Ceramics – Shadow of Enamel: an Overview

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Abstract
The demand for esthetics in dentistry is increasing day by day. Ceramics have been introduced to fulfil the requirements of the patient. With years, various modifications and improvements in ceramic in relation to properties and esthetics have been made. This review will put a light on the basic properties and esthetic ability of the ceramics so as to understand the basics of it.

Keywords: Alumina, Ceramics, Color, Metal

1 | INTRODUCTION

First ever man made materials are believed to be ceramics. They are among the earliest group of inorganic materials to be structurally modified by man. (1) The desire for the use of durable and esthetic material was always preferred and ceramics are the recent addition to it. (2) These are the most natural appearing replacement material for missing tooth and is available in different translucencies and shades so as to achieve good results. (3) However, certain drawbacks have been seen in ceramics in relation to manufacturing technique, mechanical properties and physical properties i.e. crack propagation, sintering shrinkage, restoration fracture, excessive brittleness, low tensile strength and wear of antagonists. (4)

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2 | DISCUSSION

Dentists today can choose from a variety of metal ceramic and all-ceramic materials in dentistry, available for fabrication of ceramic restorations. (5) This review outlines the developments in the evolution of dental ceramics over the last century and considers the state of the art in the several extended and innovative applications of dental ceramics.

Ceramics are compounds of metallic and non-metallic elements such as oxides, nitrides and silicates. ‘Ceramic, is an earthy material which silicate in nature nature and may be defined as: A combination of one or more metals, with a non-metallic element, usually oxygen (Gilman, 1987). (6)

In dentistry, three different types of porcelain compositions are used (depending on their applications) Table 1 (7, 8)

Structure (7, 9)
Ceramics can appear as either crystalline or amorphous solids (also called glasses). Thus, ceramics can be broadly classified as:

| Non-Crystalline Ceramics | Crystalline Ceramics |
|--------------------------|---------------------|
| (Amorphous solids or glasses) | E.g. Feldspathic porcelain | E.g. Aluminous porcelain |
| (Traditional porcelains) | (Reinforced porcelain) |
| High expansion porcelains | Low expansion porcelains |
| (For veneering metals & Magnesia core Ceramics) | (for veneering other ceramics) |

Composition (7, 8)
Ingredients used for various formulations of ceramics are:
1. Silica (Quartz or Flint) – Filler
2. Kaolin (China clay) – Binder
3. Feldspar – Basic glass former
4. Nepheline, Syenite & Leucite
5. Water – Important glass modifier
6. Fluxes – Glass modifiers
7. Color pigments
8. Opacifying agents
9. Stains and colour modifiers
10. Fluorescent agents
11. Glazes and Add-on porcelain
12. Alumina
13. Alternative Additives

Classification of ceramic materials
I. According to application (10)
- For porcelain teeth
- For Ceramo-metal restorations (Metal-Ceramic Systems)
- For All-ceramic restorations (All-Ceramic System)

II. Classes of Dental Ceramics for Fixed Prosthetics (6)
- By type: alumina, glass-infiltrated alumina, glass-infiltrated spinel, glass-ceramic, feldspathic porcelain, leucite-reinforced porcelain and aluminous porcelain
- By use: denture teeth, metal-ceramics, veneers, inlays, crowns and anterior bridges.
- By processing methods: sintering, casting or machining.
- By substructure material: cast metal, swaged metal, glass-ceramic, CAD-CAM porcelain or sintered ceramic core.

Various methods for fabricating ceramic restorations are: pressure molding and sintering, condensation and sintering, casting and ceraming, slip casting, sintering and glass-infiltration, computer controlled mining.

