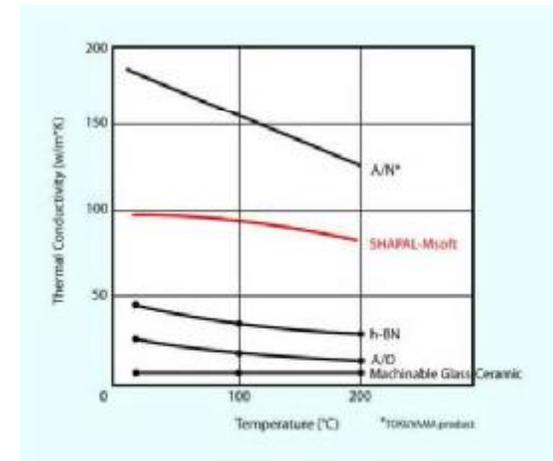
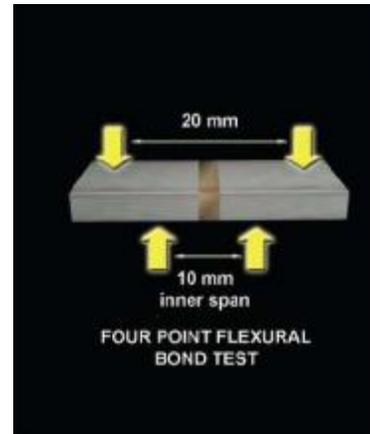


INTRODUCTION TO CERAMICS, GLASS AND REFRACTORIES

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6) Properties of Ceramics



Density (ρ): is a measure of the mass (m) per volume (V) of material in g/m^3

- **Crystallographic Density:** the ideal density of a specific crystal structure calculated from chemical composition data and from interatomic spacing data.
- **Theoretical Density:** the density of material that contain zero microstructural porosity taking into account multiple phases, defect structures and solid solution.
- **Bulk Density:** the measured density of a bulk ceramic body including all porosity, lattice defects and phases.
- **Specific Gravity:** The density of material relative to the density of water at 4°C .

Example:

A ceramic composite material consist of 30 volume % SiC whiskers in an Al_2O_3 matrix. Estimate the theoretical density (TD) if SiC has a crystallographic density of 3.22 g/cm^3 and alumina has crystallographic density of 3.95 g/cm^3 .

$$\begin{aligned} \text{TD} &= (\text{Volume fraction SiC} \times \rho_{\text{SiC}}) + (\text{Volume fraction of Al}_2\text{O}_3 \times \rho_{\text{Al}_2\text{O}_3}) \\ &= 0.3 \times 3.22 \text{ g/cm}^3 + 0.7 \times 3.95 \text{ g/cm}^3 \\ &= 0.966 + 2.765 = 3.731 \text{ g/cm}^3 \end{aligned}$$

Example:

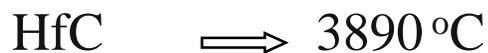
A mixture of 30 volume % SiC whiskers and 70 volume % alumina powder is hot pressed. The measured bulk density is 3.65 g/cm^3 . What is the theoretical density? How much porosity is present?

$$\begin{aligned}\% \text{ TD} &= (\text{Bulk density}/\text{Theoretical density}) \times 100 \\ &= (3.65/3.71) \times 100 \\ &= 97.8\% \text{ TD}\end{aligned}$$

$\% \text{ of Porosity} = 100\% - \text{solid}\% = 100 - 97.8 = 2.2\% \text{ porosity}$ (this include open porosity and closed porosity)

Melting Behaviour

Different materials have different melting characteristics. Some melt congruently (liquid phase and solid phase both of the same composition coexist in equilibrium at the melting temperature) and some melt incongruently (solid phase change to liquid plus a solid phase, both with compositions differ from original phase). Some sublime and other decompose. The melting or sublimation behavior is largely determined by the strength of the atomic bond.



