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Dental Ceramics

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Objectives

Upon completion of this educational activity the learner will be able to:

- Understand the various categories of dental ceramic products.
- Understand basic chemical processes for different components of dental ceramics.
- Review of basic tooth structure and anatomy as it relates to dental ceramics.
- Know types of dental ceramics used in clinical dentistry.

Course Description

This course is a review of the history of ceramics, and a basic overview of dental ceramics—and assumes some basic understanding of physical chemistry. The reader will gain understanding of refractory and glass components of ceramics and the differences between earthenware, stoneware, and porcelain. This course discusses the roles of feldspar, quartz, and kaolinite and other minerals as well as fluxes in ceramics. Various firing techniques are described as well as sintering and fusing processes. Tri-axial blends are discussed, along with a short description of dental feldspathic porcelain. The last third of the course is a focus on aspects of restorative Dental Ceramics and modern applications. The last sections are composed with authors in addition to Dr. Spiller. Much of the information is technical, yet is a great review or introduction for various dental professionals.

Martin S. Spiller, DMD

Martin Spiller graduated in 1978 from Tufts School of Dental Medicine. He is licensed in the state of Massachusetts and has been practicing general dentistry in Townsend, MA since 1984. Upon graduation from dental school, Dr. Spiller spent four years as an U.S. Army officer. During this time, he attended a dental general practice residency in which he received training in numerous dental specialties including oral surgery, endodontics, pedodontics, and orofacial surgical techniques and facial trauma. In 2000, he began work on a general dentistry website (www.doctorspiller.com). The intention at first was to educate the general public about dental procedures and the concepts behind them.



Eventually, the website became popular with professional dental students. The content of the web pages began to reflect this readership. Dr. Spiller was asked to write this course based on academic study, hard won experience in the practice of dentistry, and his proven ability to write clear and concise content.

Introduction

Pottery was the first and remains the most common ceramic. Ceramic science springs from discoveries made by potters centuries ago. Glass is the second major component in ceramics.

The name porcelain is said to have been coined by Marco Polo in the 13th century from the term porcellana which is the Italian name for the cowrie shell. Polo referred to the cowrie shell to describe Chinese porcelain to fellow Europeans because of the shell's thinness, translucency, hardness, and strength.

The term ceramic covers various hard, brittle, non metallic, heat and corrosion-resistant materials. Ceramics are made by shaping and firing a non-metallic mineral such as clay at a high temperature. The non-metallic materials used are aluminum oxide and silicon dioxide.



The Definition of Ceramics—Refractories and Glass

The two structural components of ceramics are a refractory crystalline structure, and glass. Refractory substances do not melt at normal kiln temperatures. Refractory substances retain their crystalline structure throughout all stages of ceramic production. Glass has no coherent internal structure of its own and does not melt in the kiln.

All ceramic pieces contain a refractory skeletal structure made of particles of metallic oxides. The skeletal structure is made of alumina and silica. Silica is quartz and alumina is corundum. When heated to low kiln temperatures, these refractory particles fuse together at their points of contact. The process of heating refractory particles until they fuse at their points of contact is called sintering.



Quartz



Corundum

Ceramic pieces contain various amounts of amorphous, molecularly structureless glass gel. Glass is infiltrated between the sintered refractory particles. Interestingly, glass is also composed of silicon dioxide and aluminum oxide which are the same components that make up the refractory skeletal structure in ceramics. But unlike their refractory counterparts, the silicon dioxide and aluminum oxide in glass do not retain their crystalline identities. In glass, silicon dioxide and aluminum oxide molecules combine and become part of the amorphous glass gel matrix.

Refractory particles do not melt in the kiln. They sinter at their points of contact when fired at low temperatures. Refractory materials in a ceramic body are similar to stones in a rock wall. Stones retain the shape of a wall, because they fit together in a stable way. So, refractory materials in a ceramic body retain the shape of the body before and during firing. Glass in ceramic is similar to the mortar between stones in a wall. Mortar seals the spaces between stones, keeps water out and helps keep the stones from shaking apart during an earthquake.

Glass matrix makes ceramic bodies water resistant and durable. The ratio of glass to refractory material in ceramic bodies varies. Earthenware products are fragile and water-penetrable. Because more glass is included in porcelain, it is durable and waterproof.

In dental ceramic sub-structures sintered refractory materials have little or no glass between the refractory particles. Dental ceramic sub-structures are made of alumina or zirconia fused at very high temperatures and need no glass to make them hard.

Note: A dental substructure is a framework covered with porcelain that forms the finished tooth-shaped appliance.

Pottery

Pottery was the first, and still is the foremost ceramic. Pottery is made from clay and contains both a refractory substructure and feldspathic glass. Traditional clay bodies are subdivided into three groups:

- Earthenware
- Stoneware
- Porcelain

Each pottery classification contains increasing percentages of glass and decreasing percentages of alumina and silica. Dental porcelain is another subdivision of domestic porcelain. It is impossible to understand dental porcelains and their associated cores without first understanding the art and science of ceramics, and this begins at the potter's wheel.

The first ceramics made were low-fired earthenware. Pottery is made by shaping clay, drying it, and heating it in a kiln at sufficient temperatures and amounts of time until the clay particles fuse together. This process is called firing. Clay is a special kind of mud. Not all mud is suitable to use as ceramic clay. Ceramic clay requires feldspar, quartz and kaolinite.

Potter's clays contain water which reduces friction and binds particles together. Water lends to clay plasticity. However, clay composed of only feldspar, quartz, and kaolinite lacks plasticity, because it is like very fine, wet sand. It can absorb minimal water before becoming too sloppy to hold its shape. This is known as short clay. Short clays have a fine balance between too much and too little water. Short clays are difficult to work with. Even water on the potter's hands affects the workability of the clay. Porcelain clays are short clays, because they are mostly composed of feldspar, quartz and kaolinite.

In order to make clay more workable, manufacturers add minerals such as ball-clay or bentonite. These materials have chemical configurations that allow their particles to break down in water which increases surface area available for water retention. This produces a more plastic clay.

