From Ceramics to Ceramic Steel: Genesis

Udita S Maller, Deepa Natesan Thangaraj, Sudhakar Maller

ABSTRACT

Ceramics were introduced in dentistry since the 16th century as dental porcelain, primarily for the manufacture of porcelain teeth. Improved technology saw porcelain jacket crowns, metal ceramic systems with better bonding techniques of different alloys to porcelain, bonded foil systems and then the introduction of alumina and other oxides, such as zirconia to strengthen ceramics. Superior processing methods and sintering technologies have lead to CAD/CAM ceramics and the all ceramic systems. This article provides an overview of the different methods of strengthening ceramics for a better understanding of the mechanisms involved, including that of the support system.

Keywords: Ceramic, Alumina, Zirconia, Bonding, Crack propagation, Dispersion, Sintering.

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INTRODUCTION

Dental ceramics are nonmetallic inorganic structures primarily containing compounds of oxygen with one or more metallic or semimetallic elements like Al, Si, Ca, Li, Na, K, Mg, P, Ti, Zr, etc. They are glassy in nature and different crystalline phases are used as reinforcing agents in all ceramics. Ceramics are grossly grouped into three types: Silica-based, aluminum oxide-based and zirconium oxide-based ceramics. Ceramics can also be classified according to their composition, processing methods and uses (Tables 1 to 3). Substructures could be metal, as in metal ceramics or high strength alumina or zirconia as in all-ceramics.

Silica-based ceramics, such as feldspathic porcelain and glass ceramics are used to veneer metal frameworks due to their excellent esthetic property, but they have limited flexural strength and are very brittle. The typical network of ceramics is as shown in Figure 1.

Addition of crystalline phases, such as leucite and lithium disilicate will increase the flexural and compressive strength of these feldspathic porcelains. One method of strengthening the ceramics is by altering the composition of traditional ceramics which has given us aluminum oxide-based ceramics and zirconium oxide-based ceramics.

The aluminum oxide ceramics include ceramics with an increased alumina content where aluminum oxide forms a part of the glassy matrix such as glass infiltrated aluminum oxide, densely sintered high purity aluminum oxide ceramic and glass infiltrated spinel ceramics. Addition of alumina (Fig. 2) in silicate.

Table 1: Classification of ceramics

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing methods</th>
<th>Firing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure alumina, pure zirconia, silica glass, leucite-based glass ceramics,</td>
<td>Sintering, partial sintering and glass infiltration, heat pressing, slip casting,</td>
<td>High fusing (1,300°C), medium fusing (1,101-1,300°C), low fusing (850-1,000°C),</td>
</tr>
<tr>
<td>lithia-based glass ceramics.</td>
<td>CAD/CAM and copy milling.</td>
<td>ultra low fusing (below 850°C).</td>
</tr>
<tr>
<td>Substructure material</td>
<td>Feldspathic porcelain, cast metal, swaged metal, glass ceramics, CAD/CAM, sintered</td>
<td>Amorphous glass, crystalline porcelain, hydrogen containing glass, partially</td>
</tr>
<tr>
<td>Microstructure</td>
<td>ceramic core.</td>
<td>crystalized porcelain and apatite ceramic.</td>
</tr>
<tr>
<td>Translucency</td>
<td>Opaque, translucent, transparent.</td>
<td>Anterior and posterior crowns, veneers, posts and cores, FPDs, stain ceramic, glaze</td>
</tr>
<tr>
<td>Indications</td>
<td></td>
<td>ceramic, metal ceramic, inlays, onlays and implants.</td>
</tr>
</tbody>
</table>

Table 2: Based on the core

<table>
<thead>
<tr>
<th>Ceramic block</th>
<th>Ceramic type</th>
<th>Ceramic veneer</th>
<th>Indications</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-ceram spinell</td>
<td>MgO-Al2O3</td>
<td>Aluminous porcelain</td>
<td>Anterior crowns</td>
</tr>
<tr>
<td>In-ceram alumina</td>
<td>Al2O3</td>
<td>Aluminous porcelain</td>
<td>Anterior, posterior crowns and FPDs</td>
</tr>
<tr>
<td>In-ceram zirconia</td>
<td>Al2O3 or ZrO2</td>
<td>Aluminous porcelain</td>
<td>Posterior crowns and FPDs</td>
</tr>
</tbody>
</table>

Fig. 1: Molecular structure of silica

Fig. 2: Molecular structure of silica
During firing of alumina, a welding occurs at points of contact between adjacent oxide particles (partial fusion). As the migration of atoms takes place there is a movement at grain boundaries which reduces porosities. During sintering a shift in the grain boundaries occurs which results in the formation of a closely interlocked crystalline structure of considerable strength and improved physical properties.  

