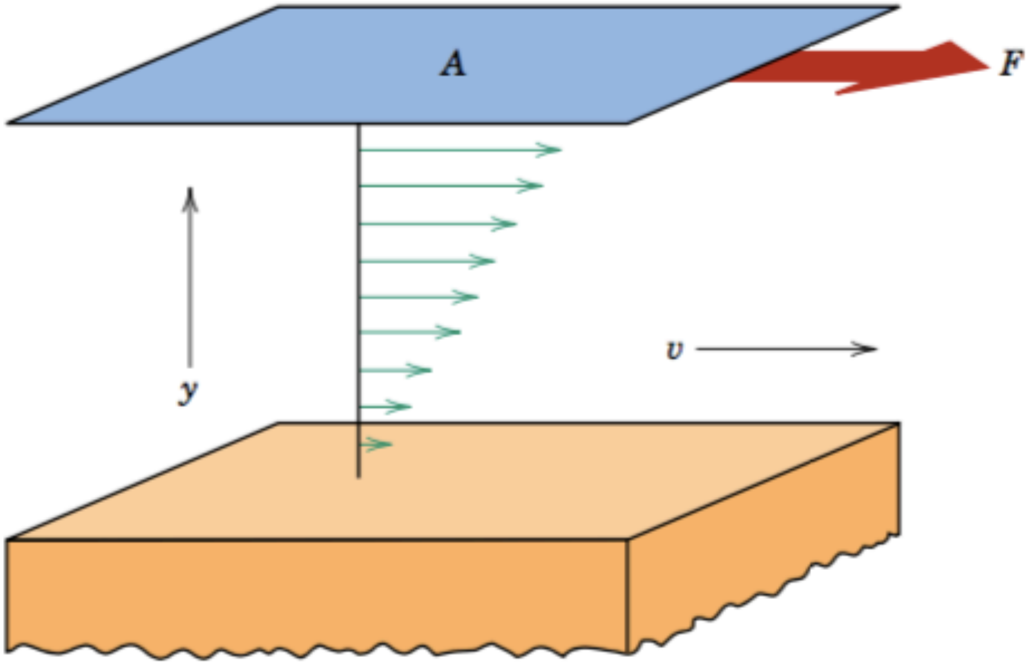
- Also, $\eta = (F/A) / (d\upsilon/dy)$

- Here, the applied shear stress = τ, the change in velocity = $d\upsilon$, and the change in distance = dy

Mechanical Properties

Mechanisms of Plastic Deformation / *Noncrystalline Ceramics*

Figure 12.32 Representation of the viscous flow of a liquid or fluid glass in response to an applied shear force.



Mechanical Properties

Miscellaneous Mechanical Considerations / *Influence of Porosity*

- As discussed earlier, the precursor material is in the form of a powder.
    - Subsequent to compaction or forming of these powder particles into the desired shape, pores or void spaces exist between the powder particles.
- During sintering, much of this porosity will be eliminated; however, often this pore elimination process is incomplete and some residual porosity will remain (See Fig. 13.22, next slide).
    - Any residual porosity will have a deleterious influence on both the elastic properties and strength.

