

Objective

The primary objective of this study is to gain an understanding of the mechanical properties, and underlying atomic structures that cause the properties, of ceramic materials through application of Modulus of Rupture tests.

Abstract

The primary drawback of using ceramic materials in structural applications is their inherent brittleness which results from strong bonding coupled with electrical balancing restrictions due to the metallic plus non-metallic nature of ceramic compounds. The Modulus of Rupture (MOR) test is the standard for determining the mechanical properties of ceramics (Flexural Strength and Flexural Modulus). Variations in Flexural Strength as a function of firing temperature and specimen size will be examined experimentally (MOR) and evaluated using the statistical t-test; large ceramic parts generally have lower strengths due to their higher probability of containing critical flaws.

Background

Ceramics are generally composed of Metallic + Non-Metallic Compounds which are primarily Ionically Bonded.

Silicon and Oxygen are Common in Ceramics due to Availability and Cost.

Common Structural Ceramics include Silicon Oxides, Nitrides and Carbides which include clay minerals such as pottery, tiles, cement and glass.

General Ceramic Properties:

Insulative, Refractory, Hard and Brittle.

Advanced Ceramic Applications:

- High-Temperature Engines.
- Tools for Machining Hard Metallics.
- Coatings that Require High-Temperature Resistance and Chemical Stability (Enamels).
- Optical uses include: Lasers, Florescent Screens and Iridescent Films.

Brittleness is the Primary Drawback of Ceramics; Ceramic Compounds are being developed which exhibit measurable ductility with excellent strength and hardness.

Three General Categories of Ceramics:

1. Crystalline Ceramics include Silicates, Oxides and Non-Oxide Compounds which form crystalline solids and are utilized in pottery, bricks and many high-tech industries such as aerospace and electronics.
2. Glasses include Silicate and Non-Silicate Compounds which are non-crystalline; Glasses are generally Amorphous.
3. Glass-Ceramics are composed of crystalline ceramics that are initially formed as glasses and are subsequently crystallized under controlled thermal processing.

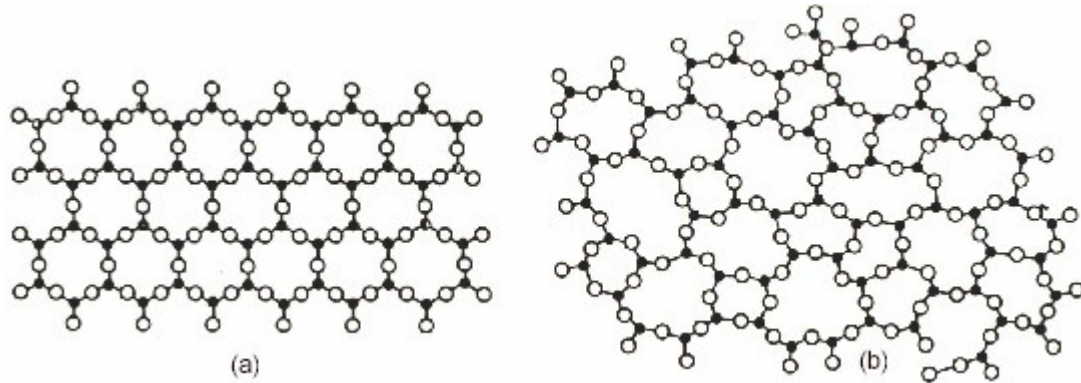


Figure 1 - (a) Crystalline Ceramic Structure, (b) Amorphous Ceramic Structure. [Askeland, 1996]

Crystalline Ceramics

Most Crystalline Ceramics are SiO_2 based and are termed Silicates.

Silicate Examples: Pottery, Whiteware, Bricks, Tile.

Table 1 - Compositions of some Silicate Ceramics. [Shackelford, 1992]

Ceramic	Composition (wt %)					
	SiO_2	Al_2O_3	K_2O	MgO	CaO	Others
Silica refractory	96					4
Fireclay refractory	50–70	45–25				5
Mullite refractory	28	72				—
Electrical porcelain	61	32	6			1
Steatite porcelain	64	5		30		1
Portland cement	25	9			64	2

Note that Silicate Ceramics are generally Oxides!

Crystalline Ceramic Formation involves **Firing** which refers to controlled heating that Dries and Facilitates Ionic Bonding of the Compounds.

Ceramic Strength is highly dependent on **Porosity** (size and number of voids) which act as crack initiation sites. Crystalline Ceramics are influenced by the Nature of the Component Ions:

- Crystals must be Electrically Balanced thus Compositions must be Balanced!
- Relative Ion Size generally determines the Crystalline Structures that form.