Note: Dental porcelain http://www.doctorspiller.com/ceramics_3.htm - Frits_ manufacturers add sugar and starch to their porcelain powders for the same reason.

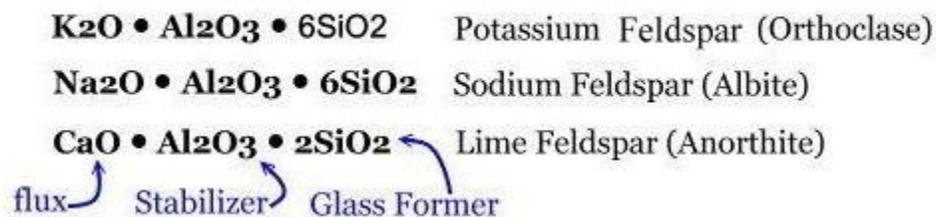
Three essential constituents of clay are feldspar, quartz and kaolinite.



Feldspar

Feldspar comprises approximately 60% of the upper eight miles of the earth's crust. Feldspars are naturally occurring glasses. Feldspars are naturally occurring crystalline rocks which have an internal, crystalline structure. When glass cools slowly, crystals form which is a process known as devitrification. Feldspar cooled over a period of millions of years. It had plenty of time to devitrify. There are twelve naturally-occurring feldspars. Their formulas are similar and can be inferred from the three formulas provided here.

Feldspars (Naturally occurring forms of devitrified glass)



Feldspars melt into a glass-like consistency and flow like a thick liquid at high temperatures. Clays containing too much feldspar are unsuitable as potter's clay since objects made from it would simply melt into a puddle in the kiln instead of maintaining its shape. Most potter's clays contain no more than 15% feldspar, and porcelain clays may contain up to 25%. The other 75% is made of non-melting refractory materials. Some glazes contain 100% feldspar, since the purpose of glaze is to melt and flow over the surface of the clay body.

Feldspars melt at ≈ 1150 C. Feldspathic glass surrounds refractory clay particles and fills the pores between them. Due to fluxes, feldspathic glasses bind to refractory particle surfaces which help bind the ceramic body together. The more feldspathic glass a ceramic body contains, the denser the fired body will be.

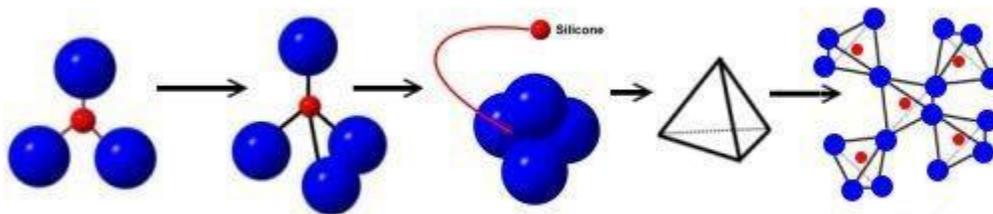


Quartz

Quartz is pure, crystalline silica. Unlike silica in feldspar, silica in crystalline quartz is not combined with flux molecules and consequently does not melt when fired in a potter's kiln. The quartz particles remain separate, un-melted, and dispersed throughout the glassy phase produced by the melting feldspar. Quartz is part of the refractory crystalline structure in ceramic bodies. It helps the piece to retain its shape in the kiln while the feldspathic glass melts around it. Quartz melts at °1713 C. Iron melts at °1510 C, and steel melts at °1370 C.

The highest temperature reached by potter's kilns is °450 C. Most dental ceramicists fire their work between °850 C and °1100 C. A refractory (quartz in the form of silica) is any ceramic constituent unable to melt at normal kiln temperatures. While quartz particles remain un-melted, availability of alkaline metal ions (fluxes) from feldspar encourages bonding of outer layers of refractory quartz particles to the surrounding feldspathic glass matrix. The presence of free flux molecules sinters refractory particles in the clay body, including alumina, quartz, and un-melted kaolinite particles.

Fusing refractory particles creates a skeletal structure throughout the clay piece helping it to maintain its original shape. Silica's chemical formula is SiO_2 . Even though silica's chemical formula shows two oxygen atoms associated with one silicon atom, silicon actually forms bonds with four oxygen atoms when in combination with other silica molecules.



Silicon shares oxygen atoms with two adjacent silica molecules forming tetrahedral crystalline structures. Tetrahedrons are bonded via shared oxygen atoms at each apex of the tetrahedron. This describes crystalline silica. Adding fluxes (alkaline metallic oxides) causes the quartz's ordered crystalline structure to become disordered, as it

does in feldspar glasses. This is the basis of glass formation.

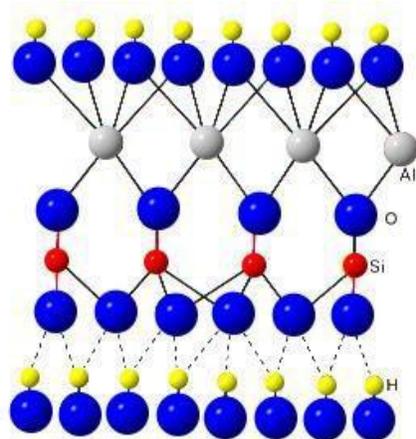


Kaolinite

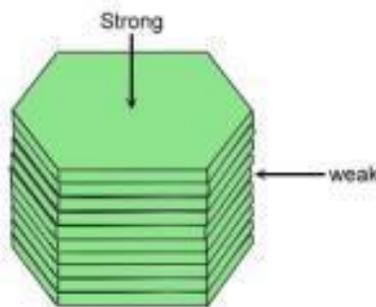
Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is found in nature. It is known as kaolin (China Clay). Kaolinite derives its name from the Chinese term for high ridge which is the place where the Chinese first discovered the purest form of kaolinite. Europeans had been using kaolinite in less purified forms to make stoneware pottery. When Europeans discovered Chinese porcelain, demand for the pure white, translucent pottery skyrocketed. Since Chinese porcelain recipes were kept secret, European quest for Chinese porcelain probably sparked the world's first case of industrial espionage.

