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RESEARCH ARTICLE

METAL FREE CERAMICS: A REVIEW.

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Abstract

For the last ten years, the application of high-technology processes to dental ceramics allowed for the development of new materials such as heat-pressed, injection-molded, and slip-cast ceramics and glass-ceramics. To select the most appropriate type of all-ceramic system for clinical use, the clinician must be familiar with the differences between systems. High-strength all-ceramic systems for fixed partial dentures (FPDs) are available for replacing a missing tooth. New core/framework materials have been developed and have evolved in the last decade. With the advancement of CAD/CAM technology, various fabrication techniques have been developed for fabricating improved, consistent, and predictable restorations in terms of strength, marginal fit, and esthetics and for managing core/framework materials that could not otherwise be managed. Concepts on the structure and strengthening mechanisms of dental ceramics are provided. The purpose of the present paper is to review advances in new materials and processes available for making all-ceramic dental restorations.

Introduction:-

Dental ceramics are known for their natural appearance and their durable chemical, mechanical and optical properties. The word "ceramic" is derived from the Greek word "Keramos" which means "burnt stuff".[1,2] A ceramic is an earthy material, usually of a silicate nature and may be defined as a combination of one or more metals with a non-metallic element, usually oxygen.[3]

All ceramics are characterized by their refractory nature, hardness, susceptibility to brittle fracture and chemical inertness. Chemical inertness is an important characteristic as it ensures that the surface of dental restorations does not release potentially harmful elements, and it reduces the risk for surface roughening and an increased susceptibility to bacterial adhesion over the time. Two other important attributes of dental ceramics are their potential for matching the appearance of natural teeth and their insulating properties.

Ceramics have been used from the medieval period. Feldspathic porcelains with reliable chemical bonding have been used in metal ceramic restorations for more than 35 years. Since the introduction of aluminous porcelain jacket crowns in early 1900s, development in both the composition of the ceramics and the methods of forming the core of all ceramic crowns have greatly enhanced our ability to produce more accurate and fracture resistant jacket crowns made entirely of ceramic material. The introduction of CAD/ CAM systems for the production of machined inlays, onlays, veneers, and crown led to development of a new generation of ceramics that are machinable. Direct bonding

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of ceramic crowns, veneers and inlays to conservative tooth preparations using low viscosity resin cements is now common practice.

There is a bright future for dental ceramics because of increased demand for tooth-colored restorations. The purpose of the present paper is to review the new materials and processes available for all-ceramic dental restorations.

I. Conventional Powder Slurry Ceramics:-

These products are supplied as powders to which the technician adds water to produce slurry, which is build up in layers on a die material to form the contours of the restoration. The powders are available in various shades and translucencies and are supplied with characterizing stains and glazes. E.g, Optec HSP, Duceram LFC, Finesse, Cerinate, Ceramco, Mirage and Vita VMK.

Optec HSP:-

Optec ceramic is a Leucite – reinforced feldspathic porcelain that is condensed and sintered like aluminous porcelain and traditional feldspathic porcelain. The leucite crystals are dispersed in a glassy matrix by controlling their nucleation and crystal growth during the initial production of the porcelain powder. Because of its increased strength, Optec HSP does not require a core, when used to fabricate all ceramic restorations as is necessary with aluminous porcelain jacket crowns. The body and incisal porcelains are pigmented to provide the desired shade and translucency. This type is recommended for inlays, onlays, low stress crowns and veneers.[4]

Duceram LFC:-

This is relatively new category of restorative material, referred to as "hydrothermal low-fusing ceramic." It is composed of an amorphous glass containing hydroxyl ions. This noncrystalline structure has greater density, higher flexural strength, greater fracture resistance and lower hardness than feldspathic porcelain, causing less abrasion against tooth structure than leucite containing systems.[4]

Finesse:-

The firing temperature of Finesse is 760^0C which is lower than that of conventional porcelain. The reduction of the fusion temperature allows for increased opalescence in the enamel porcelain. It also permits the clinician to generate a highly polished surface at chairside, thereby eliminating the need for reglazing after possible adjustments. The low-fusing porcelain offers considerably less potential for abrading any materials against which it occludes.