Due to Electrical Balancing restrictions, Crystalline Imperfections occur in Pairs:

- Schottky Defects - Vacancy Pair (Cation & Anion)
- Frenkel Defects - Cation Vacancy near a Cation Interstitial

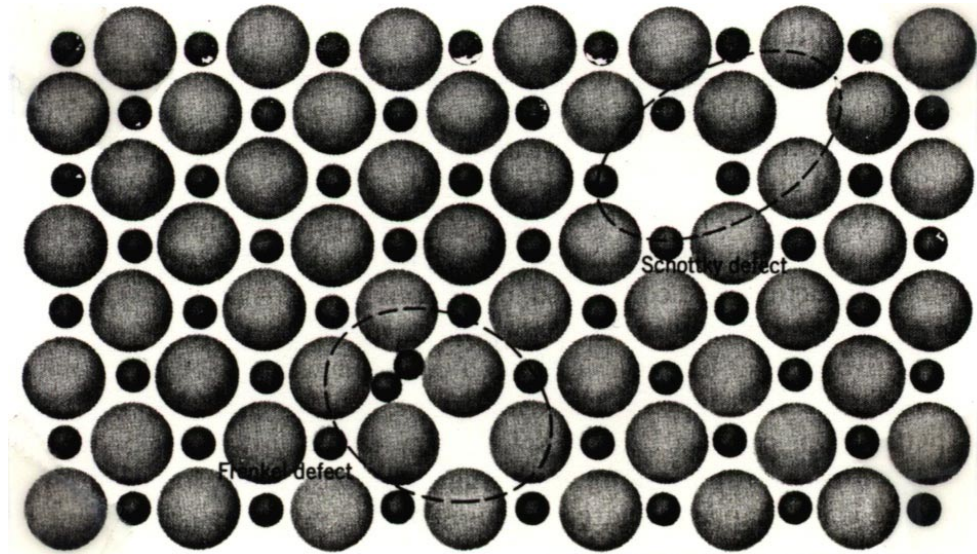


Figure 2 - Illustrations of Frankel and schottky defects. [Callister, 1991]

Electrical Balancing Restrictions are also partially responsible for Ceramic Brittleness; Dislocation Movement and Plastic Deformation are minimal.

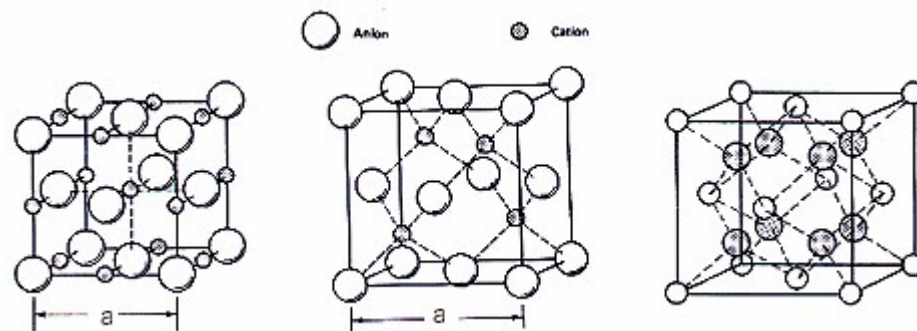


Figure 3 - Sample Ceramic Crystal Unit Cell Structures. [Callister, 1991]

Pure Oxide Compounds with very small impurity levels, such as BaTiO_3 , make excellent high-end semiconductors but are relatively expensive.

Non-Oxide Ceramics, such as Silicon Carbide and Boron Nitride, include refractories and abrasives which are developed for heat and wear resistance.

Glasses/Amorphous Compounds

Ordinary sand is primarily SiO_2 which is utilized to produce window glass.

Most Glasses are produced by the addition of oxides, such as CaO and Na_2O , which catalyze the formation of random 3-D networks of SiO_2 .

Table 2 - Compositions of some Silicate Ceramics. [Shackelford, 1992]

Glass	Composition (wt %)									
	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	CaO	MgO	K ₂ O	ZnO	PbO	Others
Vitreous silica	100									—
Borosilicate	76	13	4	5	1					1
Window	72		1	14	8	4				1
Container	73		2	14	10					1
Fiber (E-glass)	54	8	15		22					1
Bristol glaze	60		16		7		11	6		—
Copper enamel	34	3	4				17		42	—

Examples of Common Non-Crystalline Ceramics

Vitreous Silica is relatively pure SiO₂ which can withstand temperatures up to 1000°C; typically utilized in furnace windows.

E-Glass and **S-Glass** are thin pultruded fibers utilized in Composites.

