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## Ceramics in Dentistry

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### 1. Introduction

It is quite usual in dentistry to adopt a material from engineers and adapt it to clinical conditions. A good example of such an instance is dental ceramics. In Dental science, ceramics are referred to as nonmetallic, inorganic structures primarily containing compounds of oxygen with one or more metallic or semi-metallic elements. They are usually sodium, potassium, calcium, magnesium, aluminum, silicon, phosphorus, zirconium & titanium.

As we peep into the dental history, a French dentist De Chemant patented the first porcelain tooth material in 1789. In 1808 Fonzi, an Italian dentist invented a "terrometallic" porcelain tooth that was held in place by a platinum pin or frame. Ash developed an improved version of the platinum tooth in 1837. Dr. Charles Land patented the first Ceramic crowns in 1903. Vita Zahnfabrik introduced the first commercial porcelain in 1963.

Structurally, dental ceramics contain a crystal phase and a glass phase based on the silica structure, characterized by a silica tetrahedra, containing central  $\text{Si}^{4+}$  ion with four  $\text{O}^-$  ions. It is not closely packed, having both covalent and ionic characteristics. The usual dental ceramic, is glassy in nature, with short range crystallinity. The only true crystalline ceramic used at present in restorative dentistry is Alumina ( $\text{Al}_2\text{O}_3$ ), which is one of the hardest and strongest oxides known. Ceramics composed of single element are rare. Diamond is a major ceramic of this type, hardest natural material used to cut tooth enamel. Ceramics are widely used in dentistry due to its dual role - strength and esthetics.

Basically the inorganic composition of teeth and bones are ceramics - Hydroxyapatite. Hence ceramics like hydroxyapatite, wollastonite etc are used as bone graft materials. They have an entire plethora of synthetic techniques like wet chemical, sol-gel, hydrothermal methods etc. Also they are added as bioactive filler particles to other inert materials like polymers or coated over metallic implants. These ceramics are collectively called as bioceramics. There are basically two kinds of bioceramics-inert (e.g. Alumina) and bioactive (hydroxyapatite). They can be resorbable (Tricalciumphosphate) or non-resorbable (Zirconia).

Dental cements are basically glasses. Initially, silicate cements were introduced. They constitute the first dental cement to use glass as its component. The cement powder contains a glass of silica, alumina and fluorides. The liquid, is an aqueous solution of phosphoric acid with buffer salts. Fluoride ions leached out from the set cements are responsible for the anti-cariogenic property. But silicates are discontinued due to low pH during setting reaction that affects the dental pulp.

In cements called glass ionomers, the glass forms the filler and acidic polymers form the matrix. The reaction that proceeds is usually an acid base reaction. Usually they are dispensed as powder containing glass powder, and liquid containing an acid, say, polyacrylic acid. When they are mixed, the acid in liquid etches the glass and reacts with calcium and other ions forming salts and the cement sets to a hard mass. Cements are direct restorative materials - i.e. manipulated and placed onto teeth directly, unlike other restorations that are made outside and fixed to teeth, called indirect restorations. They are highly advantageous as they are quick to set, release fluoride leading to anti-cariogenic action, esthetic and chemically bond to tooth material.

The use of ceramics are encouraged by their biocompatibility, aesthetics, durability and easier customization. The specialty of ceramic teeth is the ability to mimic the natural tooth in colour and translucency along with strength. Ceramics have excellent intraoral stability and wear resistance adding to their durability.

Dental ceramics, since introduction have undergone numerous modifications in terms of chemistry. Ceramics have been able to give heed to the ever changing needs in dentistry. To delve deep into the relevance of ceramic in dentistry, one should understand the physics of forces acting in the oral cavity. The masticatory (chewing) force is the strongest force present here. Other minor forces include that of tongue and periodontal ligament, which do not relate to the use of ceramics in dentistry.

The masticatory force is generated outside oral cavity by basically strong muscles, that move the jaw, open it or close it. Closure of jaw produces two kinds of forces. It is predominantly compressive in nature. Frequently impact kind of force is also experienced. Hence a ceramic has to undergo cycles of these forces indefinitely, without fracture, to result in a successful restoration of lost teeth structures.

In order to have a complete idea of what ceramic means to dentistry, we need to look at the complete range of ceramics used in this discipline.

### 1.1 Classification of dental ceramics

Classification of ceramics in dentistry is apparently an impossible task due to vast improvements made in the compositions. Nevertheless, the table provided here gives a general idea, say a bird's eye view of ceramics in dentistry.

<b>Microstructural Classification</b>	<p>Category 1: Glass-based systems (mainly silica)</p> <p>Category 2: Glass-based systems (mainly silica) with fillers usually crystalline (typically leucite or a different high-fusing glass)</p> <p>a) Low-to-moderate leucite-containing feldspathic glass</p> <p>b) High-leucite (approx. 50%)-containing glass, glass-ceramics (Eg: IPS Empress)</p> <p>c) Lithium disilicate glass-ceramics (IPS e.max® pressable and machinable ceramics)</p> <p>Category 3: Crystalline-based systems with glass fillers (mainly alumina)</p> <p>Category 4: Polycrystalline solids (alumina and zirconia)</p>
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<b>Based on processing technique</b>	1) Powder/liquid glass-based systems 2) Pressable blocks of glass-based systems 3) CAD/CAM systems
<b>Based on Composition</b>	Silicates: These are characterized by amorphous glass phase, containing predominantly silica. Oxide ceramics: It is notable that only oxide ceramics are used in dentistry, since nonoxide ceramics are difficult to process. Oxide ceramics contain a principal crystalline phase like Alumina. Zirconia has very high fracture toughness. Glass ceramics: These are type of ceramics that contains a glass matrix phase & at least one crystal phase. Although classification of dental ceramics based on composition is not much of importance today, due to advances made, it is included for historic importance.
<b>Based on Type</b>	Feldspathic porcelain. Leucite - reinforced porcelain, Aluminous porcelain. Glass infiltrated alumina, Glass infiltrated zirconia. Glass ceramics.
<b>Based on firing temperature</b>	Ultra-low fusing < 850°C Low fusing 850°C - 1100°C Medium Fusing 1101°C - 1300°C High fusing >1300°C
<b>Based on sub-structure metal</b>	Cast Metal, Swaged metal, Glass ceramics. Sintered core ceramics and CAD-CAM porcelain. The various types of metals in metal ceramics include noble alloys like gold alloys, base metals like iron, indium & tin. Pure metals like commercially pure titanium, platinum, gold and palladium alloys and Base metal alloys (nickel, chromium).
<b>Based on reinforcing method</b>	Reinforced ceramic core systems Resin-bonded ceramics Metal-ceramics

Table 1. Classification of dental ceramics.

Material	wt %
Silica	~62
Alumina	~18
Boric oxide	~7
Potash (K <sub>2</sub> O)	~7
Soda (Na <sub>2</sub> O)	~4
Other oxides	~2

Table 2. Typical oxide composition of dental porcelain.

The classification based on microstructure will be dealt with in detail and an idea of classification by processing technique is added in this review. Other classifications are of academic interest.

Basically ceramics are used as indirect restorative materials such as crowns and bridges, Inlays/Onlays and dental implants. Recently ceramic braces are used in orthodontics.

