Fracture Toughness

Problem
A reaction-bonded silicon nitride has a strength of 300 MPa and a fracture toughness of 3.6 MPa.m^{1/2}. What is the largest-size internal crack that this material can support without fracturing? Given Y = 1

Principles of Fracture Mechanics

• Fracture toughness – measure of a ceramic material’s ability to resist fracture when a crack is present

• Plane strain fracture toughness $K_{IC}$ is defined according to the expression

$$K_{IC} = Y \sigma_f \sqrt{a}$$

$K_{IC}$ = plane strain fracture toughness (MPa√m)
$Y$ = geometric constant (usually ~1)
$a$ = length of external crack or half the length of internal one
$\sigma_f$ = applied stress

Modulus of Rupture (MOR)

• Ceramic materials are usually tested in bending
  – Sample preparation is easier
  – Significant difference in results for testing in tension, compression and bending

  **Flexural strength (modulus of rupture, bend strength, transverse rupture strength)** is a material property, defined as the stress in a material just before it yields in a flexure test

Factors affecting strength of ceramics

• Depends on the amount of defects => giving stress concentration

  • All brittle materials contain a certain population of small cracks with different sizes, orientations, geometries

  • Surface cracks
  • Porosity
  • Inclusions
  • Excessive grain sizes

Modulus of Rupture (MOR) Testing

• MOR is calculated as the “maximum fiber stress” on the tension side at failure (strength parameter)

For a rectangular cross-section:

$$\sigma = \frac{3FL}{2bh^2}$$

For a circular cross-section:

$$\sigma = \frac{FL}{\pi r^3}$$

For a three-point bending:

For a four-point bending:

Load

Area

Load

Area
Mechanical properties versus degree of crystallinity

- Crystalline phases are stronger.
- At low T’s, crystalline and non-crystalline phases are brittle.
- At high T’s approaching T_m, non-crystalline phases are ductile.

Effect of Porosity on Mechanical Properties

- Many ceramic materials are manufactured in the solid state because of their high melting points.
- They are milled into powder.
- Then sintered at HT to allow particles to bond together.
- They then contain free space: porosity.

Porosity in Al_2O_3

\[ E = E_0(1 - 1.9P + 0.9P^3) \]
Refractories Requirements

- Withstand high temperatures and sudden changes in temperature
- Withstand action of molten slag, glass, hot gases etc
- Withstand load at service conditions
- Withstand abrasive forces
- Conserve heat
- Have low coefficient of thermal expansion
- Will not contaminate the load (material with which it comes into contact with)

Phases in contact with refractories

- **Slag**: Mixture of acidic and basic inorganic oxides like SiO₂, P₂O₅, CaO, MgO, FeO, etc.; temperature varies from 1400°C to 1600°C.

- **Molten steel**: Iron containing C, Si, Mn, P, S and different alloying elements like Cr, Ni, Nb, Mo, W, Mo etc.; temperature 1600°C

- **Gases**: CO, CO₂, N₂, Ar containing solid particles of Fe₂O₃, Fe₃O₄ etc.; temperature 1300°C to 1600°C.

Properties of Refractories

- **Melting point**
  - Temperature at which a ‘test pyramid’ (cone) fails to support its own weight

- **Size/shape**
  - Affects stability of furnace structure
  - Minimize space between construction joints

- **Bulk density**
  - Amount of refractory material within a volume (kg/m³)
  - High bulk density ⇒ high volume stability, heat capacity and resistance to slag penetration

**Melting points of some pure compounds used as refractory materials**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (pure sintered)</td>
<td>2800</td>
</tr>
<tr>
<td>CaO (limit)</td>
<td>2571</td>
</tr>
<tr>
<td>SiC pure</td>
<td>2248</td>
</tr>
<tr>
<td>MgO (90-95%)</td>
<td>2193</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2338</td>
</tr>
<tr>
<td>Al₂O₃ (pure sintered)</td>
<td>2050</td>
</tr>
<tr>
<td>Fireclay</td>
<td>1871</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1715</td>
</tr>
</tbody>
</table>
Properties of Refractories

- **Porosity**
  - Apparent porosity is the volume of open pores as % of total refractory volume
  - Low porosity => less penetration of molten material
  - A large number of small pores is generally preferred to a small number of large pores.