Enamel is a ceramic coating applied for Temperature & Corrosion Protection.

Window Glass is a mixture of Oxides; 72% SiO₂ with Na₂O, CaO, MgO and Al₂O₃.

Glass Ceramics

Glass Ceramics are a new group of materials which are initially relatively ordinary glassware which is cheap and easy to form.

90% of the glassy material can be Crystallized though controlled heat treatment; small-grained, nearly pore-free ceramics form which are Strong and Shock Resistant.

Crystallization is a Nucleation and Growth process; catalysts are added to facilitate the formation of numerous grains.

Table 3 - Compositions of some Glass Ceramics. [Shackelford, 1992]

Glass-Ceramic	Composition (wt %)							
	SiO ₂	Li ₂ O	Al ₂ O ₃	MgO	ZnO	B ₂ O ₃	TiO ₂ ^a	P ₂ O ₅ ^a
Li ₂ O-Al ₂ O ₃ -SiO ₂ system	74	4	16				6	
MgO-Al ₂ O ₃ -SiO ₂ system	65		19	9			7	
Li ₂ O-MgO-SiO ₂ system	73	11		7		6		3
Li ₂ O-ZnO-SiO ₂ system	58	23			16			3



Figure 4 - Photograph of a partially crystallized Glass-Ceramic. [Smith, 1993]

Bend Test - Modules of Rupture

In ductile materials, the stress-strain behavior is found by applying the tensile test (as determined in previous experiments). The curve typically goes through a maximum which is where the tensile strength is located. Failure occurs at a lower stress after necking has reduced the cross-sectional area supporting the load. On the other hand the stress-strain behavior of brittle ceramics is not ascertained by a tensile test. There are many reasons the tensile test is not used:

1. it is difficult to prepare and test specimens having the required geometry;
2. it is difficult to grip brittle materials without fracturing them;
3. surface flaws often cause premature failures; and
4. ceramics fail after only about 0.1% strain thus specimens must be perfectly aligned in order to avoid the presence of bending stresses.

For these reasons a more suitable transverse bending test is used.

In the bend test (or flexure test) a bar specimen having either a circular or rectangular cross section is bent until fracture using a three or four point loading technique.

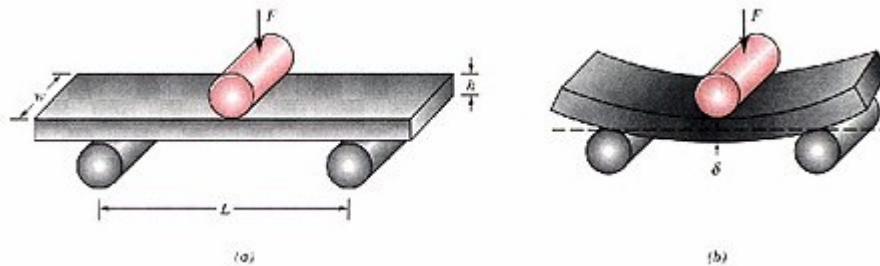


Figure 10 - (a) The bend test often used for measuring the strength of brittle materials, and (b) the deflection d obtained by bending. [Askeland, 1994]

At the point of loading, the top surface of the specimen is placed in a state of compression and the bottom surface is in tension. Stress is computed from the specimen thickness, the bending moment, and the moment of inertia of the cross section. The maximum tensile stress exists at the bottom surface of the center of the specimen, directly below the point of load application. Since the tensile strengths of ceramics are about one-tenth of their compressive strengths and fracture occurs on the tensile specimen face, the bend test is a valid substitute for the tensile test.

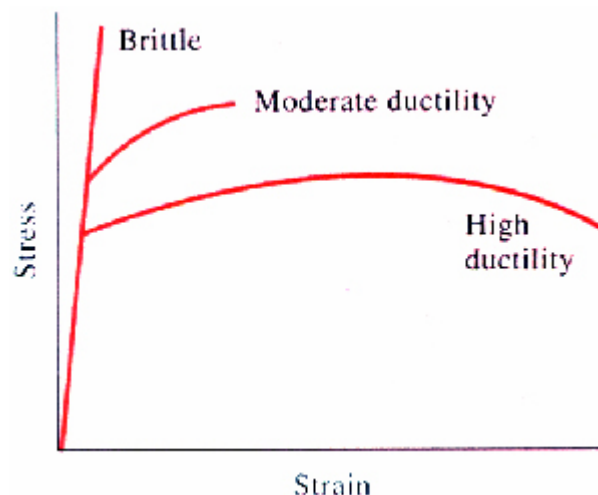


Figure 11 - The stress-strain behavior of brittle materials compared with that of more ductile materials. [Askeland, 1994]

For a 3-point bend test of a rectangular bar, the stress at fracture using the bend test is known as the Flexural Strength or Modulus of Rupture and is given by

$$\sigma_{fs} = \frac{3FL}{2wh^2}$$

Where σ_{fs} = Flexural Strength

F = Fracture Load

L = Length Between Outer Supports

w = Specimen Width

h = Specimen Height

The results of the bend test are similar to stress-strain curves; however the stress is plotted versus deflection rather than versus strain.