## 1.2 Crowns and bridges

Crown is technically a “Cap” placed on a tooth to protect it from fracture or sensitivity. On the other hand a bridge is a fixed replacement of missing teeth, with support from adjacent teeth. Both of these function similarly on biological and biomechanical terms, hence discussed together. These are of either *Porcelain fused to metal (PFMs)* or *full ceramics*. In case of PFMs, a metal core is placed in the tooth surface and ceramic is built on it. This is done by initially preparing the metallic portion by conventional casting techniques. Then the ceramic powder is incrementally painted on it and sintered. This is followed by glazing. In case of full ceramics, the wax pattern is prepared for the crown, it is invested and mould space prepared by lost wax technique. The ceramic is fused and typically pressed into the mould space.

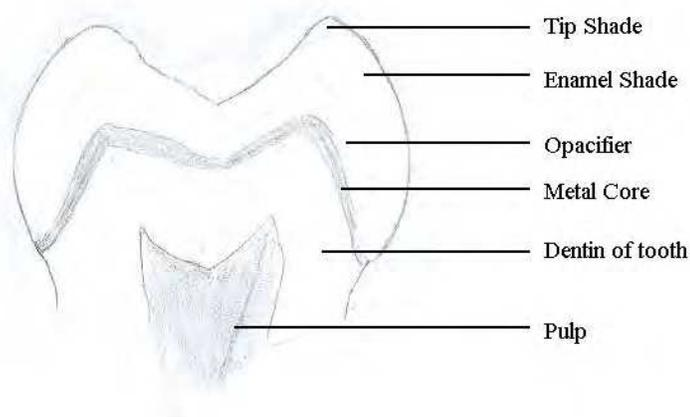


Fig. 1. Ceramic Crowns and their anatomy.



Fig. 2. Clinical picture of crown. Note pink ceramic used of gum recession.



Fig. 3. All Ceramic Crown.

Similarly, ceramic teeth are manufactured in various shades, shapes and sizes to be used in complete dentures. Also, in case of gum recession, in fixed prosthesis, pink coloured ceramics are placed in the lost gum region to make it look natural.

### 1.2.1 Category 1: Glass-based systems (mainly silica)

Chemical composition of these ceramics is based on silica network and potash feldspar ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ ) or soda feldspar ( $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ ) or both. Potassium and sodium feldspar are naturally occurring minerals composed primarily of Potash and soda. The most important property of feldspar is its tendency to form crystalline mineral leucite when melted.

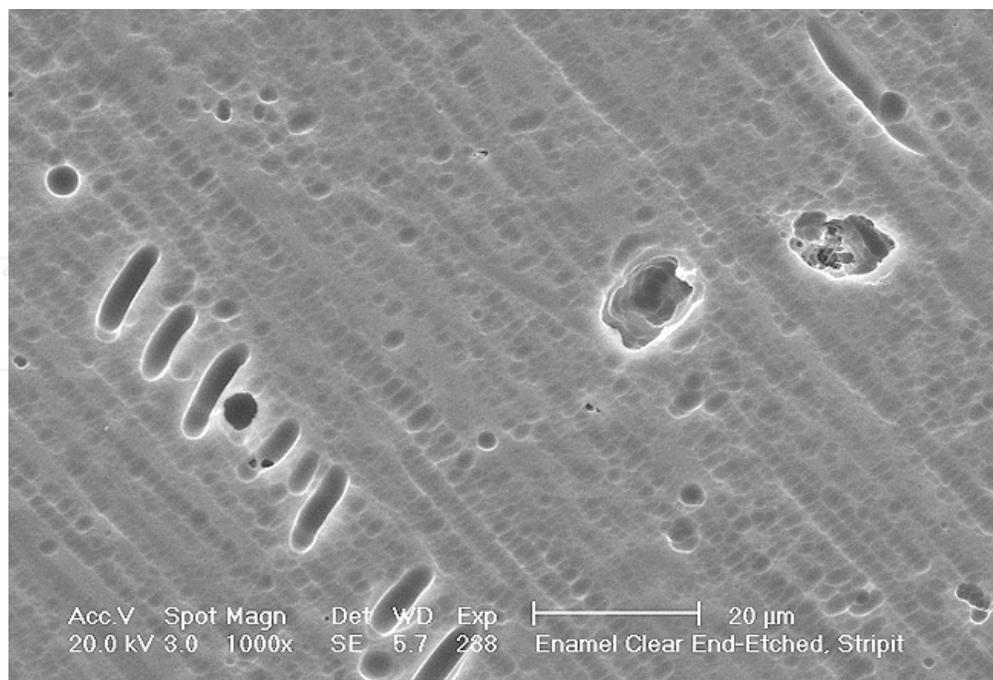


Fig. 4. Scanning electron micrograph of amorphous glass (Russel Giordano et al, 2010).

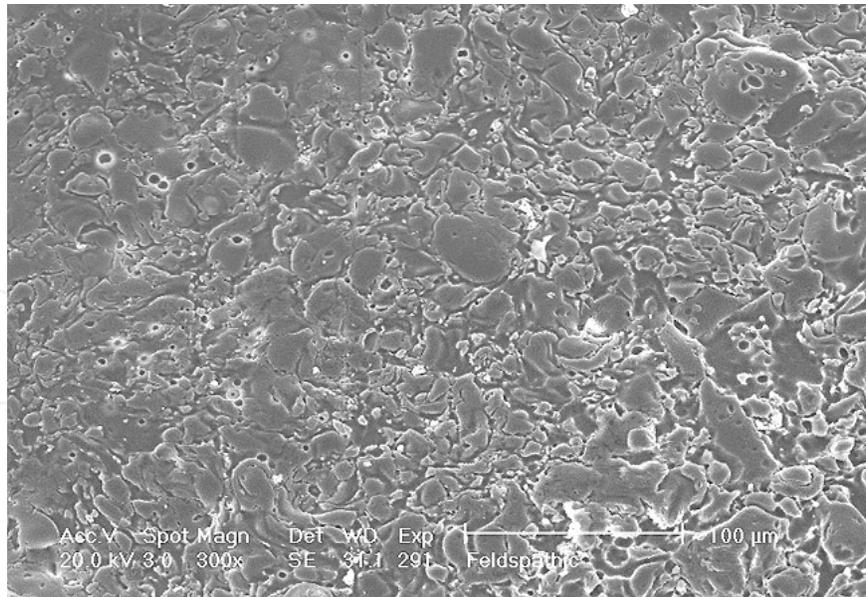


Fig. 5. SEM image of Feldspathic porcelain (Russel Giordano et al, 2010).

Mechanical properties say, flexural strength usually ranges from 60 MPa to 70 MPa. Hence, they can be used as veneer materials for metal or ceramic substructures, as well as for veneers, using either a refractory die technique or platinum foil.

Then, few other components like pigments, opacifiers and glasses are added to control fusion and sintering temperature, thermal properties and solubility. Glass modifiers like boric oxide can be added to reduce viscosity and softening temperature. Pigments are basically metallic oxides – say nickel oxide, manganese oxide, etc. Tin oxide is used for opaquing, iron oxide used for brown, copper oxide for green, titanium oxide for yellow, manganese oxide for purple, cobalt oxide for blue, nickel oxide for brown and rare earth oxides for simulating ultraviolet reflectance of natural teeth in ceramic.