Mechanical Properties

Miscellaneous Mechanical Considerations / *Influence of Porosity*

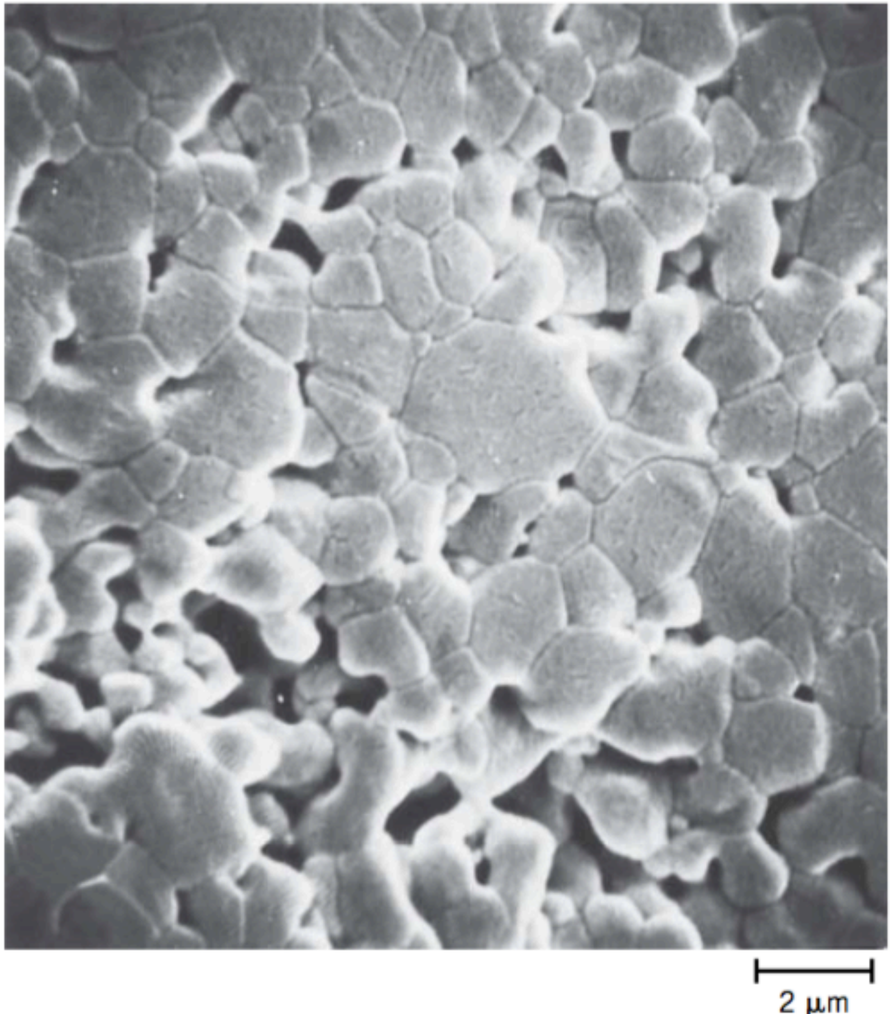


Figure 13.22 Scanning electron micrograph of an aluminum oxide powder compact that was sintered at 1700°C for 6 min. 5000×.
(From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition, p. 483. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Mechanical Properties

Miscellaneous Mechanical Considerations / *Influence of Porosity*

- For example, for some ceramic materials the magnitude of the modulus of elasticity *E* decreases with volume fraction porosity *P* according to:

$$E = E_0\,(1-1.9P + 0.9P^2)$$

where E_0 is the modulus of elasticity of the nonporous material.