ε

Thermal Properties

Thermal Conductivity (k)

is the rate of heat ($\Delta Q / \Delta t$) per unit area (A) required to develop unit temperature gradient ($\Delta T / \Delta x$)

Thermal conductivity may be expressed and calculated from the **Fourier's law**:

$$k = (1/A)(\Delta Q / \Delta t) / (\Delta T / \Delta x)$$

Where Q -heat, passing through the surface A ; Δt - change in time; k - thermal conductivity; A - surface area, normal to the heat transfer direction; $\Delta T / \Delta x$ - temperature gradient along x – direction of the heat transfer.

Fourier's law is analogue of the First Fick's law, describing diffusion in steady state.

In contrast to metals, ceramics have low thermal conductivity due to Ionic-covalent bonding which does not form free electrons, thus thermal energy is transported by phonon

Compare: k of $Al_2O_3 = 30 \text{ W/(m.K)}$ and k of $Al = 231 \text{ W/(m.K)}$ and $SiO_2 = 1.2 \text{ W/(m.K)}$. Porosity reduce k

Coefficient of Thermal Expansion (α)

$T \uparrow \longrightarrow V \text{ (volume)} \uparrow$ **Amplitude of atomic vibration about a mean position** \uparrow

Closed pack structures (**metal and Ionic ceramics**) \longrightarrow **High α**

Covalent Ceramics (open space within the structure) \longrightarrow **Low α**

Thermal Expansion (Coefficient of Thermal Expansion) is relative increase in length per unit temperature rise:

$$\alpha = \Delta L / (L_0 \Delta T)$$

Where; α -coefficient of thermal expansion; ΔL – length increase; L_0 – initial length; ΔT – temperature rise.

Compare: α of SiC = $4.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ($2.3 \text{ }^\circ\text{F}^{-1}$), Al = $23 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ($13 \text{ }^\circ\text{F}^{-1}$)

Specific Heat Capacity

Heat Capacity: is amount of heat required to raise material temperature by one unit.

Specific Heat Capacity (c): is amount of heat required to raise temperature of unit mass of material by one degree at constant pressure. **J/(kg.°K)**

$$c = \Delta Q / (m\Delta T)$$

Where; **c** –specific heat capacity; **ΔQ** – amount of heat; **m** – material mass; **ΔT** – temperature rise.

Heat Capacity of ceramic materials is higher, than that of metals.

Compare: “**c**” of Alumina = 850 J/(kg.°K) or 0.203 BTU/(lb*°F);
“**c**” of steel = 481 J/(kg.°K) or 0.115 BTU/(lb*°F)

Thermal Shock Resistance:

is an ability of material to withstand sharp changes in temperature.

If a ceramic material is rapidly cooled, its surface reaches the temperature of cooling environment and tends to contract (thermal contraction). Since the interior regions of the material are still hot, thermal contraction of the skin surface is impossible.

This leads to formation of tensile stress (**thermal stress σ_{th}**) in the skin. Such thermal stresses at the surface may cause cracks and consequent failure.

$$\sigma_{th} = \alpha E \Delta T / (1-\nu)$$

Where; α -coefficient of thermal expansion; E – modulus of elasticity; ΔT the temperature difference; ν Poisson's ratio

Thermal shock resistance of a material may be estimated in accordance to the formula:

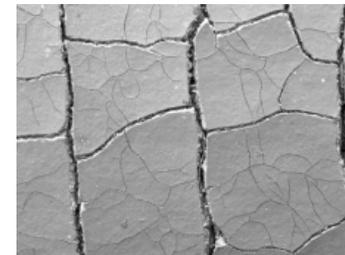
$$Rs = k \sigma_f / (\alpha E)$$

Where; Rs – thermal shock resistance; k - thermal conductivity;

σ_f – flexural strength;

For high thermal shock resistance we want a ceramic with:

High σ_f , High k , Low E , and Low α



Electrical Properties

Ceramics are used in many electrical applications as:

Insulators

prevents the flow of charge or heat. Ceramics make good insulators because the ionic and covalent bonding restricts electron and ion mobility. An example is Electrical Porcelain (50% clay, 25% silica, 25% feldspar), Alumina Al_2O_3