III. Dental porcelains are classified according to the firing temperatures (6, 11)
High fusing 1300°C (2072°F)

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Medium fusing 1101 – 1300°C (2013 – 2072°F)
Low fusing 850 – 1100°C (1962 – 2012°F)
Ultra-low fusing <850°C (1562°F)

IV. According To Use (6)
A) Metal – ceramic systems
   1. Cast metal systems : eg: Vita Metal Keramik (VMK 95)
   2. Non-Cast Metal Systems (Foil Crown Systems)
B) All – ceramic systems
V. Classified according to method of fabrication (12) (13)
   Conventional Powder & Slurry Ceramics: Using condensation & sintering.
   1) Alumina reinforced Porcelain e.g. : Hi-Ceram
   2) Magnesia reinforced Porcelain e.g. : Magnesia cores
   3) Leucite reinforced (High strength porcelain) e.g.: Optec HSP
   4) Zirconia whisker – fibre reinforced e.g.: Mirage II (Myron Int)
   5) Low fusing ceramics : (a) Hydrothermal LFC e.g. : Duceram LFC
      (b) Finesse (Ceramco Inc)

A) Mechanical e.g. : Celay
b) Automatic e.g.: Ceramatic II, DCP
   • Erosive techniques : a) Sono-erosion e.g: DFE, Erosonic
b) Spark-erosion e.g: DFE, Procera
   • Digital systems (CAD / CAM)

B) All – ceramic systems
VI. According to microstructure (12)
   1) Non-Crystalline Ceramics e.g.: Feldspathic porcelain
   2) Crystalline Ceramics e.g.: Aluminous porcelain, Glass-Ceramics

Manufacture & Dispensing
Pyrochemical reactions during manufacture of porcelain
When the ceramic raw materials are mixed together in a refractory crucible and heated to a temperature well above their ultimate maturing (fusion) temperature, a series of reactions occur.
After the water of crystallization is lost, the flux reacts with the outer layers of the grains of silica (filler), kaolin (binder) and feldspar (basic glass former) and partly combines them together.

**Manufacture of porcelain (14)**

- Feldspar fuses and further intermingles with kaolin & quartz
- Decompose to form a glass and a crystalline material (leucite)
- Molten glass begins to dissolve the kaolin and quartz
- Heating cause total dissolution of all components forming a homogenous glass
- Quenching
  - Frit (final glass product)
  - Ground to fine powder

Fritting is the process of blending, melting and quenching the glass components.

**Dispensing of dental porcelain (14)**

The conventional dental porcelain material may be generally supplied as a kit containing:

- Fine ceramic powders in different shades of enamel, dentin, core/opaque
- Special liquid or distilled water vehicle/medium for ceramic powder (binder)
- Stains and color modifiers
- Glazes and Add-on porcelains

**Steps in fabrication (6)**

Mixing ceramic powders of selected shades with distilled water or a special liquid (binder)

Various methods of fabricating ceramic restorations vary according to different formulations available: (15–18)

- Condensing and Sintering
- Pressure molding & Sintering
- Casting & Ceramming
- Slip casting, Sintering & Glass infiltration
- Milling (Machining) by mechanical and digital systems

For the fabrication of conventional porcelain restoration, there are following stages: Condensation – Sintering – Glazing – Cooling

**Condensation (Compaction)**

Porcelain powder is built into shape using a liquid binder to hold the particles together. The process of packing the particles together and removing the liquid binder is known as condensation. It is a 2-part process – Agitation of the particles & Removal of excess moisture. It is repetitious and the two components are carried out alternatively until no
further moisture comes to the surface. The movement of the particles is generated by a number of standard methods such as

- Vibration
- Spatulation
- Whipping

A working model; die of the prepared tooth is used for condensation of porcelain. A matrix is used to support the unfired porcelain both during condensation and firing.

**Binder**

It helps to hold the particles together, as the porcelain material is extremely fragile in the ‘green’ state.

Types of binder used:

- Distilled water – most commonly used, especially for dentin / enamel porcelain
- Propylene glycol – used in alumina core build-up
- Alcohol or formaldehyde based liquids – used for opaque core build up
- Proprietary modeling fluids
- Paint-on liquids for stain application.

**Sintering or Firing of Dental Porcelain**

It is defined as a process of heating closely packed particles to achieve inter particle bonding and sufficient diffusion to decrease the surface area or increase density of the structure. The partial fusion or compaction of glass is often referred to as sintering.