The pigment oxides are also called as colour frits. These are added in appropriate proportions, dictated by intensity of colour required. Then the material is fired and fused to form glass, that is powdered again.



Fig. 6. Acrylic Denture with Ceramic teeth in lab processing stage.

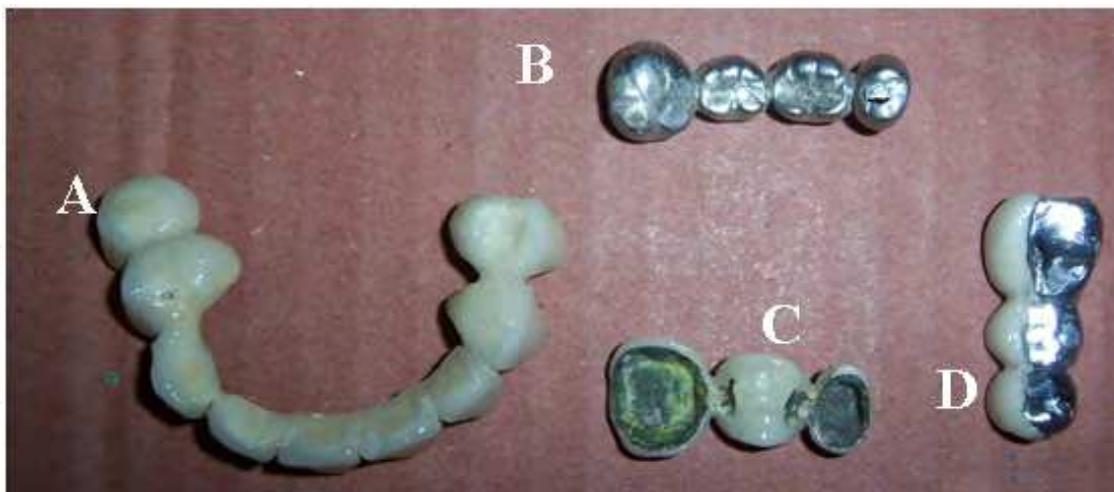


Fig. 7. Different kinds of fixed Dentures A) PFM Bridge, B) Full metal bridge, C) Inner side of PFM bridge, D) Metal bridge with ceramic facing.



Fig. 8. Porcelain teeth set for removable prosthesis.

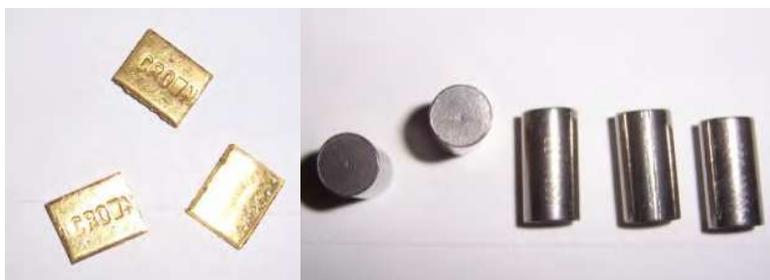


Fig. 9. Representative alloys for PFM cores.



Fig. 10. Commonly used dental shade guide showing corresponding numbers for shades.

These ceramics are strengthened by either development of residual compressive stresses within the surface or by interruption of crack propagation through the material. Residual compressive stresses are introduced by ion exchange and thermal tempering. Interruption of crack propagation is in turn achieved by dispersion of crystalline phases like partially stabilized Zirconia.

Glass ceramics made of a glass matrix phase and at least one crystal phase is produced by controlled crystallization of glass. It is available as castable machinable, pressable and infiltrated forms used in all-ceramic restorations. The first commercially available castable glass ceramic was developed by the Corning Glass Works (Dicor®) in 1950s. It paved way to dental ceramic system relying upon strengthening of glass with various forms of mica. ( $\text{SiO}_2.\text{K}_2\text{O}.\text{MgO}.\text{Al}_2\text{O}_3.\text{ZrO}_2$ , with the addition of some fluorides). Fluorides present in these ceramics are responsible for their nature-like fluorescence. Mould space is created by lost wax method and desired shape is formed. This process followed by coating with veneering porcelain. The noteworthy aspect of this ceramic is the *Chameleon effect* in which some part of color is picked up from adjacent teeth. Here, the ceraming process results in the nucleation and the growth of tetrasilicate mica crystals within the glass. The crystals are needle-like in shape and arrest the propagation of cracks. Mechanical property measurements suggest the flexural strength is in the range of 120–150MPa, may just be adequate for posterior crowns but is not sufficient for the construction of all-ceramic bridges. The passage of light through the material is affected by the crystal size and the difference in the refractive indices of the glass phase and the crystalline phase. If the crystals are smaller than the wavelength of visible light (0.4–0.7mm) the glass will appear transparent.

The refractive index of the small mica crystals is closely matched to that of the surrounding glass phase, such that the tendency for light to scatter is lower than the aluminous porcelains.

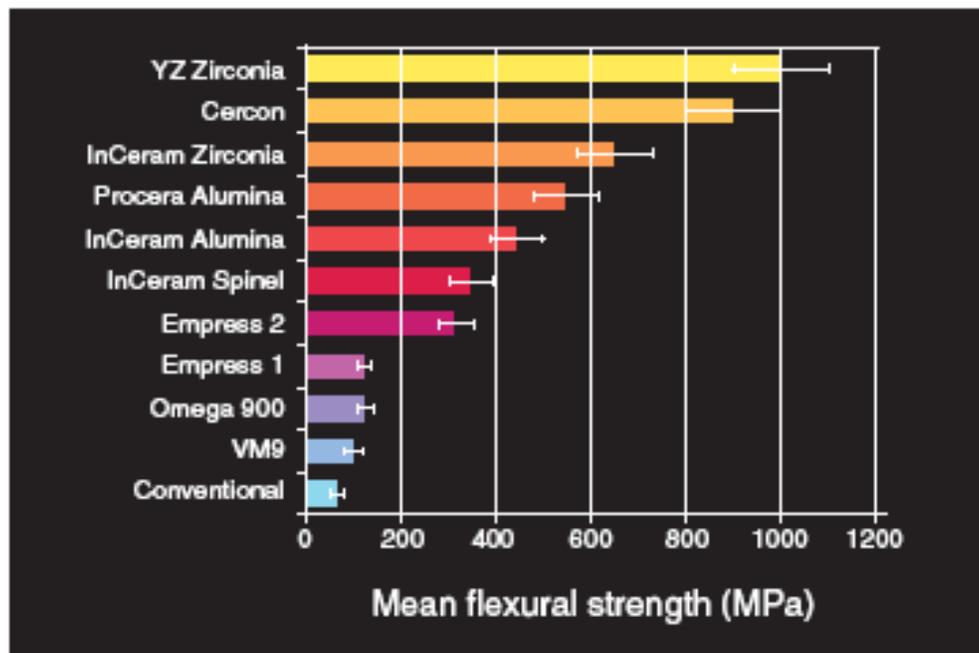


Fig. 11. Flexural strengths of various ceramics (McLaren EA et al, 2005).