Capacitors

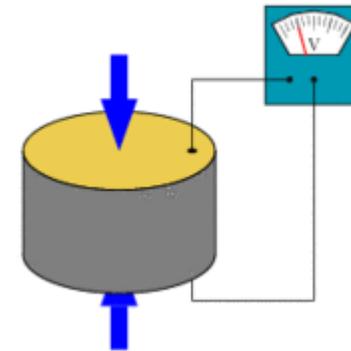
store electrical energy by virtue of separating oppositely charged plates with an insulator (also called a dielectric) in between. An example of a ceramic material used as the dielectric for a capacitor is Barium Titanate, Ba_2TiO_3

Semiconductors

have an intermediate value of electrical conductivity. The most commonly used ceramic semiconducting materials are sintered oxides of Mn, Ni, Fe, Co, and Cu. By varying the amounts of these oxides in the material the desired value of the electrical conductivity can be obtained. These are used for NTC thermistors. A **Negative Temperature Coefficient Thermistor** is a device that measures temperature by a change in the resistance of the material. As temperature increases, resistance decreases.

Piezoelectrics

have the distinct property whereby an applied stress induces an electrical voltage. The reverse piezoelectric effect is the phenomena whereby an applied voltage across the material results in a dimensional change. BaTiO_3



Magnetic Properties

Naturally occurring magnetic ceramic mineral magnetite (Fe_3O_4)

Oxide ceramics could be synthesized with strong magnetic properties

Magnetic properties of materials depends on electrical structure and crystal structure

Pauli exclusion principal \longrightarrow 2 electrons can occupy a given energy level and must have opposite spin

Half filled energy level (electronic structure with unpaired electrons \longrightarrow)

A net magnetic moment (Transition elements (Fe, Co, Mn), Rare earth(Y, Nd, Cd), Actinide (Ra,Th)

Application: Permanent magnet, Memory unit, microwave device, etc,

Optical properties

Radiation is absorbed by unbound electrons. Metals are opaque. Single-crystal sapphire with filled electronic shells and contains no grain boundaries or pores, making it as clear as glass. As a result, single-crystal sapphire is an excellent material for making windows for high power LCD projectors.

In contrast, polycrystalline Ceramics have a microstructure of crystal grain boundaries and microscopic pores which diffuses light and makes it difficult to pass through.

Other Applications: fluorescent lights, light sensors and other related products.

Spinel, a high performance, transparent and polycrystalline ceramic material



Mechanical Properties of Ceramic Materials

Elasticity: Load (stress) σ MPa

Deformation (Strain) ϵ (%) $\epsilon = \Delta L/L$

ϵ depends on $\begin{cases} \text{Atomic bond strength} \\ \text{The stress } \sigma \\ \text{Temperature } T \end{cases}$

$$\sigma = E \epsilon$$

Where E is the **Young Modulus** (Modulus of elasticity)

For shear loading (τ):

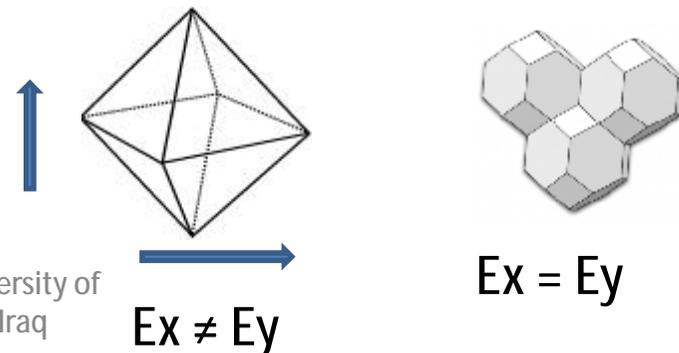
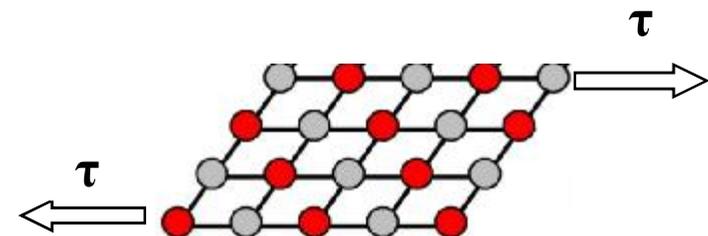
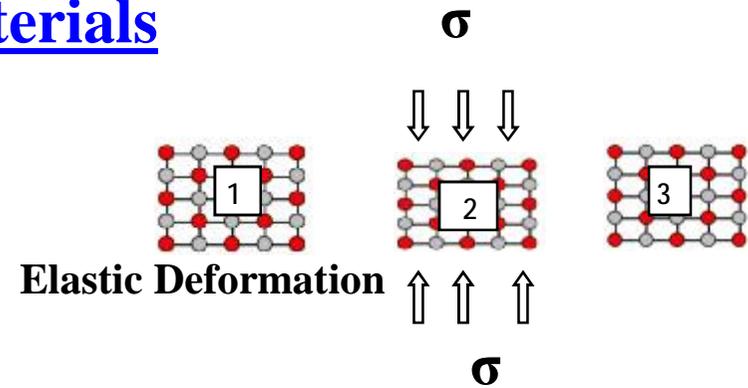
$$\tau = G \epsilon'$$