During the process of sintering, the individual particles are in contact (grain bounds) soften and fuse at sufficiently high temperature. This process relies on diffusion, which is greatly accelerated by elevated temperatures.

**Glaze**

Surface porcelain would undergo pyroplastic flow i.e. the matter surface would disappear and a smooth shiny surface would result (self-glace) if the porcelain was held in the furnace for a greater length of time at the end of high bisque stage.

Stages of maturity of porcelain has been described in (19)Table 2

**Bonding to porcelain (20, 21)**

The bonding of resins and ceramics introduced new restorative techniques and arouse considerable interest. Bonding composite resins (organic substance) to a porcelain surface (inorganic substrate) requires the modification of the porcelain surface to enhance the compatibility of resin and achieve high bond strength.

For the bonding between porcelain (inorganic substrate) and composite resin (organic substrate) the silane primer is essential.

**Silanization (20, 21)**

This refers to silane coating of an etched glass surface to increase its surface affinity to polymers. The silanes, often called Coupling agents react and bond to the silica crystals in the glass matrix through the ethoxy-, chloro-or amino- groups leaving the vinyl group to react and form a bond with the resin. When applied and subsequently dried, the resultant condensation forms a strong chemical bond.

**Repair of ceramic restorations (22–26)**

**Fracture is totally in porcelain (Simplest repair)**

- Fractured porcelain fragment
- When missing : Fabricate a piece of porcelain or porcelain veneer to replace missing portion / fractured area or direct composite bonding with shade matched composite to repair defect.
- When available – The fractured fragment and surface to be repaired are etched, silanated, coated with suitable bonding agent luted together with resin based luting agent.

**Preparation of porcelain surface for repair by bonding:**
1. Surface roughening by:
   - Diamond roughening
   - Air abrasion (50μ A12O3 - more effective)
   - Acid etching with 9.5%HF (Cerametch or Porcelain etch) for 2 to 4 min. depending on the product or 1.23% APF for 10 min.
2. Application of Silane coupling agent (e.g. Scotchprime) and allow to dry for 1 min.
3. Application of Bonding agent (e.g. Clearfil Porcelain Bond).

*Mixed (Porcelain/Metal) repair (More complicated)*

It involves exposed metal

Remaining porcelain:
   - If adequate to retain composite: Exposed metal and remaining porcelain is veneered with composite opaquer and subsequently with layers of shade matched composite (after preparation of both porcelain and metal surface for repair by bonding).
   - If inadequate to retain composite: Exposed metal surface is used as an adhesive substrate after preparation, for bonding with composite opaquer layer followed by shade matched composite.

*Preparation of metal surface for repair by bonding:*

1. Surface roughening: Microeteching (50μ A12O3) and Tin plating (noble metal)
2. Application of bonding agent capable of bonding to metal. E.g.: All Bond 2 (Bisco, Itasca, IL), C&B Metabond (Parkell, Farmingade, NY), Panavia 21 (J. Morita Co).

*Metal repair (Most difficult)*

It involves exposed metal with minimal or no porcelain

Two methods:
   - Veneering exposed metal surface with direct bonding of shade matched composite after preparation of exposed metal surface for bonding.
   - Fabrication of an overcasting: Small areas of remaining porcelain are removed if present. Crown/Pontic is reduced circumferentially (incisally, facially, and lingually) to provide room for both porcelain and metal, and provide margin for the laboratory technician. A thin metal overcasting with a fused porcelain veneer is fabricated. The metal surface of the repair area (substrate) and inner surface of the overcasting are air abraded (50μ A12O3) and bonded with suitable adhesive resin.

*Porcelain Repair Systems*

These porcelain-silane-acrylic adhesive systems are basically composite resins utilizing silane-coupling agents for clinical repair of porcelain (minor fractures) in sites. E.g. Fusion (George Taub Products, N. Jersy), Enamelite 500 (Lee Pharmaceuticals), Ultra Bond (Den-Mat Corp).