The Machinable glass ceramic is another high quality product, which is crystallized during the manufacture and provided as CAD/CAM blanks or ingots. They provide better precision than castable glass ceramic, due to reduction of casting errors. They exhibit similar mechanical properties, to castable forms but are less translucent.

### 1.2.2 Category 2: Glass-based systems (mainly silica) with fillers usually crystalline (typically leucite or a different high-fusing glass)

This is a modification to category 1, in that varying amounts of other crystals are added or grown. The primary crystal types are either leucite, lithium disilicate, or fluorapatite.

Leucite has been widely used as a constituent of dental ceramics to modify the coefficient of thermal expansion. This is most important where the ceramic is to be fused or baked onto metal (Optec HSP). But in leucite reinforced ceramic system, IPS Empress, leucite has a different role. This material relies on an increased volume of fine leucite particles to increase flexural strength. Leucite is nothing but potassium aluminum silicate mineral with large coefficient of thermal expansion compared with glasses. The property of Feldspar to form Leucite is exploited in the manufacture of porcelains for metal bonding. Newer generations of materials have much finer leucite crystals (10  $\mu\text{m}$  to 20  $\mu\text{m}$ ) and even particle distribution throughout the glass. These materials are less abrasive and have much higher flexural strengths. In Figure 5, a scanning electron micrograph (SEM) of a typical feldspathic porcelain reveals a glass matrix surrounding leucite crystals. These materials are most commonly used as veneer porcelains for metal-ceramic restorations.

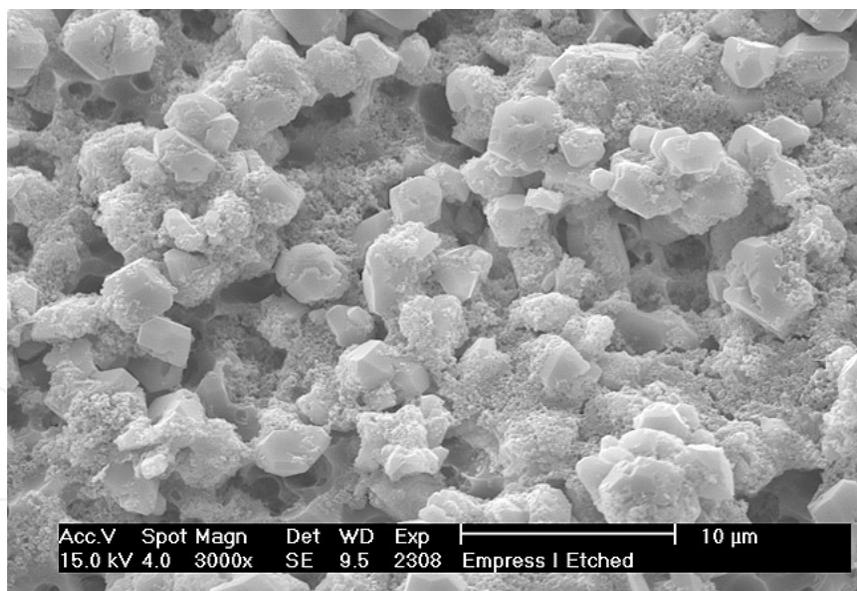


Fig. 12. SEM Image of IPS-Empress I - Etched (Russel Giordano et al, 2010).

In the sintering process (Fortress and Optec-HSP), slurry of the ceramic powder is applied to a refractory die (unlike Platinum foil coated die in the procedure of the porcelain jacket crown), dried and subsequently fired in a porcelain furnace. Multiple layers can be built up to develop characterisation. Great skill is required by the dental laboratory technician to get the best aesthetics and appropriate contour. However, the strength of Leucite ceramics are insufficient for all-ceramic restorations.

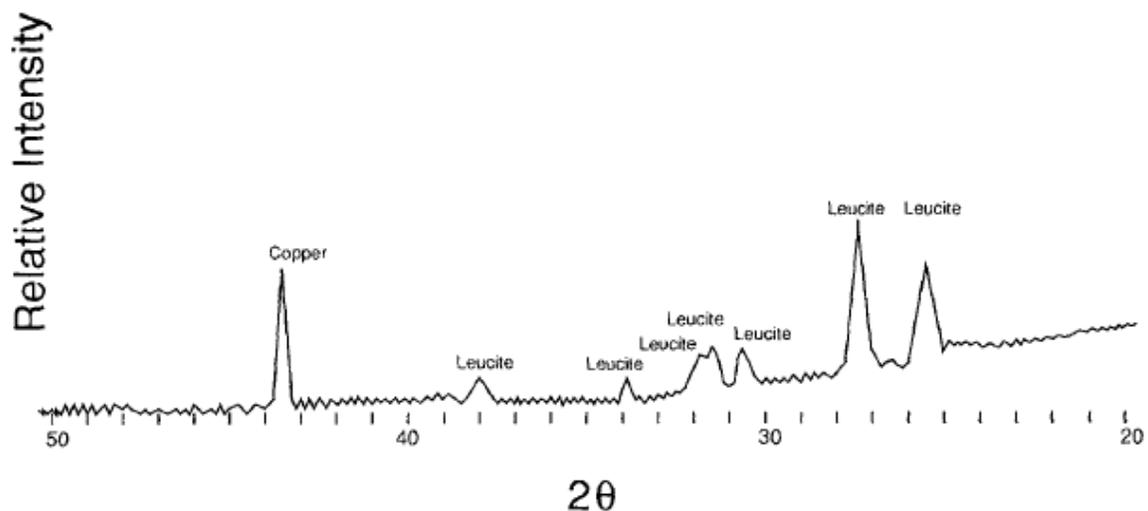


Fig. 13. XRD of Optec HSP (Peter W. PichC et al, 1994).

Lithium Disilicate and Apatite Glass Ceramics are based on  $\text{SiO}_2\text{-Li}_2\text{O}$ . (Empress II, Ivoclar-Vivadent). The crystalline phase, lithium disilicate ( $\text{Li}_2\text{Si}_2\text{O}_5$ ) makes up about 70% of the volume of the glass ceramic. Lithium disilicate has microstructure consisting of numerous small plate-like crystals that are interlocking and randomly oriented. This has a reinforcing effect on strength because, the needle-like crystals deflect cracks and arrest the propagation of cracks. A second crystalline phase, consisting of a lithium orthophosphate ( $\text{Li}_3\text{PO}_4$ ) of a much lower volume, is present. The mechanical properties of this glass ceramic are far superior to that of the leucite glass ceramic, with a flexural strength in the region of 350–450MPa and a fracture toughness approximately three times that of the leucite glass ceramic. There is a possibility for its use in all-ceramic systems. Also, processing is done by hot pressing technique.

For the alumina-based core systems feldspathic glasses can be used to provide the aesthetic surface layer, as their coefficients of expansion are closely matched. For the leucite glass ceramics the layering ceramic is identical to the core ceramic and so a mismatch in coefficient of expansion does not arise. However, this is not possible for lithium disilicate glass ceramic due to its higher coefficient of expansion. Here emerges a need for new compatible layering ceramic. This new layering ceramic is an apatite glass ceramic. The crystalline phase formed on ceraming is hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ ), which is the basic constituent of enamel. Thus, it represents a material that, at least in composition, is the closest match to enamel.