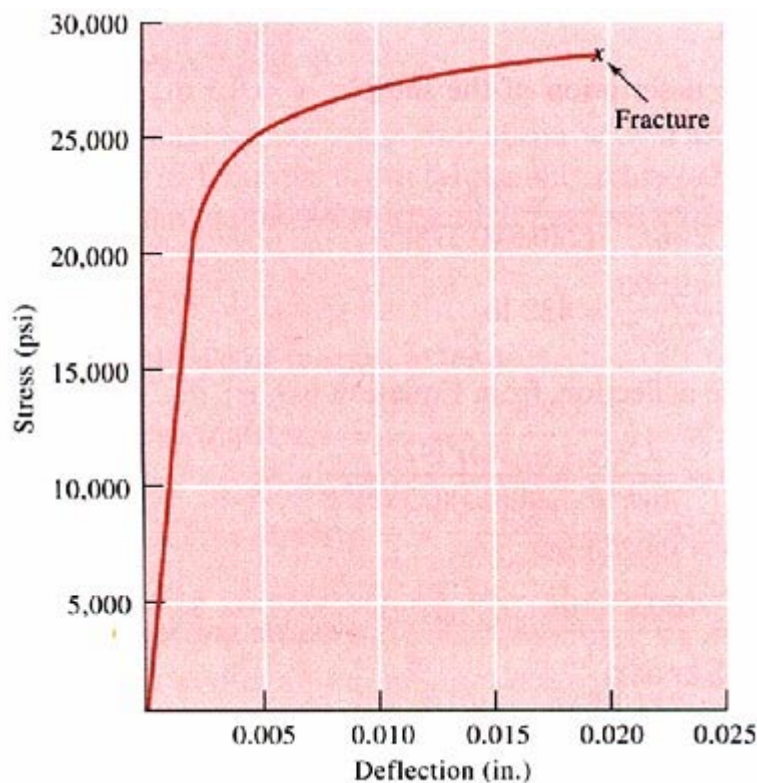


Figure 12 - Stress-deflection curve for MgO obtained from a bend test. [Askeland, 1994]

The modulus of elasticity in bending, the flexural modulus, is determined from the linear portion of the Stress-Deflection curve and is given by

Where

$$E_{fs} = \frac{L^3(F_1 - F_2)}{4wh^3(\delta_1 - \delta_2)}$$

E_{fs} = Flexure Modulus

δ = Beam Deflection

$F_1 = 2/3 F_{max}$ with δ_1 @ $2/3 F_{max}$

$F_2 = 1/3 F_{max}$ with δ_2 @ $1/3 F_{max}$

Because cracks and flaws tend to remain closed in compression, brittle materials are generally designed such that only compressive stresses act on the part.

t-Test for Determination of Mean Differences

There is often considerable variation and scatter in flexural strength for many specimens of a specific brittle ceramic material. This phenomenon may be explained by the dependence of flexural 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 also influences flexural strength; the larger the specimen, the greater the probability of critical flaw existence, and the lower the flexural strength. The t-Test is a statistical method that is applied to determine whether or not significant mean differences exist between two sets of repeated measures data. The method will be applied to determine whether or not a specimen size effect is evident in the Modulus of Rupture tests being conducted in this experiment.

A small sample-size test (less than 30 measurements) of the significance of the difference between two population means may be based on the t statistic. The t-test is generally applied when at least one of the sample sizes, n_1 or n_2 , is less than 30. If the samples (tests) are random and independent and derive from approximately Normal distributions with the same standard deviations, then the t statistic can be applied to determine if the sample means are different where:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}}$$

\bar{X}_1 = sample mean for the first data set

\bar{X}_2 = sample mean for the second data set

n_1 = number of data points in the first data set

n_2 = number of data points in the second data set

s_1 = sample standard deviation of the first data set

s_2 = sample standard deviation of the second data set

Note: $s =$

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

The decision as to whether or not one mean is greater than the other is based on the t-sampling distribution with **$n_1 + n_2 - 2$ Degrees of Freedom.**

Applying the one-sided alternative, \bar{x}_1 that is not Greater Than \bar{x}_2 , the level of significance, α , is identified $t_{\alpha/2}$ by as indicated in Figure 13.