Causes of Weakening in Crystalline Ceramics

1. Voids occur between the crystals which allow passage of gases to permeate the material and also cause the crystals to slide past one another.  
2. If one crystal is out of line or twisted as compared to its neighbor, the bonds between them may be stretched or distorted causing weakness at the boundaries.  
3. Ions with the same charge, either positive or negative may cause electrostatic repulsion leading to stresses in that region and finally cracks may occur.  

Crack Propagation

Porcelains (being brittle) are solid materials that have a very small work of fracture (i.e. require very less energy to break it). They will tolerate cracks much deeper than 0.025 mm but when the crack propagates its tip radius remains the same throughout the length and very little force is required to propagate the stress. Once porcelain is under tension, the crack propagates and a complete fracture occurs suddenly. Surface porosity, abrasion, grinding and thermal stresses are methods to introduce a flaw system.  

Methods of Strengthening Ceramics

In order to strengthen porcelain, it is essential that mechanisms should exist to prevent crack propagation under low tensile stresses. Porcelain jacket crowns would fracture where tensile stresses occur on the fit surface/internal surface. Now the inner surfaces can be reinforced with metal (cast or swaged, electroformed system) or a higher strength core ceramic. Alternatively the surface layer can also be treated. The approaches in strengthening ceramics are as follows:

1. Enamelling of metals  
2. Dispersion strengthening of glasses  
3. Enamelling of high strength crystalline ceramics  
4. Controlled crystallization of glasses  
5. Production of prestressed surface layers in dental porcelain via ion exchange, thermal tempering.
Enamelling of Metals

Metal ceramic systems (Fig. 3) were developed to reinforce the ceramics. They are:
1. Noble metal alloy systems (high gold, low gold, gold free).
2. Base metal alloy systems (NiCr,Ti) (Table 4).

Earlier methods employed to enhance bonding with precious metals were coating with tin oxide. Platinum copings were electroplated with a layer of tin oxide to which aluminous porcelain was attached. Bonded platinum foil acts as an inner skin on the fit surface which is crack free. It reduces surface and subsurface porosity in the porcelain and has the high strength of aluminous porcelain.

- Twin foil technique involves laying down of two platinum foils in close opposition to each other. One foil provides a matrix for the bonding of the porcelain which is removed after baking. The outer foil forms an inner skin to the crown. It is tin plated and oxidized to achieve a strong chemical bond with the aluminous core porcelain.31,33,34
- Noble metal foils are adapted, swaged and brazed on to dies and then bonded to feldspathic porcelain (e.g. Renaissance, sunrise, flexobond and plati-deck), better electroplating machines (ceramic plating) and other new foil systems.1,35

The advantages here include reduction of metal and labor cost, a porcelain butt fit, avoidance of metal collar, less stresses at the porcelain metal interface, reduction of internal microcracks and subsurface porosity, so lesser sites of crack propagation.

Dispersion Strengthening of Glasses

Glassy materials can be strengthened by dispersion strengthening (Fig. 4), i.e. dispersing ceramic crystals of high strength and elasticity in the glass matrix. The reinforcing crystals may be quartz or alumina. Limiting factors while choosing reinforcing crystals are fusion temperature, coefficient of thermal expansion, bonding properties with dental porcelain, mechanical strength and resistance to thermal shock during rapid firing cycles.12

| Table 4: Requisites for proper bonding of the alloy to the porcelain |
|-----------------|------------------|
| Alloy | Ceramic |
| 1. High melting temperature (100°C more than the firing temperature of ceramics) | Low fusing temperature |
| 2. Adequate stiffness, strength and sag resistance of the alloy | Wets the alloy readily |
| 3. Compatible coefficient of thermal expansion (alloy to be slightly higher than the ceramic) | Good interaction of the ceramics with metal oxides on the metal surface |