Mechanical Properties

Miscellaneous Mechanical Considerations / *Influence of Porosity*

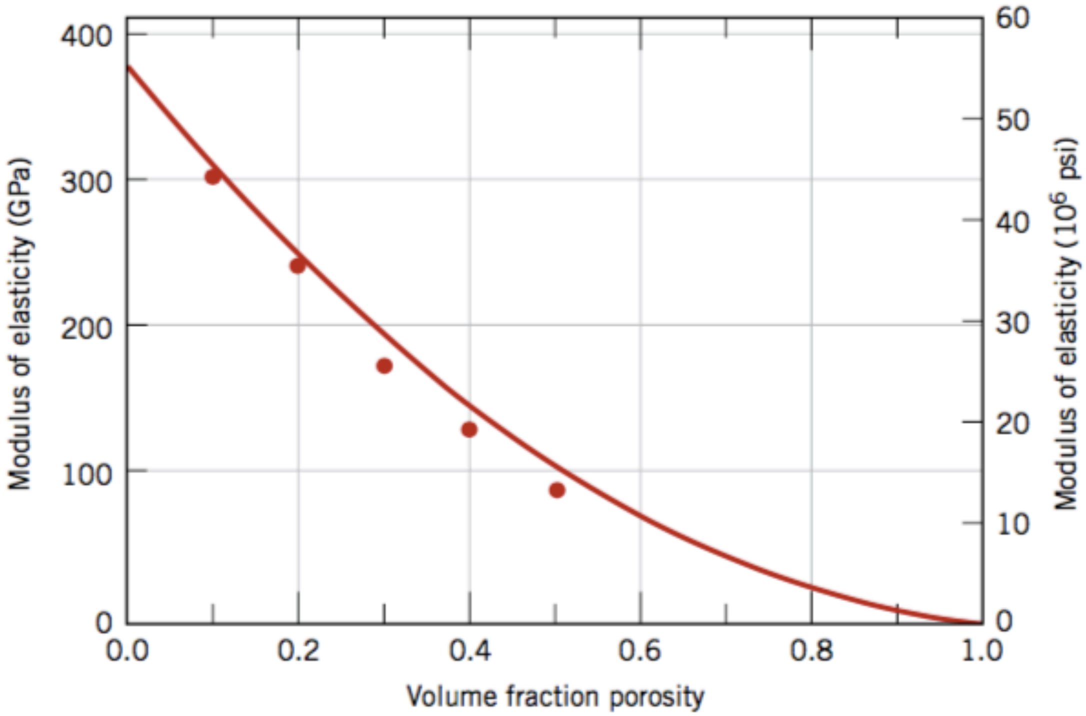
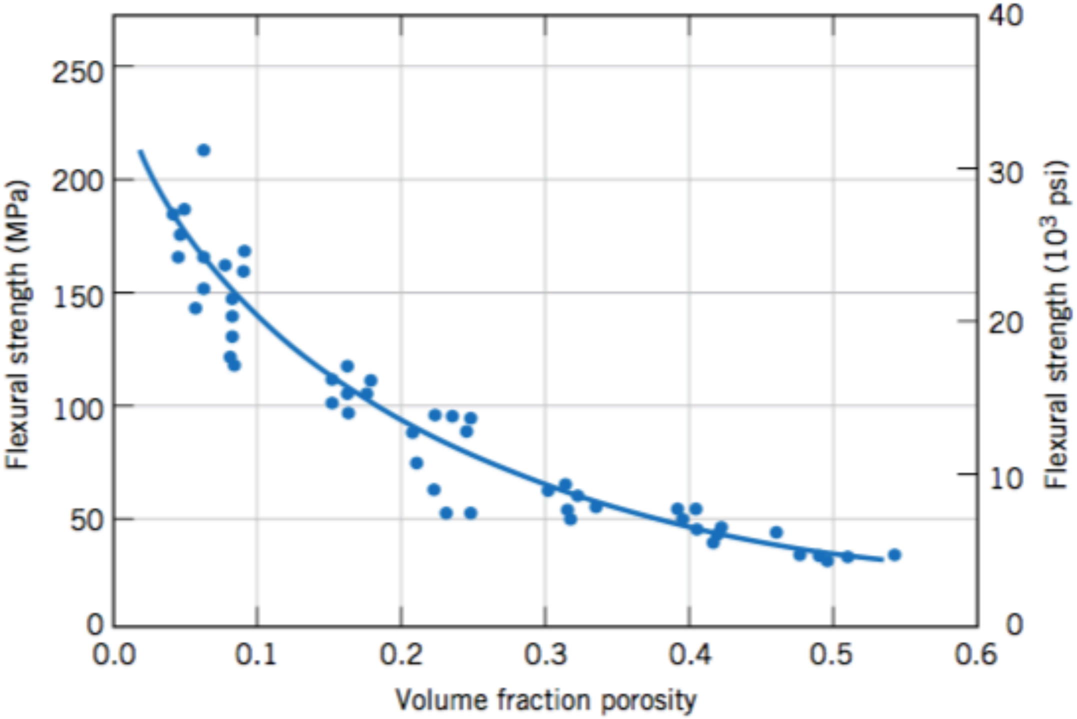


Figure 12.33 The influence of porosity on the modulus of elasticity for aluminum oxide at room temperature. The curve drawn is according to Equation 12.9. (From R. L. Coble and W. D. Kingery, "Effect of Porosity on Physical Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **39,** 11, Nov. 1956, p. 381. Reprinted by permission of the American Ceramic Society.)

Mechanical Properties

Miscellaneous Mechanical Considerations / *Influence of Porosity*

Figure 12.34 The influence of porosity on the flexural strength for aluminum oxide at room temperature.
(From R. L. Coble and W. D. Kingery, "Effect of Porosity on Physical Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **39**, 11, Nov. 1956, p. 382. Reprinted by permission of the American Ceramic Society.)



Porosity is deleterious to the flexural strength for two reasons: (1) pores reduce the cross-sectional area across which a load is applied, and (2) they also act as stress concentrators

The influence of porosity on strength is rather dramatic; for example, 10 vol% porosity often decreases the flexural strength by 50% from the measured value for the nonporous material.

Constants

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

Mechanical Properties

Miscellaneous Mechanical Considerations / *Hardness*

- Vickers and Knoop technique are usually used to measure the hardness of ceramic materials.