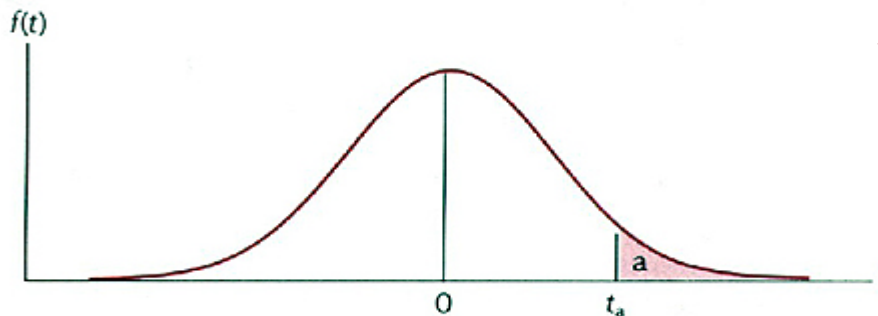



Figure 13 - Graphical Depiction of the t-Distribution. [Ott, 1988]

The following procedure can be utilized in the application of the t-test:

1. State the Null Hypothesis as $H_0: \bar{x}_1$ Not Greater Than \bar{x}_2
2. State the Alternative Hypothesis as $H_A: \bar{x}_1$ Greater Than \bar{x}_2
3. Select a Level of Significance (α): 0.05 is generally used.
4. Criterion: Using the t-table, determine the critical value of $t_{\alpha/2}$ for $n_1 + n_2 - 2$ Degrees of Freedom.
5. Calculate t based on the two data sets.
6. Decision: Reject the Null Hypothesis if $|t| > t_{\alpha/2}$; Do Not Reject the Null Hypothesis if $|t| < t_{\alpha/2}$.

Table 4 - Percentage points of the t-Distribution. [Ott, 1988]



Percentage Points of the t Distribution

df	$\alpha = .1$	$\alpha = .05$	$\alpha = .025$	$\alpha = .01$	$\alpha = .005$	$\alpha = .001$
1	3.078	6.314	12.706	31.821	63.657	318.309
2	1.886	2.920	4.303	6.965	9.925	22.327
3	1.638	2.353	3.182	4.541	5.841	10.215
4	1.533	2.132	2.776	3.747	4.604	7.173
5	1.476	2.015	2.571	3.365	4.032	5.893
6	1.440	1.943	2.447	3.143	3.707	5.208
7	1.415	1.895	2.365	2.998	3.499	4.785
8	1.397	1.860	2.306	2.896	3.355	4.501
9	1.383	1.833	2.262	2.821	3.250	4.297
10	1.372	1.812	2.228	2.764	3.169	4.144
11	1.363	1.796	2.201	2.718	3.106	4.025
12	1.356	1.782	2.179	2.681	3.055	3.930
13	1.350	1.771	2.160	2.650	3.012	3.852
14	1.345	1.761	2.145	2.624	2.977	3.787
15	1.341	1.753	2.131	2.602	2.947	3.733
16	1.337	1.746	2.120	2.583	2.921	3.686
17	1.333	1.740	2.110	2.567	2.898	3.646
18	1.330	1.734	2.101	2.552	2.878	3.610
19	1.328	1.729	2.093	2.539	2.861	3.579
20	1.325	1.725	2.086	2.528	2.845	3.552
21	1.323	1.721	2.080	2.518	2.831	3.527
22	1.321	1.717	2.074	2.508	2.819	3.505
23	1.319	1.714	2.069	2.500	2.807	3.485
24	1.318	1.711	2.064	2.492	2.797	3.467
25	1.316	1.708	2.060	2.485	2.787	3.450
26	1.315	1.706	2.056	2.479	2.779	3.435
27	1.314	1.703	2.052	2.473	2.771	3.421
28	1.313	1.701	2.048	2.467	2.763	3.408
29	1.311	1.699	2.045	2.462	2.756	3.396
30	1.310	1.697	2.042	2.457	2.750	3.385
40	1.303	1.684	2.021	2.423	2.704	3.307
60	1.296	1.671	2.000	2.390	2.660	3.232
120	1.289	1.658	1.980	2.358	2.617	3.160
240	1.285	1.651	1.970	2.342	2.596	3.125
inf.	1.282	1.645	1.960	2.326	2.576	3.090

Source: Computed by P. J. Hildebrand.