Cerinate:-

It is feldspathic ceramic that contains aluminous oxide. It is indicated for veneers crowns and inlays.

Mirage:-

It is a feldspathic ceramic that contains zirconium oxide fibers.

Ceramco:-

It is a feldspathic ceramic.

Vita VMK:-

VMK 95 is the latest generation ceramic from Vita. It is used for the fabrication of crowns veneers and bridges.

Alumina Reinforced Porcelain:-

The sintering of $A1_20_3$ powder is a solid-state sintering process that involves material transport by diffusion. The dental porcelain used had a thermal expansion adapted to alumina, and the bonding of porcelain to alumina is of a chemical nature, probably an ionic bond. Aluminous core porcelain is a typical example of strengthening by dispersion of a crystalline phase. Its dispersion in a glassy matrix of similar thermal expansion coefficient leads to significant strengthening of the core. Hi-Ceram is a more recent development of this technique.[5] Aluminous core porcelain is now baked directly onto a refractory die. The demerits of this ceramic included internal surface microcracks which are caused by the inability to adequately wet the foil, limited to anterior tooth replacement, limited ability to create multiple units and laboratory technique sensitive.

Slip Casting Technique:-

Alumina-based (In-Ceram):-

ln-Ceram is a slip-cast aluminous porcelain. The alumina-based slip is applied to a gypsum refractory die designed to shrink during firing. The alumina content of the slip is more than 90%, with a particle size between 0.5 and 3.5 micrometers. After being fired for four hours at 1100°C, the porous alumina coping is shaped and infiltrated with a lanthanum-containing glass during a second firing at 1150°C for four hours. After removal of the excess glass, the restoration is veneered with matched expansion veneer porcelain. This processing technique is unique in dentistry and leads to a high-strength material due to the presence of densely packed alumina particles and the reduction of porosity. These restorations provide an accurate fit. Because of the opaque alumina core, the translucency of the final restoration may not be as lifelike as that seen with other systems. Two modified porcelain compositions for the Inceram technique have been recently introduced. In-Ceram Spinell contains a magnesium spinel ($MgAl_2O_4$) as the major crystalline phase with traces of alpha-alumina, which seems to improve the translucency of the final restoration. The second material contains tetragonal zirconia and alumina. A variety of alumina-glass dental composites can be prepared by the glass-infiltration process. However, research has shown that the fracture toughness of the composites is relatively insensitive to the volume fraction of alumina in the range investigated.[5]

Pressable Ceramics:-

These products are melted at high temperatures and pressed into a mold created using the lost-wax technique. The pressed form can be made to full contour, or can be used as a substrate for conventional feldspathic porcelain buildup. The flexural strength has been shown to improve under subsequent heat treatments as a result of the growth of additional leucite crystals. IPS empress is a pressable ceramic used for fabrication of all ceramic restorations. They are available as ingots of various shades and are manufactured in a pre-cerammed condition. They are casted pneumatically using lost wax method (high temperature injection molding technique). They are basically reinforced with either leucite or lithium di-silicate. The main advantage of IPS empress is its lack of metal, moderate flexural strength, excellent fit and excellent esthetics. The main disadvantages are its high potential for fracture and need for special armamentarium.[6]

Lithium Disilicate Reinforced Pressable Ceramic:-

(IPS Empress Cosmo Glass Ceramic, IPS Empress Post)

The Empress II system uses a lithium-disilicate glass core material and also contains ZrO_2. The framework is fabricated with either the lost-wax and heat-pressure technique or is milled out of prefabricated blanks. Various types of tests measuring the flexural strength of the framework material demonstrated a range of 300-400 MPa. Fracture toughness describes the resistance of brittle materials to the catastrophic propagation of flaws under an applied stress. For the lithium disilicate core material, the fracture toughness (KIC) ranges between 2.8 and 3.5 $MPa/m^{½}$.[7] They are mainly used for post and core purposes and replacing teeth anterior to premolars.