- **Cold crushing strength**
  - Resistance of refractory to crushing (transportation)
  - Indirect relevance to refractory performance

- **Creep at high temperature**
  - Deformation of refractory material under stress at given time and temperature

Properties of Refractories

- **Volume stability, expansion & shrinkage**
  - There can be permanent changes during refractory service life
    - E.g. chemical reaction producing a new material of different specific gravity
  - Occurs at high temperatures

- **Reversible thermal expansion**
  - Phase transformations during heating and cooling

Classification of Refractories

- Refractories can be classified based on **chemical composition** and **physical form**

- Chemical composition is based on reactions to the type of slags
  1. Acid refractories
  2. Basic refractories
  3. Neutral refractories

Properties of Refractories

- **Pyrometric cones**
  - Used in ceramic industries to test ‘refractoriness’ of refractory bricks
  - Each cone is mix of oxides that melt at specific narrow temperature range

- **Pyrometric Cone Equivalent (PCE)**
  - Temperature at which the refractory brick and the cone bend
  - Refractory cannot be used above this temp
  - Refractoriness under load (RUL) more important

Properties of Refractories

- **Thermal conductivity**
  - Depends on chemical and mineralogical compositions and silica content
  - Increases with rising temperature

- **High thermal conductivity desirable??**
  - Heat transfer through brickwork required
    - E.g. recuperators, regenerators

- **Low thermal conductivity desirable??**
  - Heat conservation required (insulating refractories)
    - E.g. heat treatment furnaces
  - Additional insulation conserves heat but increases the hot face temperature and hence a better quality refractory is required

Acid Refractories

- **Uses: under acidic conditions**
  - They are based on SiO₂ and lie on the line between SiO₂ and Al₂O₃,
  - The more Al₂O₃ the material contains the more neutral the material becomes.

- **Examples:** fireclay, quartz, silica, aluminosilicate
SiO$_2$-Al$_2$O$_3$  

Basic Refractories  
- Uses: under alkaline conditions  
- They are based on magnesia (MgO), lime (CaO) and Cr$_2$O$_3$  
- High bulk density, high melting point and good resistance to chemical attack.  
- Examples: magnesite, chrome-magnesite, dolomite

Neutral Refractories  
- Uses: under either acidic or alkaline conditions  
- Examples: Carbon (most inert), Alumina, Mullite

Special Refractories  
- Silicon carbide, cermets and SiAlON are some examples of special refractory.  
- They are used for special applications.

Classification of Refractories  
- Physical form can be grouped into two:  
  1. Shaped refractories (refractory bricks)  
  2. Unshaped refractories (monolithic refractories)

Shaped Refractories  
- They have fixed shaped (e.g. bricks)  
  - standard shapes  
  - special shapes  
- They are machine-pressed with high uniformity in properties  
- Special shapes are most often hand-molded and are expected to exhibit slight variations in properties.
Unshaped Refractories

- They are without definite form and are only given shape upon application.
- It forms jointless lining and are known as monolithic refractories.
- Types of monolithic refractories:
  - Plastic refractories (ramming mixes), castables refractories, gunning mixes, fettling mixes and mortars

Monolithic Refractories

Castable refractories
- Consists of mixtures of coarse and fine refractory grains together with a bonding agent which is normally based on high alumina cement (HAC)
- Upon heating, binder transforms to form ceramic bond

Plastic refractories
- Mixtures prepared in stiff plastic condition
- Refractories delivered in blocks wrapped in polyethylene
- Blocks sliced into pieces, rammed into place with a rammer

Advantages
- Elimination of joints
- Faster application
- Heat savings
- Better spalling resistance
- Volume stability
- Easy to transport, handle, install
- Reduced downtime for repairs

Manufacture of Refractories

1. Crushing
2. Grinding – < 200 microns
3. Screening – e.g. settling, magnetic separation, chemical methods
4. Storage
5. Mixing
6. Moulding
7. Drying
8. Firing