ϵ' is the shear strain and **G** is the **shear modulus** (rigidity modulus)

Bond strength and thus E varies for different crystallographic directions

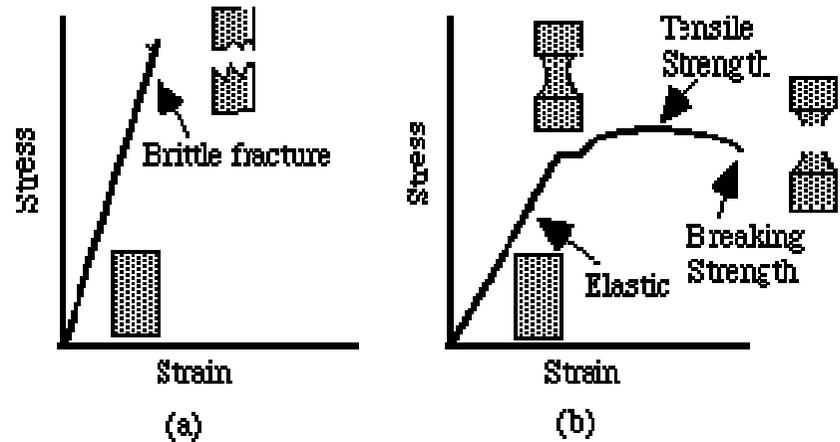
At high temp E decreases because of an increase in interatomic spacing.

Strong bond \longrightarrow E \uparrow



Ceramic materials are known for their lack of ductility. In general, they are strong in compression, but possess low fracture toughness; plastic deformation (slip) is essentially non-existent

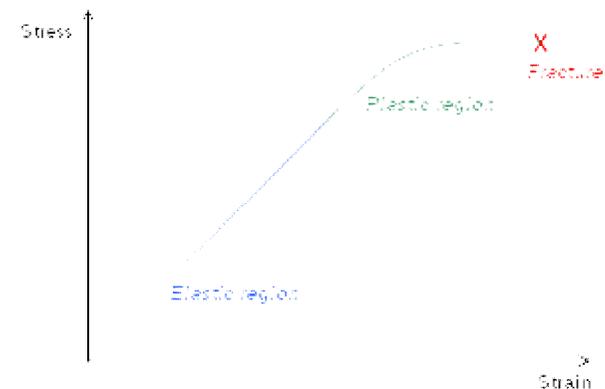
At intermediate temperature and short term loading most ceramics behave elastically with no plastic deformation up to failure – this is known as Brittle Fracture



Metals also behave elastically up to certain stress but unlike ceramics metal deform in a ductile manner as the stress is further increased.

This is referred to as Plastic Deformation.