Example: Two sets of tensile strength test data were collected as indicated below. It is thought that Zinc Coated parts are stronger than Tin Coated parts. Use the 0.05 Level of Significance to determine whether the Mean Strength of the Zinc Coated parts can be considered to be Greater Than the Mean Strength of the Tin Coated parts.

Tin Coated Parts – Tensile Strength (MPa): 55, 56, 49, 61, 58

Zinc Coated Parts – Tensile Strength (MPa): 62, 63, 53, 59, 60

Answer: $t = 5.404$, $t_{\alpha/2} = 2.306 \rightarrow$ Reject H_0 (\bar{x}_1 Not Greater Than \bar{x}_2) \rightarrow Accept H_A (\bar{x}_1 Greater Than \bar{x}_2)

Ceramic Properties

The main disadvantage of ceramics is their Brittleness; catastrophic fractures occur following minimal deformation. Ceramics are relatively Weak in Tension but are generally Strong in Compression.

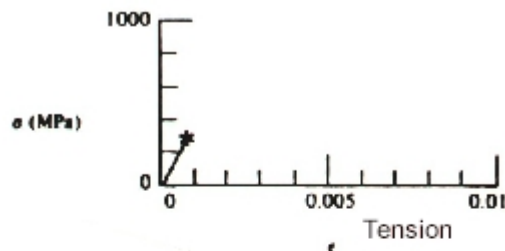
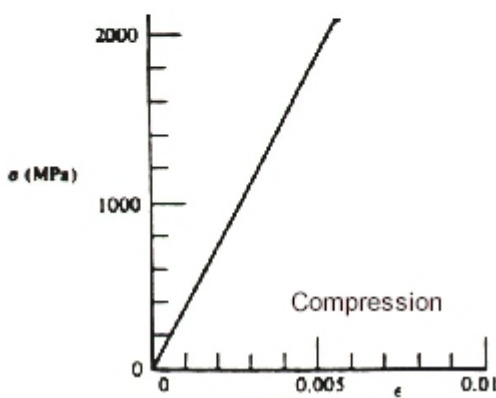


Figure 5 - Representative Compressive and Tensile Ceramics Stress-Strain Curves. [Shackelford, 1992]

Ceramic Fracture Toughness values are Low due to the presence of Pores and Microcracks; strengths are much lower than their theoretical based on breaking bonds.

Ceramic Strength is Size Dependent; large ceramic parts generally fail at lower stresses due to their higher probability of containing critical flaws.



Methods of Improving Fracture Toughness (Recent Investigations):

- Porosity (void space) Minimalization: Sintering, Crystallization, etc.
- Transformation Toughening: Stress Induced Phase Transformation resulting in Compressive Crack-Tip Stresses.
- Crack Intersections: Intersections can Blunt the Crack-Tip

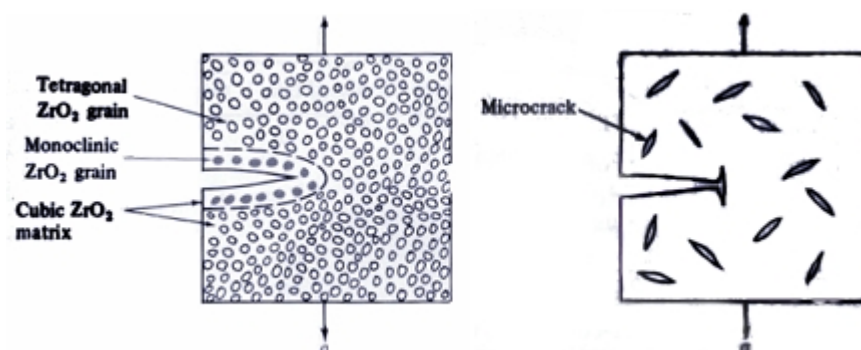


Figure 6 - Transformation Toughening and Crack Tip Blunting. [Shackelford, 1992]

H₂O can contribute to Ceramic Fracture through chemical reaction at the highly stressed crack tip (similar to creep).