1. Metal-ceramic interface
2. Dispersion strengthening
a. Quartz (10-15%) was used earlier, however, quartz undergoes changes during heating (inversion of quartz crystals) and has a high coefficient of thermal expansion and the strengthening effect of quartz is poor.

b. Alumina reinforcement: When alumina crystals are dispersed in a glass matrix and heated and cooled, different stress patterns are observed due to the differences in thermal expansion between glass and alumina. If the thermal expansion of the glass matrix matches that of alumina, sudden volume changes occur and strength may not be affected. Alumina crystals are available in two forms:
1. Calcined (alpha type)
2. Fused alumina (high purity alumina 99.6%)

c. Aluminous porcelain: A type is core porcelain and it contains 50% fused alumina.

In comparison to glass ceramics, alumina reinforced core ceramics bond better chemically to the glass and disrupt crack propagation by forcing the fracture path to pass around a crystal. Long firing or sintering schedules do not cause harm as they are more resistant to pyroplastic flow and not subject to devitrification.

d. Alumina whiskers are also used as dispersion strengtheners of glass.

Hi-ceram and In-ceram (slip casting) also have higher alumina content but differ in processing methods. Ceramics fabricated by slip casting can have higher fracture resistance than those produced by powder condensation because the strengthening crystalline particles form a continuous network throughout the framework.

e. Magnesia core consists of 40 to 60% crystalline magnesia in a glass matrix.

Controlled Crystallization of Glasses

The property of controlled crystallization of glasses has been incorporated in glass ceramics also. Here high thermal shock resistance and improved strength property has been observed. Normally glass does not crystallize on cooling from a melt but it can be made to crystallize by adding a nucleating agent like titanium dioxide, lithia, zinc oxide, silica or metal phosphates. Though the glass is amber in color and glassy it becomes translucent and tooth like after crystallization or ceramming for 1 hour at 600°C. If silver is added as a nucleating agent, the glass ceramics after ceramming at different temperature rates become photosensitive and responsive to UV light, creating a polychromatic effect.

Production of Prestressed Surface Layers in Dental Porcelain

Ion Exchange (Chemical Tempering)

Ion exchange involves the principle of diffusion in a solid where atoms or ions move from a saturated surface to an unsaturated one. When sodium ions lying on the surface of dental alumino silicate glasses are exposed to surface contact with liquids containing metallic cations, sodium ions can get exchanged for certain metallic ions (Fig. 5). Dental porcelains with sufficient soda content (Na₂O) may be chemically treated in a potassium nitrate salt bath and the potassium ions will diffuse into the surface of the porcelain and be exchanged for some of the sodium ions. The larger potassium ions result in crowding of atoms at the surface of the porcelain and a prestressed surface layer is produced. This surface compression gives an increase in strength on the surface of porcelain, it is also very dependent upon time/temperature cycling.

Thermal Tempering

Rapid cooling or quenching of a surface of an object while it is still hot creates residual surface compressive stresses on the surface of the ceramics. As the core is hot and soft and still in its molten state it tends to shrink and tries to pull the outer surface which is rigid now. On solidification, residual tensile stresses are created on the inner core and residual compressive stresses on the outer surface. Hot glass phase ceramics are quenched in silicone oil or other special liquids.

Enamelling of High Strength Crystalline Ceramics

During firing some form of crystallization takes place in ceramics (sintered or high alumina), resulting in an
interlocking crystalline system which is better able to withstand high stresses than feldspathic porcelain. High alumina cores with aluminous porcelain veneers have been used in combination. These laminates are much stronger than regular porcelain, similar to metal ceramic systems. The bonding at the interface is chemical in nature and an ionic bond ensures no porosity as the wetting of the porcelain enamel on high alumina is good. Nowadays aluminous core ceramic is directly baked on a refractory die (flexural strength, 139 MPa; shear strength: 145 MPa).12,21

Other methods to improve strengthening are as follows:
- Good condensation techniques (powder condensation),9 programmed firing schedules, high pressure compaction,43 vacuum fired porcelain and better condensation in the wet stage which are all very essential to minimize shrinkage and avoid excessive air bubbles.
- If the surface is undisturbed, the strength of the glazed surface specimen is found to be higher.12,34
- Thermal stresses occurring during improper cooling can cause cracks and weaken the porcelain. Water (saliva) can act as a network modifier and weaken the structure.25
- Crack propagation can be prevented by crack tip blunting/transformation toughening, using alumina.44
- Proper design of the restoration minimizes stress concentrations.1,2

Recent Advances
Since, the discovery of transformation toughening capabilities of zirconia (Ceramic steel),11 its application in strengthening ceramics has taken place.15 Pure zirconia can exhibit a polymorphic phase transformation.