A veneer porcelain made of fluorapatite crystals in an aluminosilicate glass may be layered on the core to create the final morphology and shade of the restoration. The shape and volume of crystals increase the flexural strength to approximately 360 MPa, or about three times that of Empress. This material can be translucent even with the high crystalline content; this is due to the relatively low refractive index of the lithium-disilicate crystals. The material is translucent enough that it can be used for full-contour restorations or for the highest esthetics and can be veneered with special porcelain. Veneer porcelain consisting of fluorapatite crystals in an aluminosilicate glass may be layered on the core to create the final morphology and shade of the restoration. The fluorapatite (fluoride-containing calcium

phosphate,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) crystals contribute to the veneering porcelain's optical properties and CTE, so it matches the lithium-disilicate pressable or machinable material. Both the veneering and lithium-disilicate materials are etchable due to the glassy phase. Initial clinical data for single restorations are excellent with this material, especially if it is bonded. A material with similar properties and structure called 3G OPC is available as a pressable glass-ceramic from Pentron.

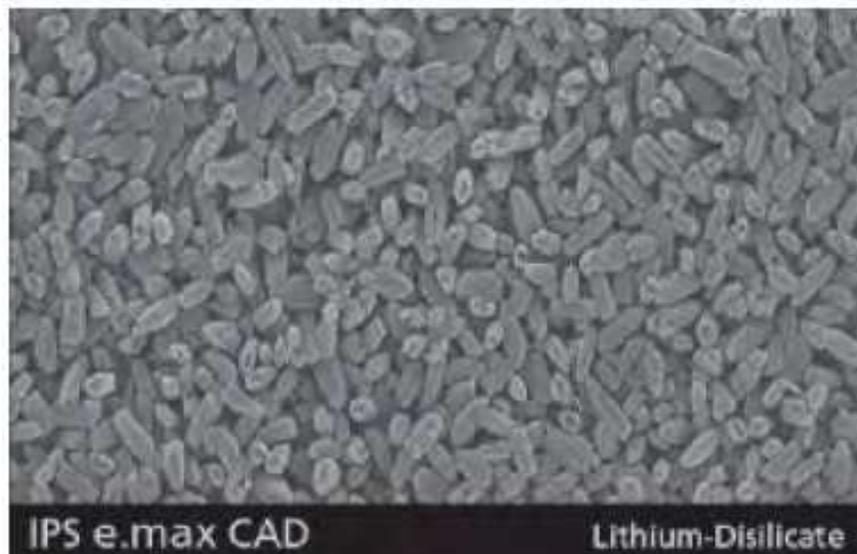


Fig. 14. SEM image of IPS e.max. CAD (McLaren Et al, 2009).

Advantage of PFM is its high strength in clinical service. It uses the sub-structure metal to withstand stresses. Thermal compatibility is good. Lower crack propagation leading to better fracture resistance. But, on the other side of the coin, there is inadequate structure for ceramics due to thickness of metal. This results in reduction of more tooth structure while preparing it for the restoration. Metallic hue can be visible in anterior teeth. Metal will be exposed in case of gingival recession. Patients with allergy to metals can react adversely. As we add more layers between materials, more number of fractures can occur. Bonding failures at porcelain-metal interface can occur due to oxidation of interface metallic surface.

It is good to have a glance into preparation of tooth structure for a full crown, to understand the pros and cons of ceramics. This procedure involves reduction of size of the tooth to accommodate the crown. Briefly, the aim of the procedure is to achieve good retention of restoration on crown, resistance of tooth to fracture, facilitate good chewing, protection of dental pulp while maintaining conservation of tooth structure. Unlike metals that are strong in thin sections, ceramics are strong only in bulk. Hence, when a particular region of crown is involved in mastication, more of tooth material is reduced at that particular region, called functional cusp bevel, to provide bulk to the ceramic. In such cases, amount of tooth reduction will be the sum of clearance for metal and ceramic in PFM and only for ceramic in all ceramic crowns. This definitely projects the tooth conservation in all-ceramic crowns.

In order to overcome the disadvantages of PFMs, and to achieve closer tooth colour match, All-Ceramics were developed. Natural teeth always permit diffuse transmission and regular

transmission. Prosthetic teeth must also possess a similar depth of translucency, which is realized in all-Ceramic restorations. Aluminous porcelain, Glass Ceramics, Castable, Machinable and Pressable Glass infiltrated, CAD-CAM and Cercon Zirconia system are few examples of all-ceramic systems.

### 1.2.3 Category 3: Crystalline-based systems with glass fillers

Aluminous porcelain contains a glass matrix phase and at least 35 vol% of Alumina. It is a commonly used core ceramic and has a thin platinum foil when employed with all ceramic restorations. Aluminous core is stronger than feldspathic porcelain.

Construction of the Procera AllCeram core involves die production from the impression, digitising the geometry of coping using computer software, and transferring this information to a laboratory in Stockholm. The coping is produced by a process, which involves sintering 99.5% pure alumina at 1600–1700°C such that it is completely densified. The coping is then returned to the dental laboratory for building in the crown's aesthetics using compatible feldspathic glasses. The flexural strength of the  $\text{Al}_2\text{O}_3$  core materials is in the region of 700MPa, and thus similar to that achieved with the In-Ceram Zirconia.

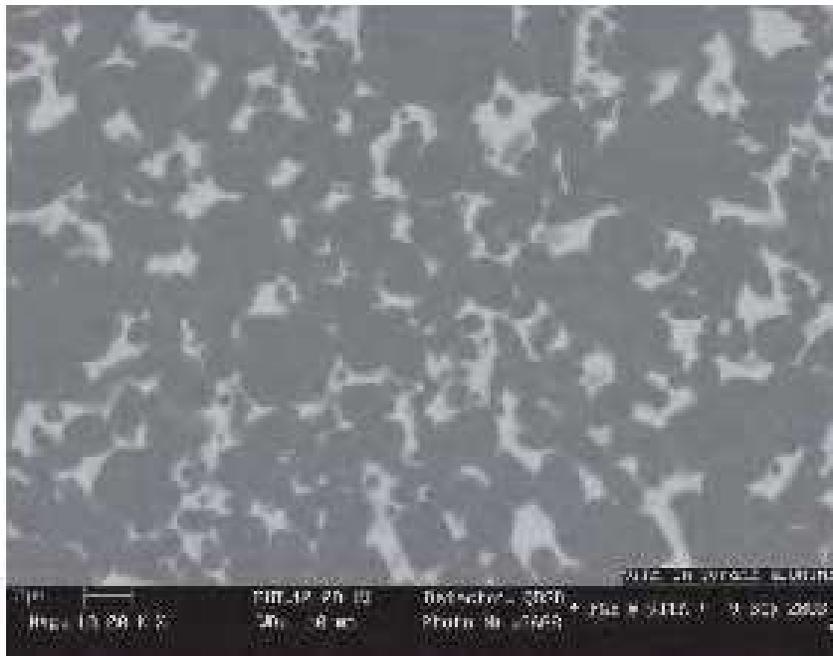


Fig. 15. High density of In-Ceram powder. (McLaren Et al 2009).