Some metals, Al for instance, have a smooth transition from elastic strain, others like low carbon steel for instance have discontinuity at the outset of plastic strain – this is called the Yield Point



The reasons that ceramics are so brittle:

- Ceramic materials inherently have cracks, flaws, pores and inclusions. These act as stress risers and failure initiates at one of these and propagates quickly (because there is no energy absorbing mechanism as there is in metals,) causing brittle fracture.
- The covalent bond is directional and electrons are shared. Hence, bonds will not reform easily and so brittle fracture will occur.
- Since the crystal structures tend to be complex, there are limited slip systems.
- Potential slip planes may involve like charges moving over each other which will cause separation and so brittle fracture will occur.

Mechanical behavior is described by the **Griffith theory** of brittle fracture:

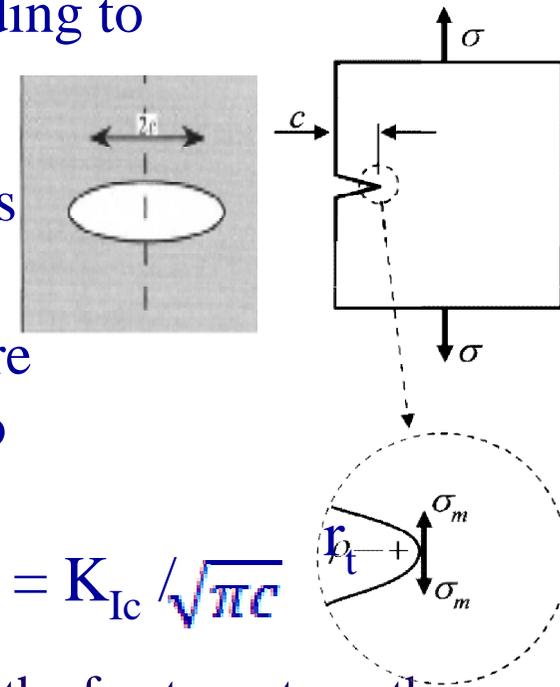
All ceramics are assumed to contain pre-existing microscopic defects (voids, cracks, grain corners) that act as stress concentrators. The local stress at the tip of a pre-existing flaw increases with decreasing tip radius of curvature and with increasing crack length according to

$$\sigma_m = 2\sigma (c/r_t)^{1/2}$$

Crack propagation occurs when σ_m at the tip exceeds the local tensile strength σ (applied stress). C is the flaw size, r_t the crack tip radius. Plane strain fracture toughness, K_{Ic} , is a measure of a material's ability to resist fracture when a crack is present. Recall

$$K_{Ic} = \sigma_f \sqrt{\pi c} = \sqrt{2E\gamma} \quad \text{and} \quad \sigma_f = (2E\gamma / \pi c)^{1/2} = K_{Ic} / \sqrt{\pi c}$$

γ is the fracture surface energy or work of fracture, σ_f is the fracture strength. Values for K_{Ic} for ceramic materials are usually (at least) an order of magnitude less than that for metals. Since there is no stress amplification under compression, ceramics are usually used under compressive loading.



Example

a) A sharp edge notch 120 μm deep is introduced in a thin magnesia plate. The plate is then loaded in tension normal to the plane of the notch. If the applied stress is 150 MPa, will the plate survive? (b) Would your answer change if the notch were the same length but was as internal notch instead of an edge notch? The fracture toughness of MgO is around $2.5 \text{ Mpa}\cdot\text{m}^{1/2}$?

Answer

(a) To determine whether the plate will survive the applied stress, the stress intensity at the crack tip needs to be calculated and compared to the fracture toughness of MgO.

K_{Ic} in this case is given

$$K_{Ic} = \sigma\sqrt{\pi c} = 150\sqrt{3.14 \times 120 \times 10^{-6}} = 2.91 \text{ MPa} \cdot \text{m}^{1/2} :$$

Since this value is greater than K_{Ic} for MgO, it follows that the plate will fail.

(b) In this case, because the notch is an internal one, it is not as detrimental as a surface or edge notch and

$$K_{Ic} = \sigma\sqrt{\pi c/2} = 150\sqrt{3.14 \times 60 \times 10^{-6}} = 2.06 \text{ MPa} \cdot \text{m}^{1/2}$$

Since this value is $< 2.5 \text{ MPa} \cdot \text{m}^{1/2}$ it follows that the plate would survive the applied load.