*Sandblasting (Grit blasting/ Microetching)*

Gritblasting refers to the process of air abrading a material with alumina particles (25-250μm) or glass beads at a specific pneumatic pressure. Microetching also refers to the use of sandblasting to prepare all types of surfaces for bonding restorations. This technique is used for:

   - Removal of investment material and cleaning the ceramic copings by abrading away surface contamination, which hinders good contact and bonding.
   - To increase the surface area by the creation of numerous ridges and crevices, thus providing more surface area for bonding.
   - Pretreatment and roughening of metal, resin and porcelain surfaces increases microscopic roughness for providing mechanically retentive surface for resins adhesive (to lock into crevices) to enhance bond strengths and repairs with various materials.

*Welding of ceramic materials*

Laser induced surface homogenization of dental ceramics can be used to remove local surface defects
and polishing marks without the need to reconstruct a complete construction firing.

The surface characteristics of Dental Ceramics following firing:

- Main vacuum firing: Irregular wave-like structures with dendrite crystal features.
- Furnace Gloss firing: Dendrite crystal structures are leveled off, but the crystal features are not removed.
- Laser Gloss firing: A full leveling of the surface is achieved.

Laser-induced modification of ceramic materials can be done by a process of heat induction using a suitable laser such as CO\textsubscript{2} laser (its emission wavelength is almost totally absorbed by ceramics). During focused CO\textsubscript{2} laser beam, a local glaze firing occurs on the ceramic surface.

\textit{Properties of dental ceramics Table 3}

\textbf{Color stability}

Ceramics are the most stable tooth colored materials. The metallic oxides used as colorants do not undergo any change in shade after firing is complete. Adherence of exogenous stains is resisted by the smooth glossy surface. In fact over a period of years, a porcelain restoration may develop a mismatch with adjacent teeth caused by changes in color of the adjacent natural teeth with age. (27)

\textbf{Brittleness}

It is the relative inability of a material to sustain plastic deformation before fracture of the material occurs. Ceramics are brittle at oral temperatures (5\textdegree{} to 55\textdegree{} C). In other words it fractures at or near its proportional limit. (28)

\textbf{Strength (29)}

1. Compressive strength : 350-550MPa
2. Tensile strength : 20-60MPa
3. Impact strength : Impact resistance, Elastic moduli and Tensile strength of ceramics are 40 GPa and 50 to 100 MPa respectively.

\textit{Abrasion Resistance (27)}

1. Natural tooth - 343 KHN
2. Porcelain - 460 KHN

When not glazed properly, it causes wearing of natural tooth and metal restorations.

\textit{Dimensional Stability}

Porcelain has a coefficient of thermal expansion, slightly less than that of the tooth structure. It does not exhibit microleakage and is comparable to a cemented metal restoration. It also does not imbibe or synergize water. (30)

\textit{Shrinkage}

1. Volumetric shrinkage - 35 – 45 \% 
2. Linear shrinkage - 11 – 14 \%

Shrinkage can be minimized by using proper condensation, lesser binder, build-up of restoration 1/3\textsuperscript{rd} larger than original size and firing in successive stages. (27)

\textbf{Degradability}

Porcelain is generally resistant to degradation in the oral environment and is susceptible to mechanical degradation by brittle fracture (chipping), and chemical degradation by fluoride attack. (31)

\textbf{Abrasion resistance and wear}

The hardest dental material which is commonly used is fused porcelain. Wear resistance by opposing restoration or natural teeth is better in fused porcelain than other dental materials. On the other hand, it will cause metal restorations and tooth structure to wear more rapidly; particularly when not adequately glazed or when glaze is removed during occlusal adjustment (should be smoothened by polishing). (27)

\textbf{Coefficient of thermal expansion (CTE)}

Coefficient of expansion of porcelain is slightly less than that of tooth structure. When different porcelain formulations are veneered together (all-ceramic) and over metal copings (metal – ceramics), coefficient of thermal expansion should be matched to prevent development of interfacial stresses leading to separation or fracture. (32)
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Strength properties of dental ceramics (33)

Dental ceramics are inherently fragile in tension. While the theoretical strength of porcelain is dependent upon the silicon – oxygen bond, the practical strength is 10 to 1000 times less than the nominal strengths.