1. Monoclinic (P21/c) → from room temperature to heating to 1,170°C
2. Tetragonal (p42/nmc) → 1,170°C to 2,370°C
3. Cubic (fmmm) → above 2,370°C till the melting point.

On cooling from 950°C there is an increase in volume leading to a catastrophic failure. Pure zirconia is alloyed with stabilizing oxides, such as CaO, MgO, Y2O3 or CeO2 which allows the tetragonal structure to remain stable at room temperature, thus efficiently arresting the crack propagation and leading to high toughness.15,44,45

Three forms of zirconia-based ceramics systems are currently available.10

1. Yttrium cation doped tetragonal zirconia polycrystals (3Y-TZP).
2. Magnesium cation doped partially stabilized zirconia (Mg-PSZ).
3. Zirconia toughened alumina (ZTA).
1. 3Y-TZP usually contains 3 mol% Ytria (Y2O3) as a stabilizer. Flexural strength → 800 to 1,000 MPa. Fracture toughness → 6 to 8 MPa. Higher sintering temperature and longer sintering time lead to large grain sizes. Grain size is a critical factor in controlling strength during phase transformation. Processing methods is by:46,47
   - Soft machining of presintered blanks (CAD/CAM) followed by sintering at high temperature using specifically programmed furnaces (1,300°C-1,550°C) for 2 to 5 hours.
   - Hard machining of fully sintered blocks which are processed by hot isostatic pressing at temperature between 1,400 to 1,500°C under high pressure in an inert gas atmosphere. The blocks are then machined using a specifically designed milling system.
2. Mg-PSZ has not been successful due to presence of porosity associated with a large grain size (30-60 µm), poor phase stability and lower mechanical properties which induce wear. The microstructure consists of tetragonal precipitates within a cubic stabilized zirconia matrix. Percentage of MgO is around 8 to 10 mol%.10
3. ZTA zirconia is combined with an alumina matrix to form ZTA. Processing of this ceramic is by slip casting or machining. Flexural strength (slip cast method) → 630 ± 58 MPa, (machined) → 476 ± 50 MPa. The microstructure has large alumina grains together with clusters of small zirconia grains. Crack pattern is transangular for zirconium oxide and intragranular for aluminum oxide. Newly developed ZTA (bioceramics) has better mechanical properties because there is uniform dispersion of zirconia grains in an alumina matrix (sol gel processing).10

An advancing crack triggers the $t \rightarrow m$ transformation. This volume change creates microcracks in the alumina matrix which are surrounding by transformed particles, thus enhancing the fracture toughness by microcracking.10

Bonding of Ceramics with Tooth Structure
The goal of bonding ceramics to dentin/enamel using adhesive systems is to transfer functional stresses to the tooth, thus, strengthening the systems without necessarily improving the strength of the materials.3,34,48-50

CONCLUSION
An overview of the transition from porcelains to high strength ceramics and their usage has been described briefly. The various methods of strengthening ceramics with the introduction of zirconia in dentistry is also discussed with
Alumina/Zirconium Reinforced Ceramics

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Containing Ceramics</td>
<td></td>
</tr>
<tr>
<td>Feldspar ceramic</td>
<td>9.5% hydrofluoric acid for 2 to 2.5 minutes, 1 minute washing; silane application honeycomb bonding.</td>
</tr>
<tr>
<td>Leucite reinforced IPS Empress</td>
<td>9.5% hydrofluoric acid for 60 seconds, 1 minutes washing; silane application</td>
</tr>
<tr>
<td>Lithium disilicate IPS Empress II</td>
<td>9.5% hydrofluoric acid for 20 seconds, 1 minutes washing; silane application</td>
</tr>
</tbody>
</table>

its underlying chemistry for a better insight. Recent advances in bonding of ceramics to the tooth structure has also been elucidated. With the advent of digital designing and copy milling it shows that zirconia ceramics are rightly called ceramic steels now.

REFERENCES


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