Porosity reduces the elastic modulus

E and can be estimated from the relation

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

Where E_0 is the modulus for nonporous material, P volume fraction of pores. The relation is valid for materials with up to 50% porosity

Some materials are made up of more than one composition or phase and have E value intermediate between the moduli of the constituent phases. Example glass bonded ceramics, composite materials, dispersion strengthened materials.

E can be estimated from the **law of mixture** where

$$E = E_1V_1 + E_2V_2 + E_3V_3 + \dots$$

The strength of multi-phase material can also be estimated from the relation

$$\sigma = \sigma_1V_1 + \sigma_2V_2 + \sigma_3V_3 + \dots$$

Question: What would have the greater effect on the elastic modulus of an Al_2O_3 material, 5vol% intergranular glass or 5 vol% porosity? E for Al_2O_3 is 380 GPa and for glass is 69 GPa

Elastic Modulus (E) of some materials

Material	GPa
Nylon	2.8
Bulk Graphite	6.9
Fused Silica	69
ZrO ₂	138
Al ₂ O ₃	380
SiC	414
Diamond	1035

Recall in the case of metals, mechanical properties were determined from tensile tests, in which a stress-strain curve is generated. **Ceramics are not normally tested in tension because:**

- It is difficult to machine to the required geometry
- It is difficult to grip brittle materials without inducing fracture
- Ceramics typically fail after only ~ 0.1% strain

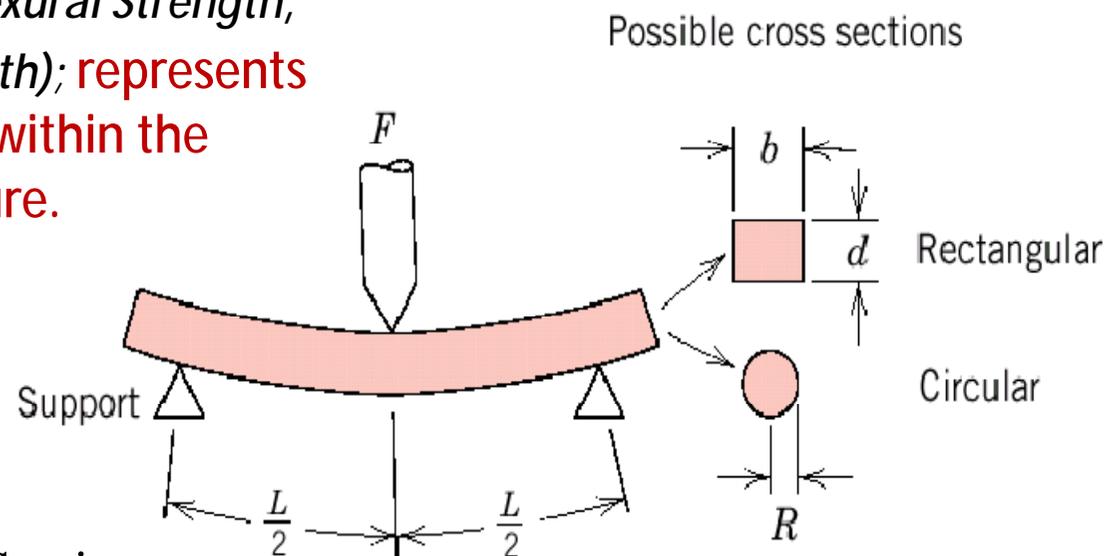
For these reasons, the mechanical properties are determined using a different approach, the three point bend test or four point bend test:

σ_f *Modulus of Rupture MOR (Flexural Strength, Bending Strength, Fracture Strength); represents the highest stress experienced within the material at its moment of rupture.*