In ceramics, microcracks are caused by:

- The condensation, melting and sintering process
- The high contact angle of ceramics on metal
- Differences in the coefficient of thermal expansion between alloy or core and veneers
- Grinding and abrasion
- Tensile stresses during manufacture, function and trauma

Method of strengthening ceramics (20)

- Enamel ing of metals - Metal-ceramic restoration
- Dispersion strengthening - Alminous porcelain, Slip-casting alumina (In-Ceram), Non-shrink ceramics (Cerestore).
- Crystalization of glasses - Dicor, Dicor plus
- Chemical toughening - Ion exchange
- Bonding to foils - Platinum foil, Foil Crown systems (Renaissance)

Methods of Strengthening brittle materials (6)

Development of residual compressive stresses

- Ion exchange (Chemical tempering)
- Thermal tempering
- Thermal compatibility (Thermal expansion coefficient mismatch)

Interruption of crack propagation

- Dispersion of crystalline phase
- Transformation toughening

Methods of designing components to minimize stress concentrations and tensile stresses:

Minimizing tensile stress Reducing stress raisers.

Esthetic Properties of Dental Ceramics

The principal reason for the choice of porcelain as a restorative material is its aesthetic qualities in matching the adjacent tooth structure in translucency, colour and chroma.

Color reproduction

Perfect color matching is extremely difficult, if not impossible. Correct color matching of natural teeth by the observer (clinician / ceramic technician) is dependent upon his subjective assessment and even with the use of the most modern types of shade guide and colour corrected lighting, he will experience difficulty in producing consistent shade matchings. (6)

Color production in natural teeth (27)

The structure of tooth influences its color. The bulk of tooth structure is comprised of 2 layers of calcified tissues; enamel and dentin, surrounding a central core or pulp chamber.

Variation of tooth color is also apparent in different regions of the tooth such as the incisal, middle and cervical/gingival third Table 4

Specimens of each shade (collectively called a shade guide) are provided for the dentist, who in turn, attempts to match the tooth colour as nearly as possible. Shade guides made of solid porcelain are used most often by dentists to describe a desired appearance of a natural tooth or ceramic prosthesis.

Colour reproductivity (6)

Without intrinsic and extrinsic colorants, dental porcelain match the color of its respective shade tab. To produce an acceptable match with corresponding shade guides, several factors play important
role which include porcelain type, batch, underly-
ing metal, manufacturers, thickness and perceptible
differences in color imparted by extrinsic colorants
before and after firing whereas varied firing tem-
peratures condensation techniques, repeated firings
and firing cycles do not affect the color of dental
porcelain.

Problems in reproducing natural teeth colors in ce-
eramics restorations:

- Duplication of enamel color and translucency
  is difficult as no material available as yet can
  produce the optical effect created by the closely
  packed prismatic nature of natural enamel.
- No biologically inert cements are available, that
  are transparent and which match the refractive
  indices of the tooth structure.
- Color assessment is a complex psycho-
  physiologic process, which is subject to
  numerous variables.

Side effect of dental ceramics (34–36)
Ceramics are inert; nevertheless they do pose certain
problems:

1 Side effects to Laboratory technician and dentist
   - Prolonged exposure to finely divided inorganic
dust in the atmosphere.
   - Silicosis affect workers exposed to silica dust.
   - Inhalations and prolonged exposures to sil-
ica are associated with malignancies especially
lung cancer.

2 Side effect to patients
   - Wear of opposing teeth due to abrasive nature of
porcelain (especially rough, unglazed surface).
   - Localized tissue changes – silica granulomas,
which occurs as a result of introduction of den-
tal ceramic particles into tissue (Schmidt and
Joachimi, 1987) – possibly a delayed hyper
sensitivity reaction due to fluorescing agents
(Radioactive uranium salts used earlier).
- Systemic effects – due to leaching of silica or
fluorescing agents

3 Effects of material deficiencies
   - Substantial tooth reduction for bulk, translu-
cency and esthetics.
   - Fracture of ceramic material – due to inherent
brittleness of ceramics.