Pure alumina cores are produced by Techceram Ltd. In this system the impression can be sent to Techceram Ltd, who will produce a special die onto which the alumina core is deposited using a thermal gun-spray technique. This process produces an alumina core with a density of 80–90%, which is subsequently sintered at 1170°C to achieve optimum strength and translucency. The alumina coping is then returned to the dental laboratory, where the ceramist will develop the final contour and aesthetics using conventional feldspathic glasses. The clinical significance is the better translucency than glass alumina ceramics.

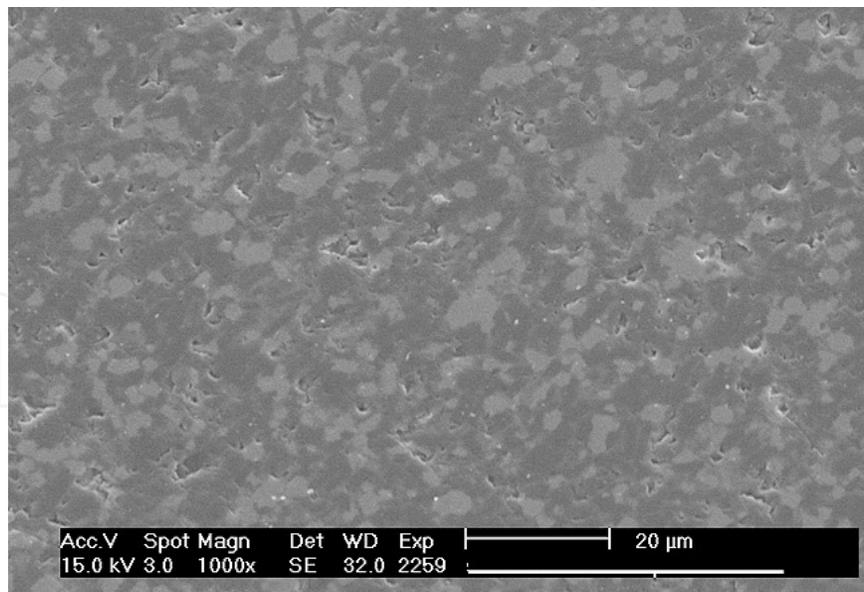


Fig. 16. SEM image of In-Ceram surface (Russel Giordano et al, 2010).

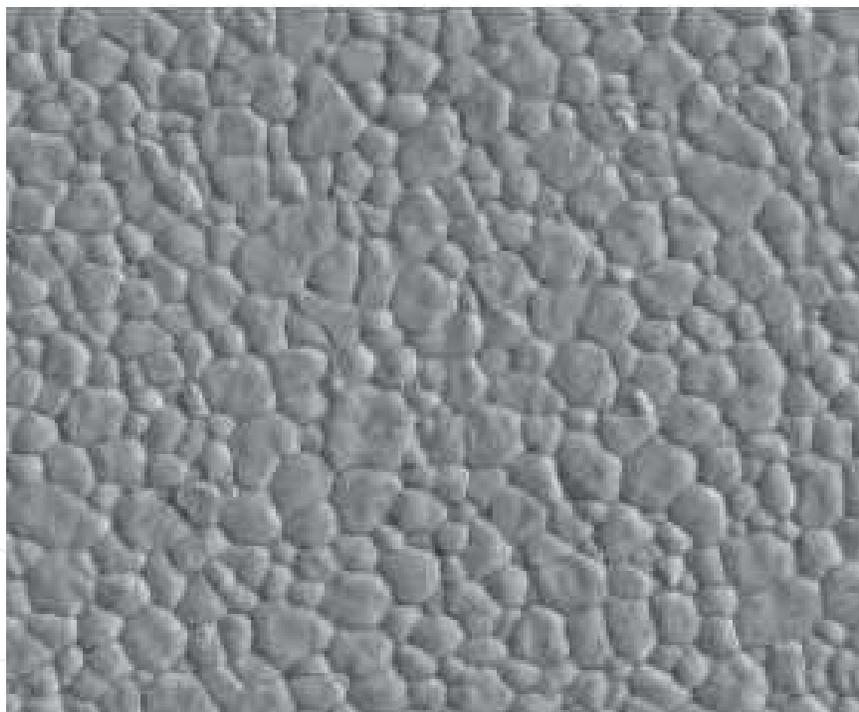


Fig. 17. SEM image of Sintered Zirconia (Lava) (McLaren Et al, 2009).

The use of modern Aluminous Crowns rose in the mid 1960's by McLean. The Nobel Biocare company (Sweden) introduced systems of pressing alumina onto a metal die, removing the pressed shape from the die and then sintering it. They are used to make cores to build up ceramic superstructures for dental implants (CeraOne®), and the second for conventional crowns (Procera®). Here, there is no glassy phase present between the particles. Feldspathic veneering porcelains are then fired onto this core to provide the necessary colour and form for the final restoration.

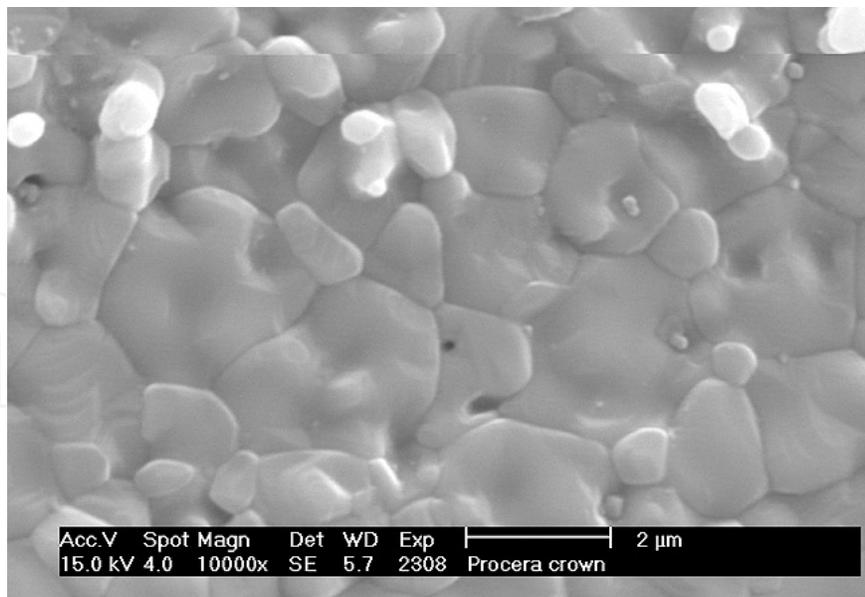


Fig. 18. SEM Image of Procera Crown (Russel Giordano et al, 2010).

The Pressable glass ceramics (IPS Empress 1 & 2) involve pressure molding in the manufacture. Heated ceramic ingot is pressed through a heated tube into a mold, where the ceramic form cools and hardens to the shape of the mold, which is later recovered after cooling. Hot pressing usually occurs over a 45mins at a high temperature to produce the ceramic sub-structure. Then it is stained, glazed or coated by veneering porcelain, according to esthetic needs, which results in translucent ceramic core, moderately high flexural strength, excellent fit & excellent esthetics.