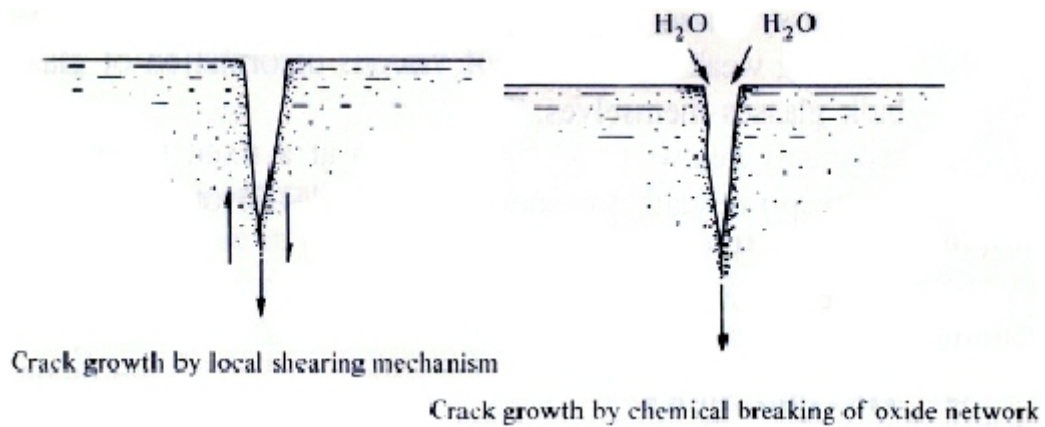


Figure 7 - Contribution of H_2O in Ceramic Fracture. [Shackelford, 1992]

Thermal Shock refers to Fractures resulting from Rapid Temperature Changes.

When a part is Quenched, internal stresses are created due to differing expansion-contraction rates. Thermal Shock causes sudden, Catastrophic Fracture of Ceramics; Ceramics should be cooled slowly!

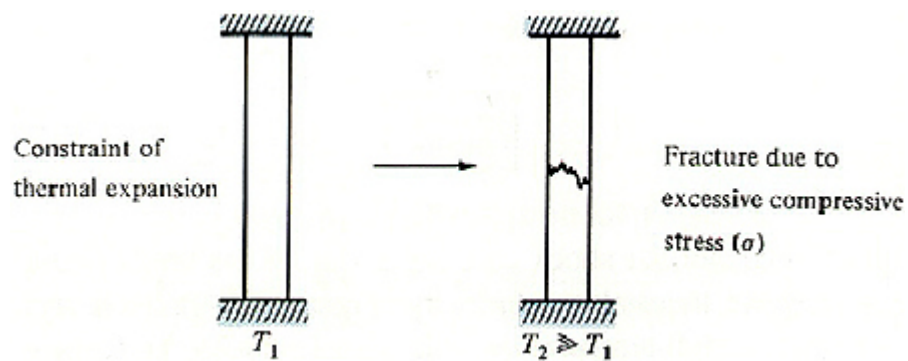


Figure 8 - Depiction of Thermal Shock in a Constrained Ceramic Column. [Shackelford, 1992].

Optical Properties

Ceramics are often Transparent due to their lack of Conduction (Free) Electrons; Free Electrons absorb visible light energy.

Metals are generally opaque due to the presence of Free Electrons. Opacity in Ceramics is generally due to the scattering effect of pores.

Viscous Deformation of Glasses

Glasses thermally expand similar to crystal with atomic structures similar to liquids. Glasses Deform by Viscous Flow where the Rate of Deformation is Proportional to the Applied Stress.

Viscosity, η , is a measure of a non-crystalline material's resistance to deformation.

T_G , Glass Transition Temperature (Near the Annealing Point)

Below T_G glassy materials are true Glasses,

Above T_G glassy materials become Supercooled Liquids.

T_s , Softening Temperature - Elongation continues with increasing temperature up to T_s where the glass becomes a True Fluid.

Glasses are generally shaped in the **Working Range**: 700°C to 900°C.

Residual Stresses can be relieved in ~15 minutes in the **Annealing Range**: ~450°C.