Fireclay Bricks

- Common in industry: materials available and inexpensive
- Consist of 25 to 45% Al₂O₃ and 50- 80% SiO₂.
- Application areas
  - Iron and steel industry, non-ferrous metallurgy, glass industry, pottery kilns, cement industry
Classification of Fireclay Bricks

<table>
<thead>
<tr>
<th>Brick</th>
<th>%SiO₂</th>
<th>%Al₂O₃</th>
<th>Other constituents</th>
<th>PCE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super duty</td>
<td>49-53</td>
<td>40-44</td>
<td>5-7</td>
<td>1746-1760</td>
</tr>
<tr>
<td>High duty</td>
<td>50-80</td>
<td>35-40</td>
<td>5-9</td>
<td>1690-1746</td>
</tr>
<tr>
<td>Medium duty</td>
<td>60-70</td>
<td>26-36</td>
<td>5-9</td>
<td>1635-1690</td>
</tr>
<tr>
<td>Low duty</td>
<td>60-70</td>
<td>23-33</td>
<td>6-10</td>
<td>1521-1593</td>
</tr>
</tbody>
</table>

High Alumina Refractories

- Al₂O₃ varies from 45 to 95%.
- Commonly used refractory mullite (70 – 85% Al₂O₃).
- High alumina => high refractoriness

- Uses: BF, cement and lime rotary kilns, electric arc furnace roofs, ladle, glass making furnaces

Insulating Materials

- Material with low heat conductivity: keeps furnace surface temperature low.
- Achieved by introduction of a high degree of porosity.
- How?

Selecting the Right Refractory

Selection criteria

- Type of furnace
- Type of metal charge
- Presence of slag
- Area of application
- Working temperatures
- Extent of abrasion and impact
- Structural load of furnace
- Stress due to temp gradient & fluctuations
- Chemical compatibility
- Heat transfer & fuel conservation
- Costs

Corrosion of Refractories

- Refractories are used in many cases within high temperature corrosive environment.
- Changes in the state of the environment (as “redox” conditions or oxygen “activity”) influence the chemical reactions
- Along with chemical reactions during corrosion, physical changes occur that may be accelerated by the corrosion process.

Corrosion of Refractories

A refractory wear by loss of thickness and mass from the exposed face of the refractory as a consequence of chemical attack by a corroding fluid in a process in which the refractory and the corroding fluid react approaching chemical equilibrium in the zone of contact between the refractory and the fluid

1. Phenomenological approach – chemical and physical process
2. Use of equilibrium phase diagram
**First Fundamental Principle on Refractory and Slag Compatibility**

- “Acid” refractories tend to resist “acid” slags better than “basic” slags.
- “Basic” refractories tend to resist “basic” slags better than “acid” slags.

Acidity and Basicity in Solution Chemistry at RT

Acidity and Basicity in Corrosion Chemistry at ET

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**Second Fundamental Principle on Porosity and Corrosion Rates**

- Most refractories contain voids or porosity.
  - Porosity may be open or closed
- No porosity => corrosion reaction limited only to the **hot face**
- Porosity causes the corrosive media to penetrate the refractory causing destructive reactions behind the hot face.
- Slag corrosion rates increase linearly with the percentage of apparent porosity within the refractory

**Implications in ceramic processing??**

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**Third Fundamental Principle on Reactions and Temperature Gradients**

- Very steep temperature gradient => very little penetration of slag
  - corrosion reactions restricted to the slag/refractory interface.
- Steep gradients are seen in thin-wall refractory linings
  - E.g. boilers

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**Summary**

- Slag corrosion by liquids occurs whenever a threshold temperature is exceeded which is usually when melting occurs between the refractory and the slag.
- Corrosion results in solution of refractory constituents in the liquid phase resulting in loss of thickness of the refractory lining.
- The rate of corrosion is dependent on the chemical environment and on the hot face temperature of the refractory.

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**Summary**

- Corrosion is primarily a chemical process, and the potential for corrosion can be estimated by reference to phase equilibrium diagrams.
- These diagrams can allow prediction of the “threshold temperature” for liquid formation.
- Microscopic techniques allow identification of particular corrosion reactions.