Kaolinite has a crystalline structure, and it contains silicon just as does feldspar and quartz. In pure form, kaolinite melts at $^{\circ}1770\text{C}$. However, in clay form, because clay contains highly-fluxed feldspar, kaolinite's melting point drops to between $^{\circ}1200\text{C}$ and $^{\circ}1450\text{C}$. Kaolin is a hydrated aluminum silicate.

Note in the illustration above, there are layers to kaolinite's structure. The upper layer is composed of aluminum oxide (Al_2O_3). This is also called gibbsite layer. The lower layer is composed of silica (SiO_2). The illustration above is a vertical slice through the crystalline structure. Crystalline slabs stack one on top of another forming a three-dimensional crystal lattice.



The gibbsite layer binds to the silica layer by sharing oxygen atoms, and each hydroxyl group in the silica layer weakly binds to the hydrogen atoms in an adjacent gibbsite layer. This causes the crystalline structure to resemble a vertically stacked set of hexagonal plates. The plates can support pressure applied to the top (compression), but do not do well when pressure is applied to the sides (shear). The plates tend to slide over one another due to weaknesses in hydroxyl bonds. Orientation of these plates is influenced by the pressure of potters' hands as the potter forms the clay on the wheel. The durability of stoneware pottery owes much to this fact. The orientation of clay crystals sets during the wedging and throwing processes.



Heat application does interesting things to kaolinite's crystalline structure. As temperature increases toward the fusing temperature of feldspar (with its load of flux molecules), some hydroxyl groups in the silica are driven off and combine with hydrogen atoms attached to adjacent gibbsite layers. This produces water which volatilizes and abandons the arena. This process destabilizes bonds between gibbsite and silica layers and allows silica and aluminum oxide to react separately.

The presence of alkaline metal ions in feldspar disrupts free silica radicals from forming stable crystals, instead forcing formation of amorphous glassy gel (glass). The more flux in the medium, the more kaolinite crystals dissolve, and more glass is formed. Quite a bit of silica in kaolinite melts into glass in porcelain clays which include 25% feldspar.

The leftover gibbsite layer, which has lost its hydrogen atom, becomes refractory crystalline aluminum oxide, also known as alumina. Not all kaolinite will melt. Much of it remains behind as plate-like crystalline inclusions in the glass gel matrix. When the clay body melts at high temperature, it consists of the following constituents:

- Feldspathic glass formed from the melting of the feldspar.
- Glass from the kaolinite. The de-bonded silica layer from the melted kaolinite.
- Refractory alumina crystals. The de-bonded gibbsite layer from the melted kaolinite.
- Refractory kaolinite particles in the form of flat plates.

- Refractory quartz particles.

Two forms of glass mix together and form one homogenous, melted body throughout the ceramic body structure. Alumina, quartz, and kaolinite are refractories. These un-melted particles sinter and form a brittle skeletal structure which allows the ceramic body to retain its shape throughout all phases of firing giving the finished body a great deal of strength.

Fluxes

Na₂O, K₂O and CaO are alkaline metal oxides. They are strong bases when added to water. These oxides are used as fluxes. Fluxes have active molecular structures at high temperatures and attach to and combine with the surface structure causing the crystals' surface molecules to dissolve until the entire crystal melts away. Fluxes cause crystalline structures to melt at lower temperatures than would otherwise be possible. Without fluxes present, other constituents in the ceramic body would not be able to melt at normally attainable temperatures. Fluxes are a major constituent of glass.

Aluminum Oxide

Aluminum oxide (Al₂O₃) exists in two separate forms within clay and porcelain bodies. When chemically combined with other feldspar constituents, aluminum oxide acts as a stabilizer, and is a part of the glass melt. Aluminum atoms bond with silicon via a shared oxygen atom and are an integral part of the amorphous silicon matrix. In this form, it does not affect glass transparency.

However, aluminum oxide is also added to clays as a separate constituent in the form of kaolinite. Because of large amounts of flux contained in feldspars, some of the kaolinite also melts into a glass. The by-product left over when the kaolinite melts is a precipitate of pure crystalline aluminum oxide called alumina. Alumina crystals remain un-melted (they are refractory particles) and scattered throughout the glass melt. In this form, aluminum oxide causes glass to become opaque.

Silica

Silicon dioxide (SiO₂), like alumina, exists in two separate forms within clay and porcelain bodies. When chemically combined with flux and aluminum oxide, silica exists as a molecular component in the amorphous melted glass gel. In this form, it is called a glass former. Silica also exists as un-melted crystalline, quartz particles scattered throughout the glass melt. This is part of the refractory substructure which supports clay and porcelain bodies.

Greenware

When the potter has finished throwing her pot, she lets it dry out. Before firing, the ceramic body is in a fragile greenstate and is called greenware. In its green state, the piece has not become ceramic. It is fragile microscopic particles held together, because they have been forced into their most compact form by the potter's hands. When greenware is dry, it is placed into a kiln for low-temperature firing known as a biscuit bake. During this low-fire process, little if any feldspathic glass is produced.

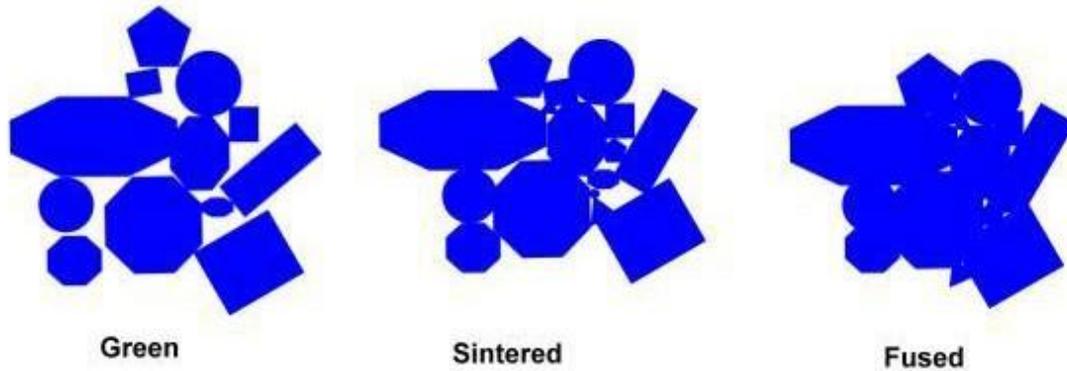
Sintering

Temperature increases short of the melting point of feldspar cause outer molecular layers of these particles to become active. Surface molecules move rapidly which causes un-melted particles (refractories and crystalline feldspar) to become slippery. The outer particle layers act like they are coated with a liquid, and the liquid surface tension minimizes the surface area by drawing particles close together. This causes shrinkage in the ceramic piece.