Three Points Bending Test

$$\frac{\sigma}{\frac{3FL}{2bd^2}} \text{ For Rectangular}$$

$$\frac{FL}{\pi R^3} \text{ For Circular Cross Section}$$



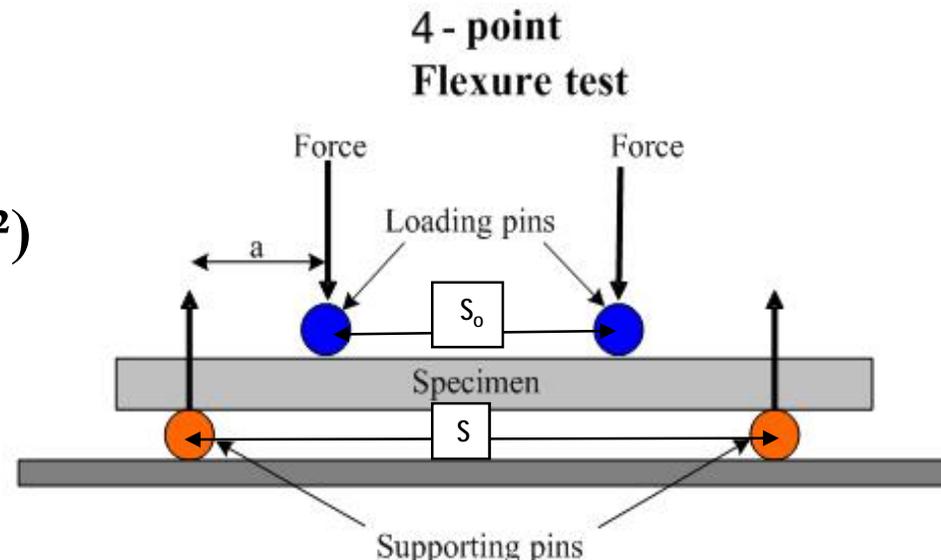
4 – points Flexure Test

For rectangular specimen

$$\sigma_f = 3Fa/(bd^2) = 3F(S-S_0)/2(bd^2)$$

For round specimen

$$\begin{aligned}\sigma_f &= 16Fa/(\pi R^3) = 2Fa/(\pi r^3) \\ &= F(S-S_0)/(\pi r^3)\end{aligned}$$



Example: A three-point transverse bend test is applied to an alumina cylinder with a reported flexural strength of 390 MPa. If the specimen radius is 2.5 mm and the support point separation distance is 30 mm, estimate whether or not the specimen would fracture when a load of 620 N is applied.

Solution:

$$\begin{aligned}\sigma_f &= FL/(\pi R^3) = 620\text{N}(30 \times 10^{-3}\text{m}) / (3.14 (2.5 \times 10^{-3}\text{m})^3) = 379 \times 10^6 \text{ N/m} \\ &= 379 \text{ MPa}\end{aligned}$$

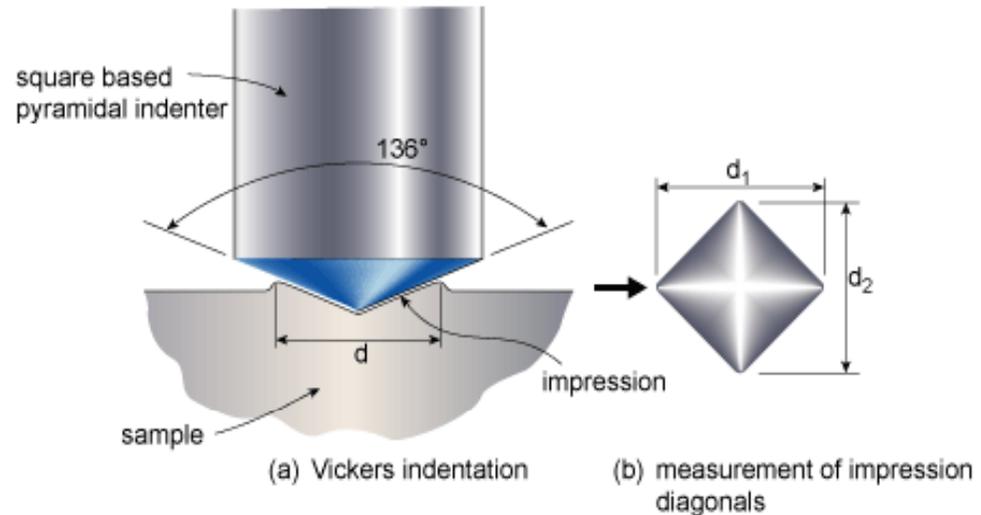
Since this value is less than the given value for σ_f (390 MPa), fracture is not predicted.