Extended & innovative applications of ceramics in
dentistry (37, 38)

- Posterior esthetic restorations (Inlay & Onlays)
- All-Ceramic Post & Core systems (Zirconia
  ceramics)
- In Dental Implants:
  1. Ceramic coating for dental implants
  2. Implant supported ceramic restorations
- Ceramic Orthodontic Brackets
- Ceramics for Oral Mucosal Stimulation
- As fillers:
  1 Glass-ceramic inserts for composite resins,
  2 Silanized ceramic fibres in Ceromers (Eg:
Targis)
  3 Network or scaffold of ceramic fibers in
Polymeric Rigid
  4 Inorganic Matrix Material (PRIMM).
  5 Glass ionomer cements
  6 Investments
3 | SUMMARY

Ceramic materials have been used in dentistry for well over 200 years. They are the most biocompatible dental restorative materials, because they are chemically very stable. A desirable feature of ceramics is that their appearance can be customized to simulate the colour, translucency and fluorescence of natural teeth. A major problem with the use of ceramics as tooth replacement materials is that they exhibit a very low flexibility before fracture and also they exhibit large firing shrinkage.

4 | CONCLUSION

Presently there is no restorative system which can ideally replace the natural tooth structure. In the last few years, ceramic research has gained attention for restorative use. Ceramics will play an important role in restorative dentistry. Improvements in fracture resistance and wear properties enhance their restorative use.

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**TABLE 1: Types of porcelain compositions according to their applications**

| Denture | Tooth Porcelain | Feldspathic Porcelain | Aluminous porcelain |
|---------|-----------------|-----------------------|---------------------|
| Begins as a mixture of powders of feldspar, clay and quartz. (This is referred to as high fusing porcelain in some dental material text books) | Used for ceramo-metal restorations; begins as a mixture of powders of potassium feldspar and glass. It can also be used for fabricating porcelain veneers and inlays. | Used in PJS's. It is composed of mixture similar to that of feldspathic porcelain with increased amounts of aluminium oxide |

**TABLE 2: Stages of Maturity**

| Characteristic features | Low Bisque | Medium Bisque | High Bisque |
|-------------------------|------------|---------------|-------------|
| Porosity                | Grains of porcelain start to soften and coalesce at the contact points | Flow of glass grains increase and the residual entrapped furnace air become sphere shaped. | Firing shrinkage is complete, and has adequate strength, for any corrections by grinding prior to glazing. |
| Particle cohesion       | Incomplete | Considerable  | Complete    |
| Strength                | Minimal    | Majority or definite | Complete |
| Surface texture         | Weak & friable | Moderate | High |
| Colour & Translucency   | Opaque     | Less opaque and colour developed | Colour & translucency developed |

**TABLE 3: Properties of Dental Ceramics**

| Properties of ceramics          | Desirable properties | Principal deficiencies |
|---------------------------------|----------------------|-------------------------|
| Good esthetic qualities         | Britleness           |                         |
| High hardness                   | Low fracture toughness |                         |
| High compressive strength       | Low tensile strength-susceptible to fracture during placement, mastication and trauma |                         |
| Good chemical durability        |                       |                         |
| Excellent biocompatibility      |                       |                         |
### TABLE 4: Tooth color variation in different areas of a tooth

| Incisal third | Middle third | Cervical/gingival third |
|---------------|--------------|-------------------------|
| Enamel covering with little or no dentin underneath produces a wrap around effect which results in increased translucency in the incisal third and approximal areas. | This region consists predominantly of dentin, hence the overlying enamel takes on some of the dentinal hue (yellow-orange) which is modified by the translucent blue grey enamel resulting in a composite colour. | Enamel thins down towards the cervical line, hence the underlying dentinal hue results in a deep hue ranging from orange-yellow to often a distinct brown depending on the degree of calcification of dentin. |