As various particles draw together, their surfaces begin to bond at points of contact, and they remain this way as the ceramic body cools. This process is known as sintering, and sintering is responsible for the formation of coherent skeletal internal structures that characterize pottery and domestic porcelain. Sintering is also an important process in fabrication of dental porcelain and ceramic dental cores.

Even though outer layers of refractory particles behave as if they are coated with a slippery liquid, sintering begins prior to the actual formation of any liquid phase. Kaolinite ordinary melts at °1200 C but sinters at temperatures as low as °600 C. Sintering is caused by diffusion of rapidly moving atoms between neighboring refractory particles. If the fusing temperature of clay is °1250 C, potters use a biscuit (sintering) temperature in of °1060 C.

Once greenware has been fired at low temperature, clay particles sinter together. This is the first stage of ceramic formation. In the picture below, the center, sintered image corresponds to the potter's biscuit bake. In each successive firing stage, the spaces between particles are reduced. The size of the clay pieces shrinks. Shrinkage has thermodynamic consequences. As clay particles move closer together, the "pile of rocks" becomes thermodynamically more stable and less prone to fracture or collapse. The piece will slump less during handling and firing, and its stronger microscopic structure is less prone to fracture.



Fusing

Once the potter has biscuit-fired (sintered) the greenware, the piece is not fragile and can more easily be handled for further processing. It is not yet fully fired. Most the feldspar remains in crystalline form. The potter applies a watery mixture of feldspar or highly-fluxed silica particles over the surface of the ceramic body. This is called a glazecoat. Once the glaze coat dries to a powder, the ceramic piece is put back into the kiln and fired to a higher temperature. Both the glaze coat and the feldspar particles melt into glass. The second firing is called glaze firing but could also be termed "fusion firing". Fusion happens even in the absence of glaze coating.

During this high-temperature firing, glass formed from melting feldspar particles flows into pores between sintered refractory particles. Glass attaches to the sintered refractory particles and further fuses them more tightly together. Alumina, quartz, and un-melted kaolinite particles maintain a skeleton that sustains the ceramic piece's original shape.

The presence of the refractory alumina and silica particles is extremely important because without this refractory skeleton, the ceramic body will distort, slump, or even melt into a puddle. Ceramic bodies without internal refractory structures are composed exclusively of feldspathic glass, and are prone to fracture due to any shock. During firing, the glaze coat melts and forms a thin glass coating over the entire body surface. Glaze fills in any surface porosity and gives the ceramic body a sleek glass coat making it smooth and waterproof.

Tri-axial Blends

The most important materials in potters' clays are feldspar, quartz, and kaolinite. The proportions of these minerals determine ceramic characteristics. A common way potters determine how a particular glaze will look or act on their clay piece is to run tri-axial blend experiments. The numbers in the table below are the percentages of components

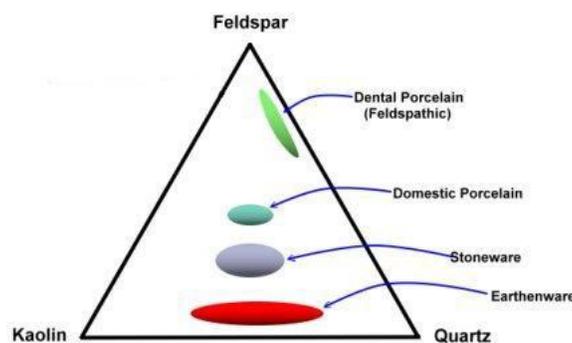
A, B and C used in the blend. The tiles in the image beneath it are the results of the tri-axial blend experiment.



The tiles on the three triangle apexes show colors of pure glazes. The tiles between them show colors of the mixtures corresponding to the percentages in the table. In this case, we are looking only at colors that result from mixtures of axial glazes, however, the same experiment could be performed to ascertain if a specific glaze mixture crazes, or devitrifies due to formation of crystals. This experiment is not limited to three axes. Although very difficult, it is possible to run tetra-axial and pentaxial blends.

Classes of Clay (Aluminous Silicates)

The tri-axial blend above demonstrates five divisions between each axis, but, it is possible to divide blends into much finer gradations. The tri-axial blend image below shows compositions of three aluminous silicate classifications ranging from those containing the least glass to those containing the most.



Earthenware

Earthenware fires at relatively low temperatures and is porous. Earthenware vessels were probably the first form of pottery made over 14,000 years ago. In order to hold liquids, earthenware must be glazed. Red clay flowerpots are good examples of

earthenware. From the diagram above, one can see that earthenware clay contains little feldspathic glass which binds particles together and fills pores between sintered alumina and silicon particles.

The red color comes from iron oxide which acts like a flux to lower the clay's fusing temperature. Earthenware does not need to be fired at high temperatures firing, because there is so little feldspathic glass in this clay. Glazes on these bodies are formulated to fuse at low temperatures, slightly above the sintering temperature of the clay itself. This is one of the reasons earthenware products are so inexpensive.

Stoneware

Stoneware is a hard, strong and vitrified ware which fires above °1200 C. It has low porosity, a defining characteristic of stoneware. Glaze can be applied to a previously sintered piece and both glaze and body mature in a second high-temperature fusion firing at the same time. This creates a well integrated glazed surface.