Hardness

Hardness is one of the most frequently measured properties of a ceramic. Its value helps to characterize resistance to deformation, densification, and fracture.

Hardness is usually measured on conventional microhardness machines with Knoop or Vickers diamond indenters. These machines make impressions whose diagonal size is measured with an attached optical microscope

Vickers Hardness

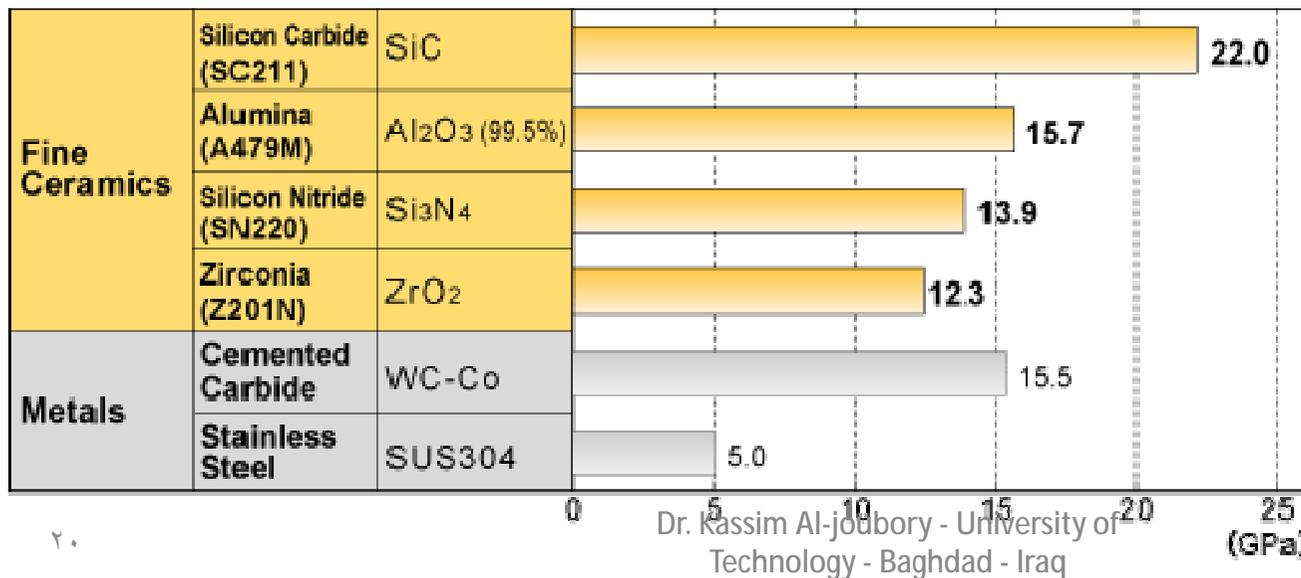


$$HV = \frac{2F \sin \frac{136^\circ}{2}}{d^2}$$

$$= 1.854 \frac{F}{d^2} \text{ approximately}$$

F = Load in kgf (N)

d = (d₁ + d₂)/2



Creep

Creep is the slow and continuous deformation of a solid under tensile stress with time that only occurs at higher temperatures, that is, $T > 0.5T_m$, where T_m is the melting point

Factors affecting the mechanical properties of ceramics

- **Temperature:** In polycrystalline material increasing temperature increases atoms separation thus the force required to separate the atoms reduces
- **Grain size:** Both the strength σ and toughness K_{Ic} increases as the grain size is reduced. $\sigma \propto d^{-1/2}$
- **Surface Defects:** from machining, thermal etching, heat treatment weaken ceramics
- **Porosity and internal flaws:** Source of failure, reduces σ and E
- **Impurities and inclusions:** different thermal expansion coefficient cause thermal mismatch and lead to microcracking reducing both strength and E
- **Silicate phase at grain boundaries:** decrease strength and increase creep at high temperature