The 1980s witnessed the development of slip casting system using fine grained alumina. The cast alumina was initially sintered and then infiltrated with a Lanthana based glass. Onto this alumina core, a feldspathic ceramic could be baked to provide form, function and esthetics to the crown. Glass infiltrated ceramic is used as one of the 3 core ceramics namely, In-Ceram Spinell, In-Ceram Alumina and In-Ceram Zirconia. They use the technique of slip-cast on a porous refractory die and heated in a furnace to produce a partially sintered coping or framework which is infiltrated with glass at 1100°C for about 4 hrs to strengthen the slip-cast core. They possess high flexural strength and can be successfully cemented using any cement. CAD/CAM involves a technique wherein the internal surface is ground with diamond discs to the dimensions obtained from a scanned image of the preparation.

In-Ceram® (Vident, [www.vident.com](http://www.vident.com)) consists of a family of all-ceramic restorative materials. The family encompasses a range of strengths, translucencies, and fabrication methodology designed to cover the wide scope of all-ceramic restorations, including veneers, inlays, onlays, and anterior/posterior crowns and bridges. In-Ceram Spinell (alumina and magnesia matrix) is the most translucent with moderately high strength and used for anterior crowns. In-Ceram Alumina (alumina matrix) has high strength and moderate translucency and is used for anterior and posterior crowns. In-Ceram Zirconia (alumina and zirconia matrix) has very high strength and lower translucency and is used primarily for three-unit posterior bridges. In addition, these materials are supplied in a block form for producing milled restorations using a variety of machining systems.

In-Ceram is in a class called interpenetrating phase composites. They consist of at least two phases, which are intertwined and extend continuously from the internal to external surfaces. This class has better mechanical and physical properties relative to the individual components; a tortuous route through alternating layers of both components is required in order for these materials to break.

Interpenetrating phase materials are generally fabricated by first creating a porous matrix; in the case of In-Ceram, it would be a ceramic "sponge." The pores are then filled by a second-phase material, lanthanum-aluminosilicate glass, using capillary action to draw a liquid or molten glass into all the pores to produce the dense interpenetrating material.

The system met with great success as an alternative to conventional metal-ceramics. It uses a sintered crystalline matrix of a high-modulus material (85% of the volume) in which there is a junction of the particles in the crystalline phase. This is different from glasses or glass-ceramic materials in that these ceramics consist of a glass matrix with or without a crystalline filler in which there is no junction of particles (crystals). Slip casting may be used to fabricate the ceramic matrix, or it can be milled from a presintered block. Flexural strengths range from 350 MPa for spinell, 450 MPa for alumina, and up to 650 MPa for zirconia. Clinical studies support In-Ceram Alumina as an almost all purpose ceramic. In-Ceram Alumina had the same survival rates as porcelain-fused-to-metal restorations up to the first molar, with a slightly higher failure rate for the second molar. In-Ceram Zirconia should be used on molars only due to its very high opacity, which is not suitable for anterior esthetics. For anterior teeth, the alumina magnesia version of In-Ceram (called Spinell) is ideal due to its higher translucency.

#### 1.2.4 Polycrystalline solids

Solid-sintered monophase ceramics are formed by directly sintering crystals together without any intervening matrix to form a dense, air-free, glass-free, polycrystalline structure. Several processing techniques allow the fabrication of either solid-sintered aluminous oxide (alumina,  $\text{Al}_2\text{O}_3$ ) or zirconium oxide ( $\text{ZrO}_2$ ) framework. The first fully dense polycrystalline material for dental applications was Procera® AllCeram alumina (Nobel Biocare, [www.nobelbiocare.com](http://www.nobelbiocare.com)), with a strength of approximately 600 MPa. The alumina powder is pressed and milled on a die and sintered at about 1600°C, leading to a dense coping but with approximately 20% shrinkage.

The use of zirconia has increased rapidly in the past few years. This is Zirconia, partially stabilized with small amounts of other metal oxides. Partially stabilized zirconia allows production of reliable multiple-unit all-ceramic restorations for posterior teeth, since they produce high stress. Zirconia may exist in several crystal types (phases) depending on the addition of minor components. Typically for dental applications, about 3 wt% of yttria is added to pure zirconia.

Zirconia has unique physical characteristics that make it twice as strong and tough as alumina-based ceramics. Values for flexural strength range from approximately 900 MPa to 1100 MPa. There is no direct correlation between flexural strength (modulus of rupture) and clinical performance. Another important physical property is fracture toughness, which has been reported between 8 MPa and 10 MPa for zirconia. This is significantly higher than

other dental ceramics. Fracture toughness is a measure of a material's ability to resist crack growth. Zirconia has the apparent physical properties to be used for multiple-unit anterior and posterior FPDs. Clinical reports on zirconia have not shown any problem with the framework, but have shown the chipping and cracking of porcelain. Using a slow-cooling protocol at the glaze bake to equalize the heat dissipation from zirconia and porcelain increased the fracture resistance of the porcelain by 20%. Zirconia may be in the form of blocks that are milled to create the frameworks (CAD/CAM). Mostly, they are fabricated from a porous block, milled oversized by about 25%, and sintered to full density in a 4 - 6 hours cycle. Alternatively, fully dense blocks are milled. However, this approach requires approximately 2 hours of milling time per unit whereas milling of the porous block necessitates only 30 to 45 minutes for a three-unit bridge.



Fig. 19. Dental Ceramic Furnaces.

### 1.3 Inlays and onlays

Basically, Inlay is an indirect filling placed on teeth. Onlay is a more extensive filling (Involving more than one cusp in case of molars). They work in similar fashion. These are made of many kinds of previously mentioned ceramics. They are fabricated by CAD/CAM technique.

### 1.4 Implants

Implant is basically a pillar/post placed into bone to act as a replacement to root of a tooth, on which a denture – fixed/removable is placed. Usually these are made from titanium and its alloys. Basic criteria for a material to be used as an implant is strength and bone biocompatibility. Recently Zirconia implants are introduced in to the market. With an increasing consciousness and fear for metal allergy, Zirconia implants are gaining momentum. Their advantage is their non allergic nature. In clinical studies, no difference in performance is reported. Their basic disadvantage over titanium is their brittleness. Also



Fig. 20. Picture of titanium implant in place - clinical picture.

hydroxyapatite coated titanium implants are already into the market. These aim at better tissue response and osseointegration. Forces experienced by the implants are basically compressive and bending. Even though alumina has good mechanical properties, it is inert towards bone, hence not used in implant dentistry.

Zirconia implants (Ceraroot® etc) are compressed, sintered and milled to produce the necessary shape and surface texture. In case of dental implants, it is a proven fact that shape and surface texture influence the osseointegration. Right from introduction of implants in dentistry, lots of shapes have been tried. Lots of patented designs are found regarding these designs and surfaces. The researches are focused on chemistry, morphology and surface characteristics for betterment of implant success.

### 1.5 Braces

The science of braces - called Orthodontics, describes the corrective procedure as unaesthetic metamorphosis to an esthetic result. The aim of ceramic braces is to reverse the above description. The primary use of these brackets is esthetics. Ceramic braces as such do not experience masticatory forces, But are subjected to the orthodontic forces like sliding over wires, torquing etc. Due to its high wear coefficient, when wrongly placed can cause attrition of opposing teeth. They are basically polycrystalline alumina or Zirconia.