Note its position in the tri-axial diagram above. Stoneware contains more feldspar than earthenware which accounts for its hardness and high density. There is more feldspathic glass that binds alumina and silica together. Modern dinnerware is made with stoneware clays.

Domestic Porcelain

Domestic porcelain is made from China Clay. From the tri-axial diagram, one can see it contains more feldspar than ordinary stoneware, and there is more feldspathic glass in the clay. The large amount of glass in the mix reduces porosity to nearly zero, and produces a very dense, hard, and translucent glassy body. Vessels made from porcelain clay have very thin walls, through which light can shine, and ring like a bell when struck. There is so much feldspathic glass in porcelain there is often no need for a glaze layer.

However, porcelain still retains a refractory matrix which fortifies its strength and helps the glass to retain its shape. Large amounts of glass are disadvantageous for the potter. Porcelain clays are very short and difficult to throw. (To throw clay is to form it on a potter's wheel).

Porcelain clay is prone to slumping while being fired. The glass wants to flow at high temperature, because there is less refractory material in the mix which acts as a skeleton support the shape of the ceramic piece. The firing temperature must be precisely controlled in order to fully vitrify the glass while preventing it from slumping.

Dental Feldspathic Porcelain

In the early 1900's, when dental porcelain was first formulated, it had the same general composition as domestic porcelain. Kaolin is a hydrated aluminum silicate, and it is opaque. Even small quantities of kaolin in the mixture cause porcelain to lack translucency. By 1938, little or no kaolin was left in porcelains chosen for dental use.

For a long time, dental porcelain was manufactured exclusively with feldspathic glass and finely ground quartz. By the 1960's, aluminum oxide had been added back into the mixture. Quartz particles remain unchanged during firing. The purpose of aluminum oxide and quartz is to strengthen glass by reducing the distance a crack can propagate before running into a hard particle. Aluminum oxide and quartz also act as a skeletal structure to reduce slumping.



Dental porcelains are used to create crowns, bridges, and veneers. They are biocompatible, esthetic, insoluble, and have a hardness of 7 on the Mohs scale. Zirconia-based restorations are recommended for three-unit porcelain molars fused to metal or in complete porcelain groups only.

Dentists specify a shade or combination shades for different parts of restorations. Shade systems used are the Vita Classical and Vita 3D Master guides.

There are two types of porcelain restorations:

1. porcelain-fused-to-metal
2. complete porcelain restorations

With porcelain-fused-to-metal restorations, the metal is masked with an opaque layer and then consecutive layers are built up. The powder corresponding to the desired shade of dentin base is mixed with water and then fired. Further layers are applied to mimic the natural translucency of tooth enamel. Porcelain may be fused to gold for extra strength. Many systems use aluminum oxide, zirconium oxide, or zirconia cores.

Recent developments in dental CAD-CAM technology have required specialized porcelains formed into sintered blocks. CAD/CAM restorations created with CEREC technology are durable.

Focus on Dental Ceramics

History

The history of restorative dentistry can be traced back as far as ancient Egyptian times. Examples of tooth replacement prostheses made from gold wire, ox bone or wood have been found. More recent types of restorations had a renaissance about two hundred years ago when air-fired porcelains and cast gold restorations were made to restore and replace teeth. It seems that in ancient times the main requirement was to replace teeth lost as a result of gum disease, whereas in recent times it is to restore teeth damaged by decay.

The use of ceramics for the restoration of teeth has been a part of dentistry's modern period of evolution. This period started in the late seventeen hundreds but major advances have mainly come about this century. The demand for esthetic restorations led to improvements in ceramic formulation and firing techniques.

The types of ceramic systems and application in modern dentistry is summarized by John W. McLean *New Dental Ceramics and Esthetics* and is the source of most of the subsequent technical information (McLean, 2007).

Dental Ceramics

Dental ceramics in restorations are essentially oxide based glass-ceramic systems. They have three essential features/requirements:

1. Ease of fabrication of complex shapes
2. Sufficient mechanical and corrosion resistance
3. Appropriate esthetic appeal.

Tooth Structure Review

Enamel

Teeth themselves are a complex hard tissue structure originally born from specialised cells called ameloblasts, odontoblasts and cementoblasts. The ameloblasts form the enamel, which is the hard outer coating seen as the clinical crown of the tooth. These cells occur in a layer on the outside of the tooth bud.

The enamel is laid down on the inside of the ameloblasts. When the tooth erupts, these cells are lost and enamel can no longer be formed. This has important implications

because any wear or loss of enamel due to decay etc, cannot be repaired by the body.

Dentin

The dentin is formed by the odontoblasts. These cells are on the inner side of the tooth bud, between the enamel and the dental pulp. The dentin is formed by these cells as an inward growth. The dentin could be viewed as the main foundation of the tooth, supporting the enamel, providing protection to the pulp, and through its covering below the gums, giving rise to the attachment via a ligament to the surrounding bone. The dentin has an ability to continue laying down dentin internally at the expense of the pulp chamber size, throughout life. It cannot however, replace dentin that has been physically lost.

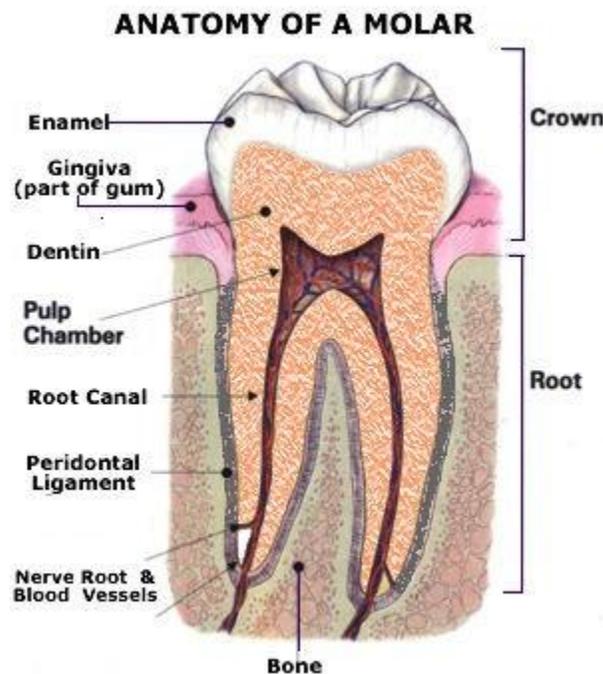


Figure 1. Cross Section of Molar

Mechanical Differences

The mechanical properties and their inter-relationship of the three hard tissues mentioned above, enamel - dentin - bone, present an interesting display of nature's ingenuity for dealing with stresses applied to the teeth as a result of chewing and also tooth grinding during periods of concentration or psychological stress. The enamel is relatively hard and brittle ($E \sim 65 - 70 \text{ GPa}$) the dentin much softer and more compliant ($E \sim 15 - 19 \text{ GPa}$) and bone even more compliant ($E \sim 12 \text{ GPa}$).