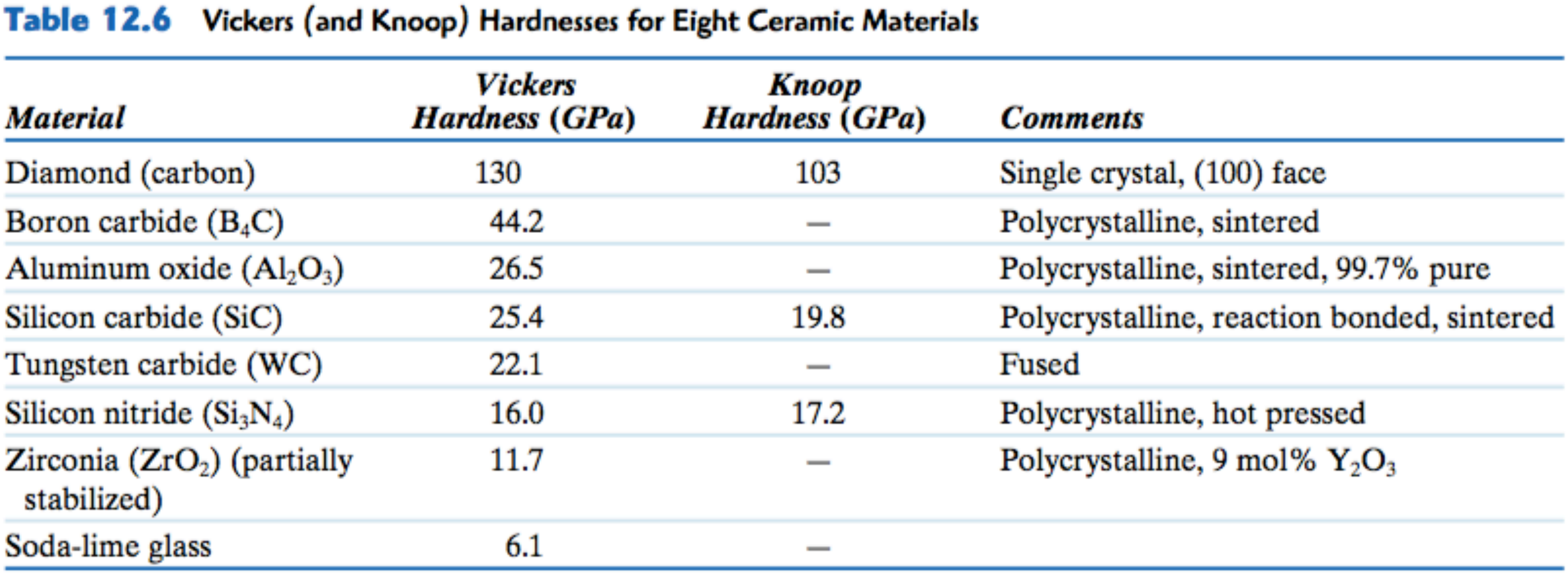


Table 12.6 Vickers (and Knoop) Hardnesses for Eight Ceramic Materials

Material	*Vickers Hardness (GPa)*	*Knoop Hardness (GPa)*	*Comments*
Diamond (carbon)	130	103	Single crystal, (100) face
Boron carbide (B_4C)	44.2	—	Polycrystalline, sintered
Aluminum oxide (Al_2O_3)	26.5	—	Polycrystalline, sintered, 99.7% pure
Silicon carbide (SiC)	25.4	19.8	Polycrystalline, reaction bonded, sintered
Tungsten carbide (WC)	22.1	—	Fused
Silicon nitride (Si_3N_4)	16.0	17.2	Polycrystalline, hot pressed
Zirconia (ZrO_2) (partially stabilized)	11.7	—	Polycrystalline, 9 mol% Y_2O_3
Soda-lime glass	6.1	—	

Mechanical Properties

Miscellaneous Mechanical Considerations / *Creep*

- Often, ceramic materials experience creep deformation as a result of exposure to stresses (usually compressive) at elevated temperatures. In general, the time–deformation creep behavior of ceramics is similar to that of metals.

- However, creep occurs at higher temperatures in ceramics. High-temperature compressive creep tests are conducted on ceramic materials to ascertain creep deformation as a function of temperature and stress level.