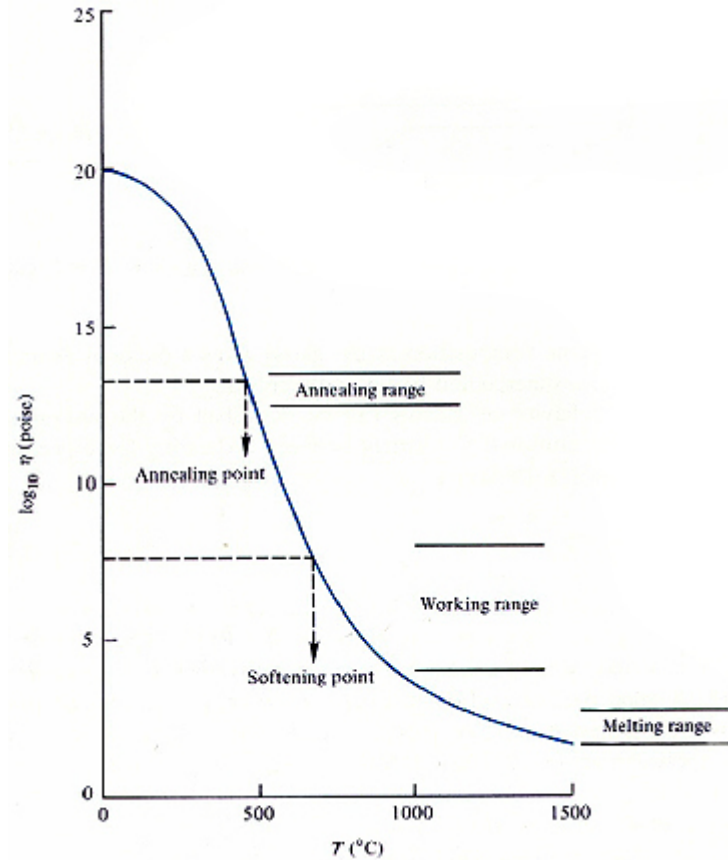


Figure 9 - Viscosity of a typical soda-lime-silica glass from room temperature to 1500°C. Above the glass transition temperature (~450°C in this case), the viscosity decrease in an Arrhenius Fashion. [Shackelford, 1992]

Procedure

MATERIALS & EQUIPMENT

Room Temperature Curing Advanced Silicon Oxide (SiO_2) Castable Ceramic (Rescor 750), 8500 Series Instron, 3-Point Bend Test Fixture (Short-Beam Shear), PC with Data Acquisition.

SAFETY

Safety Glasses Must be Worn by ALL Students in the Lab During Testing!

Instructions on using the Instron and Labtech Notebook (Data Acquisition) are available at [\[Composites Site\]](#).

Modulus of Rupture (MOR) tests will be conducted in this experiment. The MOR tests will involve three-point bending of specimens through application of a compressive load at the specimen center. Modifications to the Tensile Testing procedure for the Instron include the following:

- Note: The Instron Cross-head has been positioned to accommodate the MOR test fixture.

- Limits should be set accordingly with Minimum Load set at –2250 pounds. (will use the 10 kN load cell)
- Waveform in Position Controller set to Amplitude of –1.0 inches.
- Data Acquisition program file is "mor10k.ltc".
- Note that Strain will not be measured (no Extensometer).

Measure and record the Span Length, L , for the base of the fixture (all of the specimens are nominally 2.0 inches long, but L is based on the Span Length). Prior to each test, measure and record the specimen's center Width and Height.

Each section will be testing 4 specimens as indicated below (one replication per cell for each section).

Nominal Specimen Width (Inches)	Firing Temperature (°C)	
	110	950
0.50	1	1
1.50	1	1

Lab Requirements

1. Conduct the 4 MOR tests indicated in the Procedure Section collecting the Load versus Deflection (Stroke) data for each specimen through brittle fracture.
2. Develop a results table that includes the following information for the 4 samples tested: T , L , w , h , F_{\max} , F_1 , δ_1 , F_2 , δ_2 , σ_{fs} , and E_{fs} .
3. How does the stiffness of the ceramic compare to the stiffness values of the other material types that have been investigated in this course?
4. Obtain the Flexural Strength results of all sections of ME 3701 for the current semester and assemble all of the data into a single table (5 replication/cell).
5. Applying the t-Test to the combined Flexural Strength results of all sections, investigate whether or not there's a curing temperature effect at a 0.05 Level of Significance:
 - a.) For the $w = 0.50$ inch Specimens.
 - b.) For the $w = 1.50$ inch Specimens.

Discuss the Results. Are the results what you expected? Why or why not?

6. Applying the t-Test to the combined Flexural Strength results of all sections, investigate whether or not there's a size effect at a 0.05 Level of Significance:
 - a.) For the Specimens Cured at 110°C.
 - b.) For the Specimens Cured at 950°C.

Discuss the Results. Are the results what you expected? Why or why not?

Homework

1. What are the characteristic properties of ceramic materials?

2. What is the primary difficulty of using ceramics in structural applications and what are some of the methods applied to overcome this difficulty.
3. Why would a ceramic with large pores be expected to be weaker than an equivalent ceramic with small pores?
4. Briefly explain why Ceramics tend to be Electrically Insulative and Non-Corrosive.
5. If Dislocations are so important in Metals, why are they Not Important in Ceramics?
6. What is Thermal Shock?
7. What is the purpose of the t-test in this experiment?
8. Why would we expect larger ceramic specimens to fail at lower stress levels?
9. What occurs during the Firing of Ceramic materials?
10. Where would you expect failure to initiate in a Modulus of Rupture test using a 3-Point-Bend test fixture. Briefly explain your answer.