Dental Restorative Materials

Dentists of ancient times replaced lost tooth structure with gold and ceramics, surprisingly successfully considering the constraints. The gold and ceramic materials then, as now were used because they could be custom fabricated to fit the needs of individual tooth requirements for form and esthetics. Materials can be used independently or in combination with ceramic baked onto gold alloy subframes. Other metal alloys are also used in this metal-ceramic technique.

Silver Amalgam

The first material that was easily produced and relatively inexpensive was silver amalgam. This material, popularized by an American dentist, G. V. Black, in the 1890's has been used very widely throughout the world as a cheap and effective restorative to replace tooth structure lost through decay. The main disadvantages with this material are the concerns over its mercury content and its lack of esthetic appeal.

Composite Resins and Glass Ionomers

The other two groups of restorative materials to be used widely are the composite resins and the glass ionomers. The composite resins developed in the 1950's when a breakthrough monomer was produced. Known as BisGMA, this resin monomer has become the backbone of most dental composite resins. These materials use various glass or ceramic particles as fillers to enhance their mechanical properties and give them tooth coloring and other esthetic properties such as translucency etc.

The glass ionomers are a relatively recent development although their predecessor silicate cements have been in use for about the same time as the BisGMA resins. These materials are relatively weak, but are used to cement gold and ceramic crowns to teeth, with other versions being used as direct restoratives, depending on their filler content and the recommended application. They have a major advantage in that they have a reasonably constant fluoride release, acting as a strong decay inhibitor.

Issues Facing Ceramics as Dental Restorative Materials

The aim of this paper is therefore to review the role of ceramics in dentistry. The first consideration is why use ceramics. The reasons are as follows:

- Biocompatibility
- Esthetics
- Durability
- Relative ease for customized units.

Biocompatibility

The biocompatibility issue is essential to prevent adverse reactions within the patients. The dental ceramics in use today have relatively low firing temperatures, usually greater than 900°C and are resistant to dissolution in the mouth. Formulations have been developed with firing temperatures as low as 640°C, however, these materials tend to show considerable surface degradation in the oral environment and hence are not useful.

Esthetics

Ceramic materials have long been admired for their esthetic and natural appearance qualities. The use of dentally colored glasses can provide replacement structures that can be made to imitate tooth structure in both color, translucency and response to different lighting sources.

Durability

Durability is an area that has led to considerable research for ceramic systems. The need is for individually constructed restorations, that are small, unique, inexpensive and will be subjected to cyclic loading in wet and sometimes abrasive conditions. The critical problem for all ceramic materials, not the least those used in dentistry is the huge difference in theoretical strength, based on the covalent nature of their structure, and the usual strengths found in general use (7000-70000 MPa versus 7-700

MPa). This was originally determined by Griffith, who reported that the theoretical strength for all solids could generally be regarded as a constant with a value approximating $E/10$.

The advances in industrial ceramics for such conditions have been remarkable to say the least, in recent decades. However, nobody is going to allow their front teeth to be restored with a ceramic that is dark grey, black or opaque white. The advances in industrial ceramics have included improvements in fracture toughness, wear resistance, machinability, solubility, hardness and flexural strength. With the exception of hardness, these are the same improvements that have been sought in dental ceramics. Another major requirement apart from esthetics is that the ceramic not be too hard otherwise abrasive wear of the opposing natural tooth will be too severe.

Failure of Ceramic Dental Restorations

The clinical observations tend to show catastrophic mechanical failure in patients showing malfunction. There are reports that ceramic restorations such as inlays and crowns fail due to occlusal (biting together) injury not unlike that of a small spherical indentation. Perhaps the most important consideration to note are the possible driving

forces associated with stresses formed from elastic components within the field of the initial crack.

In general, the contacts between teeth are the same as small spherical indenters, changing with age and wear to broader, flatter contacts. The cusps of teeth are naturally rounded. As teeth become worn they tend to exhibit small milled facets and so the contacts can become much broader. A spherical indenter rather than a sharp indenter is therefore the system of choice when measuring the behavior of the ceramic system in question.

Ceramic Materials Used in Dental Restorations

The Felspathic Porcelains

Several summaries for the composition of dental porcelain have been written. They cover the composition of felspathic porcelain as a veneering porcelain in all-ceramic and metal-ceramic crowns. They describe a history of modifying the basic Potash Feldspar-Quartz-Kaolinite mix by the removal of mullite and free quartz, while increasing sodium oxide and alkaline earth oxides as bivalent glass modifiers, to improve translucent properties while trying to maintain strength. Fluxing agents have also been added to lower the melting temperatures and make them easier to handle in the dental laboratory. These materials are now substantially glassy and Binns (1983) describes their classification as a porcelain as “somewhat of a misnomer”.

The K₂O content was also varied to accommodate the need to match the coefficient of thermal expansion for metal alloys used in dental metal-ceramic techniques. The increase in K₂O content allowed a greater proportion of leucite crystals (coefficient of thermal exp. $27 \times 10^{-6}/^{\circ}\text{C}$) which led to the overall coefficient of thermal expansion rising to something in the order of $13.5 - 15.5 \times 10^{-6}/^{\circ}\text{C}$.