Fig. 21. Ceramic braces, colour codes showing the correct tooth to be cemented to.

### 2. Classification based on processing techniques

For ease of understanding, classification according to processing techniques is advocated. Generally, there are

1. Powder/liquid glass-based systems
2. Pressable blocks of glass-based systems
3. CAD/CAM systems

This system is more relevant clinically. In spite of same chemistry and microstructure, the processing history determines the properties relevant to clinical performance. Specifically, machined blocks of materials have performed better than powder/liquid versions of the same material.

1. Powder/liquid systems

These can be conventional or slip casted. The conventional construction of a porcelain crown involves compaction, firing and glazing. Briefly compaction involves mixing of powder with water and binder to form a paste by spatulation, brush application, whipping or vibrating, that is aimed at compaction, which is painted over the die that is previously coated with platinum foil. This paste is made from different porcelain powders to mimic the esthetics of natural teeth. Usually, an opaque shade (to mask metal core), a dentin shade and then enamel shade is used. The enamel shade is selected from shade guide matched to patients actual tooth shade.

The objective of condensation techniques is to remove water, resulting in a more compact arrangement with high density of particles that reduces the firing shrinkage. The particle shape and size affect the handling characteristics of the powder and have influence on firing shrinkage. The binder helps to hold the fragile particles together in this so-called green state.

Firing initially involves slow heating of crown in the open entrance to the furnace, to drive off excess water before it forms steam that cracks the ceramic. Dried compact is placed in the furnace and the binders are burnt out. Some contraction occurs in this stage. When the porcelain begins to fuse, continuity is achieved at contact points between the powder particles. The material is still porous, and is usually referred to as being at the low bisque stage. As the higher temperature prevails for longer time, more fusion takes place as the molten glass flows between the particles, resulting in more compaction and filling the voids. A large contraction takes place during this phase (~20%), and the resultant material is apparently non-porous. The high shrinkage is caused by fusion of the particles during sintering, and resultant close contact between particles. Longer sintering will lead to pyroplastic flow and loss of form and will become highly glazed. A very slow cooling rate is employed to avoid cracking or crazing.

The furnaces can be programmed to automate these procedures. Vacuum-firing produces a denser porcelain than air firing, as air is withdrawn during the firing process, resulting in fewer voids and a stronger crown and more predictable shade. Areas of porosity in air fired porcelain alter the translucency of the crown, as they cause light to scatter. Also, air voids become exposed on grinding of the superficial layer, compromising esthetics by giving a rough surface finish.

Glazing is done to eliminate residual surface porosity that might encourage bacterial colonization and its sequel. Glazing results in surface that is smooth, shiny and impervious. To accomplish this, either low fusing glasses are applied to crown after construction and fused, or final firing is done under controlled condition that fuses the superficial layer to make it impervious.

With regard to slip casting, the "slip" is a homogenous dispersion of ceramic powder in water. The water pH adjustment creates a charge on the ceramic particles, which are coated with a polymer to cause the fine suspension in water. In the case of In-Ceram, the slip is applied on a gypsum die to form the underlying core for the ceramic tooth. The water is absorbed by porous gypsum, leading to packing of particles into a rigid network. The alumina core is then slightly sintered in a furnace to create an interconnected porous network. The lanthanum glass powder is placed on the core and glass becomes molten and flows into the pores by capillary action to produce the interpenetrating network. The last step in the fabrication involves application of aluminous porcelain on the core to produce the final form of the restoration. Other powder dispersions, such as those created with zirconia, may be poured into a gypsum mold that removes the water and leads to formation of homogeneous block of zirconia.

## 2. Pressable ceramics

Pressed ceramic restorations are fabricated using a method described previously, similar to injection molding. Empress restorations and other materials with a similar leucite/glass

structure are fabricated in this manner. Pressables may be used for inlays, onlays, veneers, and single-unit crowns.

### 3. CAD/CAM

Numerous ceramics have found their way into this system, due to its short processing time. Some of them are described here. **Glass/Crystal ceramics** are made from fine-grain powders, producing pore-free ceramics. This was the first material specifically produced for the CEREC system. It has an excellent history of clinical success for inlays, onlays, and anterior and posterior crowns. These blocks are available as monochromatic, polychromatic with stacked shades as in a layered cake, and in a form replicating the hand-fabricated crowns whereas an enamel porcelain is layered on top of dentin porcelain. **Glass/Leucite** is a feldspathic glass with approximately 45% leucite crystal component. **Lithium disilicate** is not initially fully crystallized, which improves milling time and decreases chipping risk from milling. The milled restoration is then heat-treated for 20 - 30 mins to crystallize the glass and produce the final shade and mechanical properties of the restoration. This crystallization changes the restoration from blue to a tooth shade. The microstructural and chemical composition is essentially the same. **Framework Alumina** are fabricated by pressing the alumina-based powder into a block shape. These blocks are only fired to about 75% density. After milling, these blocks are then infused with a glass in different shades to produce a 100% dense material, which is then veneered with porcelain. **Porous Alumina** frameworks may be fabricated from porous blocks of material. Pressing the alumina powder with a binder into molds produces the blocks. The blocks may be partially sintered to improve resistance to machining damage or used as pressed in a fully "green" state (unfired, with binder). The frameworks are milled from the blocks and then sintered to full density at approximately 1500°C for 4 to 6 hours. The alumina has a fine particle size of about 1µm and strength of approximately 600 MPa and is designed for anterior and posterior single units, as well as anterior three-unit bridges. **Porous Zirconia** frameworks milled from porous blocks are fabricated similarly to alumina blocks. As is the case with the alumina block, the milled zirconia framework shrinks about 25% after a 4 - 6 hours cycle at approximately 1300°C to 1500°C. The particle size is about 0.1 µm to 0.5 µm.

### 3. Conclusions

Any reader of this review, who is well versed in materials science, will be tempted to enter dentistry to introduce newer and better ceramics to dentistry. As one can comprehend, no material is ideal in all aspects, to natural structure of teeth. However, mechanical and biological properties of ceramics have exhibited a significant improvement in the past few decades. Recent surges in all-ceramic crowns for esthetics and durability is a highlight of such improvements. Also, with dentistry, frequently gaining new faces are catered by these ceramic materials. Further scope of research in dental ceramics can be directed to stronger and osseointegrative ceramic implants, more esthetic and strong crowns and veneers, to mention a few. Definitely, future is bound to witness a bigger revolution in field of dental ceramics, with introduction of newer ceramics and nanotechnology for the betterment of dental restorations on the lines of form, function and esthetics, along with improved biocompatibility.

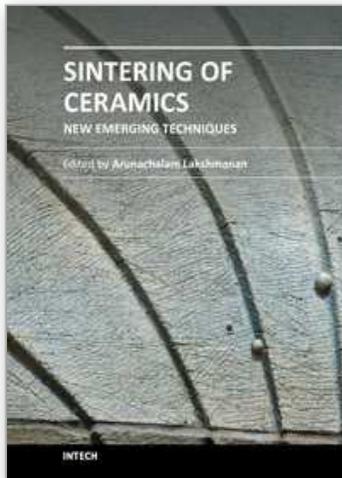
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## **Sintering of Ceramics - New Emerging Techniques**

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The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB<sub>2</sub>, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.

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