The felspathic porcelains used in all-ceramic systems have coefficients of thermal expansion ranging from $5.5 - 7.5 \times 10^{-6}/^{\circ}\text{C}$ when used over castable glass and alumina based core materials, to $16 \times 10^{-6}/^{\circ}\text{C}$ when used over the newer pressed leucite systems.

The Leucite Systems

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.

The recent introduction of the pressed leucite reinforced ceramic system, IPS Empress, has leucite in a different role. This material relies on an increased volume of fine leucite particles to increase flexural strength.

Similar versions using finely dispersed leucite grains to increase toughness, strength and modify wear patterns and rates to make them similar to enamel wear rates are now available for metal-ceramic restorations.

The Castable Glasses

The development of glass ceramics by the Corning Glass Works in the late 1950's has led to the creation of a dental ceramic system based on the strengthening of glass with various forms of mica. The Dicor® crown system uses the lost wax system to produce a glass casting of the restoration. The casting is then heat treated or “cerammed”, during which tetra silicic fluromica crystals are formed to increase the strength and toughness of the glass ceramic.

This procedure is designed to take place within the economic confines of a commercial dental laboratory. A second dental version was developed to be used for CAD/CAM dental procedures. This cerammed glass is provided in an already heat treated state

from the manufacturer. In this latter technique an optical scan of a prepared tooth is loaded into a computer and a milling system is used to produce the restoration. The restoration is then “bonded” to the remaining tooth structure using a dental BisGMA based composite resin.

The Alumina Based Systems

The Aluminous Jacket Crown

The modern Aluminous Jacket Crown, probably more commonly known as the Porcelain Jacket Crown (PJC) was popularized in the mid 1960's by McLean. This report also points out the importance for the use of alumina in dental ceramics and how it modifies the flaw systems at the surface and within the ceramic. The aluminous porcelains reported by McLean are also very prone to strength degradation when they contain porosity.

Pure Alumina Core - Heat Cured After Pressing

The Nobel Biocare company from Sweden have introduced two systems that essentially use a system of pressing alumina onto a metal die, removing the pressed shape from the die and then sintering it. One system is used to make alumina profiles that are then used as cores to build up ceramic superstructures for single tooth implants, CeraOne®, and the second is to make cores for conventional crowns, a process known as Procera®. Unlike the other dental ceramic materials, there is no glassy phase present between the particles. Feldspathic veneering porcelains such as Vitadur Alpha® and Duceram® are then fired onto this alumina core to provide the color and form for the restoration.

The Glass-Infiltrated Alumina System for Cores

During the 1980's, Dr. Michael Sadoun and Vita Zahnfabrik, developed a slip casting system using fine grained alumina. The cast alumina was sintered and then infiltrated with a Lanthana based glass. This provided a glass infiltrated alumina core (In-Ceram®) on which a felspathic ceramic could be baked to provide the functional form and esthetic component of the restoration. In-Ceram has the highest flexural strength and fracture toughness of all the currently available dental ceramic systems available to most commercial dental laboratories. The system also has the greatest versatility for dental use of any metal free ceramic restorative.

The driving force for these developments has been the immense difference in reliability between metal-ceramic systems and all-ceramic systems and a public perception that metal-free restorations are more esthetic. The disadvantages of the metal ceramic systems include radiopacity, some questions concerning metal biocompatibility and lack of natural esthetics, of course important features in today's consumer conscious dental market. Typical mechanical properties of dental ceramics and tooth structures are listed in Table 1.

Table 1. Strength of tooth structures and dental ceramics.		
Material	Flexural Strength (MPa)	Fracture Toughness (MPa.m-2)
Porcelains		
Feldspathic	60-110	1.1
Leucite	120-180	1.2
Glass Ceramics		
Lab cast/Cerammed	115-125	1.9
Premade/HIP	140-220	2.0
Alumina		
Alumina/Glass Infiltrated	400-600	3.8-5.0
Spinel/Glass Infiltrated	325-410	2.4
Tooth Structures		
Dentin	16-20	2.5
Enamel	65-75	1

These are examples of the different directions that have been chosen to improve mechanical properties while maintaining esthetic and economic considerations.

Types of Dental Restorations

The types of restorations involved include:

- Simple Feldspathic Veneers
- Porcelain Jacket Crowns and Bridges
- Metal-Ceramic Crowns and Bridges
- Inlays and Onlays
- Implant Superstructures.

Veneers

The simple veneers are essentially an enamel replacement used mainly for esthetic reasons on anterior teeth. They are approximately 0.5 mm thick and are glued or “bonded” to the tooth using a dental composite resin. They are very reliant on the mechanical integrity of the supporting tooth to provide enough stiffness to prevent loads flexing the restored tooth and exceeding the critical strain limit of the ceramic veneer. In general, dentists are not aware of the flexibility range for teeth and these restorations are often inappropriately used.

Porcelain Jacket Crowns

Porcelain Jacket Crowns are a more extensive restoration. These are used to replace virtually all the enamel component and some dentin. This means that they are almost always supported by dentin in a vital tooth, or cast gold in a non-vital tooth. They are at least 1 mm thick and depending on the system used are either made from a single material, as found in Dicor and IPS Empress crowns or are bilaminar such as In-Ceram® and Procera Crowns. In-Ceram® and Procera® use variations of alumina as a toughened and high strength underlying core to support feldspathic veneering porcelain which gives the final shape and esthetic attributes required for the restoration. In-Ceram® and Procera® are also the only systems that can be used to construct three unit bridges, where missing tooth is replaced using the adjacent teeth as abutments.

Metal-Ceramic Restorations

Metal-ceramic restorations as described earlier use an alloy, originally based on gold, to form a tough and rigid base for the veneering ceramic. This ceramic usually contains leucite as a coefficient of thermal expansion modifier to reduce stress between the metal and ceramic during the firing process. The modern versions are now using finer and denser dispersions of leucite to improve mechanical properties for wear and flexural strength.

Inlays and Onlays

Inlays and onlays are made from a variety of the systems mentioned above, with no real preference, although systems containing dispersions of leucite seem to be gaining ground.

General Discussion

Implant superstructures can be made using the metal-ceramic systems or the alumina based ceramic systems.

Despite the substantial improvements in the mechanical properties of dental ceramics there is still an unacceptable degree of failure of these materials in service. These failures often arise because of the dentists and technicians attempts to achieve esthetic design, particularly of complex multi-tooth bridges. Other failure mechanisms are due to impact failure from opposing teeth or high localized stresses due to hard particulates caught between the teeth, poor adhesion between the ceramic and the underlying tooth or metal support. There is still considerable scope for the further improvement of dental ceramics but not without very careful consideration of the esthetics and simplicity of fabrication.

2016 Advancements in Dental Ceramics

In a 2016 published article, titled *Advancements in All-Ceramics for Dental Restorations and Their Effect on the Wear of Opposing Dentition*,” in European Journal of Dentistry, the authors: Haroon Rashid, Zeeshan Sheikh, Syed Misbahuddin, Murtaza Raza Kazmi, Sameer Qureshi, and Muhammad Zuhaib Uddin share their research that:

“Despite the recent technological advancements, there has not been a valid in vivo method of evaluation involving clinical wear caused due to ceramics upon restored teeth and natural dentition...[though] some advancements have been made to re-enforce these materials with crystalline materials. Regarding sintered ceramics, porcelain can also be reinforced using alumina and magnesia, it can be re-enforced into dental ceramics by a mechanism termed as ‘dispersion strengthening.’ Zirconia can be re-enforced into conventional feldspathic porcelain to achieve highest levels of strength. This mechanism of incorporating zirconia is termed as ‘transformation toughening.’ Zirconia stabilized with yttria has high fracture toughness, strength, and thermal shock resistance. It has decreased translucency and low fusion temperature. Majority of zirconia re-enforced ceramics are radio-opaque, and copings are required to be veneered for better esthetic outcomes.”

When discussing the process of strengthening in glass ceramics, the authors explain:

“[In the] crystallization of glass to form “tetra-silicic fluoromica crystals” the procedure of crystal growth and nucleation is termed as ceramming. These crystals lead to increase in strength, abrasion resistance, fracture toughness, and chemical durability of the material.”

The authors continue:

“Until recently, Ivoclar Vivadent developed two more [pressable] ceramics named as IPS e.max-Press and IPS e.max. IPS e.max-Press is processed in the laboratory with pressing equipment which provides very high accuracy of the restoration fit. The microstructure of this material can be distinguished as needle-like disilicate crystals which are embedded into a glass matrix. The flexure strength of IPS e.max-Press is more as compared to IPS Empress.

Lastly in regards to advancements in machined ceramics, the authors reveal:

“The development of computer-aided design and computer-aided machining method for the fabrication of inlays, onlays, crowns, and bridges has lead us to the development of next generation of machinable ceramic material. The crowns fabricated using these systems can be delivered to the patient in a single appointment since these are made chair-side. There are several drawbacks which include the expense of the equipment used, and also the process requires a high level of expertise. If a zirconia coping is to be used, the color difference between the core of zirconia and adjacent tooth must be matched using a specific layering technique for the veneering ceramic, and appropriate shade selection technique should be practiced.”

Conclusion

This review, while seemingly quite technical in nature, barely scratches the surface of the complex aspects of the physics and chemistry involved in dental ceramics. This course is intended to be a review for the dentist and an introduction for staff who may want more technical knowledge. Dental ceramics is a fascinating blend of science, biochemistry, physics, casting techniques, and the wide array of restorations available in modern dentistry. The horizon will never be reached, as there will always be room for dental ceramics to improve alongside ever-changing technological advances.

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Course Test: Dental Ceramics

1. Which of the following is not an essential constituent of potter's clay?
 - a. Feldspar.
 - b. Glass.
 - c. Quartz.
 - d. Kaolinite.

2. Water's main function in clay is to:
 - a. Hydrate feldspathic substances.
 - b. Break down kaolinite into gibbsite and silica.
 - c. Reduce friction between clay particles.
 - d. Create alkaline metal oxides from the non-hydrous fluxes.

3. Sintering means:
 - a. Shock cooling of molten glass to make frits.
 - b. The molecular bonding of ceramic particles below their melting point.
 - c. Melting of non-refractory clay constituents.
 - d. Condensation of constituent particles to form greenware.

4. Which of the following statements is false?
 - a. Stoneware is harder than earthenware, because it contains more feldspar.
 - b. Earthenware is porous and requires glaze to make vessels waterproof.
 - c. Dental porcelains contain no aluminum oxide.
 - d. Domestic porcelain is made from short clay.

5. Fluxes in glass:
 - a. Are alkaline, metallic oxides.
 - b. Disrupt the crystalline structure of silica.
 - c. Raise the melting temperature of feldspar.
 - d. None of the above.

6. Earthenware clay contains little feldspathic glass which binds particles together and fills pores between sintered alumina and silicon particles.
 - a. True.
 - b. False.

7. In porcelain, kaolin causes lack of translucency. By 1938, little or no kaolin was left in porcelains chosen for dental use.
- True.
 - False.
8. When clay melts at high temperature, it consists of the following constituents:
- Feldspathic glass.
 - Glass from kaolinite.
 - Refractory alumina and quartz crystals.
 - All of the above.
9. Quartz is feldspathic.
- True.
 - False.
10. Refractory particles create a skeletal structure throughout the clay piece helping it to maintain its original shape.
- True
 - False
11. Refractory skeletal structures are made of particles of:
- Alumina.
 - Silica.
 - Alumina and silica.
 - All the above.

12. Porcelain clays are very short and difficult to throw.
 - a. True.
 - b. False.

13. Issues facing dental ceramics fabrications:
 - a. Biocompatibility
 - b. Esthetics
 - c. Durability
 - d. all of the above.

14. Tooth structure is harder than porcelain.
 - a. True
 - b. False

15. A veneer can be bonded to tooth structure or a metal subframe.
 - a. True
 - b. False