Leucite Reinforced IPS Empress:-

Leucite (K_2O-Al_2O_3-$4SiO_2$) is a mineral formed by incongruent melting of feldspar (K_2O-Al_2O_3-$6SiO_2$). They increase thermal expansion of conventional porcelain used for metal ceramic restoration. But they are used as reinforcing material in IPS empress is reinforced with leucite in amounts varying from 35-55%.[8] The high concentrations of leucite crystals increase the resistance to crack propagation. The dispersion of leucite becomes homogenous in glass matrix after pressing. The leucite content is higher than used in conventional dental porcelains. The fine pressed ceramic consists of leucite crystals 1-5 um in size and dispersed in a glassy matrix.[4]

Optec Pressable Ceramic:-

Optec OPC is also a type of feldspathic porcelain with increased leucite content, processed by molding under pressure and heat. The OPC system can be used for full-contour restorations (inlays, veneers, full crowns). Alternatively, it can be used as a core material, which is veneered using conventional powder- slurry techniques with a high-leucite-content feldspathic porcelain, similar to Optec HSP porcelain. Because of its high leucite content, it causes higher abrasion of natural teeth than that of conventional feldspathic porcelain. Optec OPC produces strong, translucent, dense and etchable ceramic restorations which are useful in fabricating ceramic veneers.[4]

V. Glass Infiltrated Ceramics:-

The conversion of a glass to a glass ceramic is essentially a two-stage process involving the formation of nuclei and the further growth of crystals upon these nuclei, and is accomplished by following a heat treatment schedule. This process is achieved by first heating the glass to a temperature appropriate to the formation of nuclei, which may be some 20°C to 80°C higher than the annealing point. The time given for nucleation depends mainly on the viscosity-temperature relationship for the glass and may vary from five minutes to several hours. After nucleation, the temperature is raised slowly to the crystal growth temperature. The rate of heating must be sufficiently slow to allow the developing crystals to form a skeleton, thereby preventing deformation. The glass ceramic is then allowed time to develop crystals and finally cooled slowly to prevent cracking.

Major Glass-Ceramic Systems:-

β-spodumene glass ceramics:-

Extensive use of glass ceramics based on the crystallization of the low-expansion crystal phase 3-spodumene solid solution ($Li_2O.Al_2O_3.nSiO_2$) has been made, particularly for cookware and counter-top cooking surfaces.

β-quartz glass ceramics:-

Although chemically very similar to the β-spodumene glass ceramics, the materials comprised mainly of 3-quartz solid solution crystals are ultra fine-grained and very low in thermal expansion.

Cordierite glass ceramics:-

This nonalkali glass ceramic combines good electrical resistivity with high mechanical strength and moderately low thermal expansion. The phases produced by heat treatments in excess of 1200^0C are primarily cordierite, rutile, magnesium aluminum titanate, and cristobalite.

Mica glass ceramics:-

A family of nonporous, machinable materials has been developed based on the crystallization of a number of fluorine-containing mica crystals. Glass ceramics with unique microstructures have been obtained through the growth of plate like crystals within a glass matrix. These micas include fluorphlogopite $KMg_3AlSi_3O_{10}F_2$, potassium tetrasilicic mica KMg and nonalkali micas (Ca, Sr, Ba) 0.5 $Mg_3AlSi_3O_{10}F_2$.[5]

Lithium disilicate or photosensitive glass ceramics:-

This ceramic was developed by overheating a photosensitively opacified glass which resulted in the formation of an opaque polycrystalline ceramic with improved mechanical, electrical, and chemical properties. The glass contains CeO_2 as a sensitizer and silver metal as a nucleation catalyst.

Lithium disilicate and Apatite Glass Ceramics:-

In order to be able to extend the use of resin-bonded ceramic restorations and possibly use them for bridge constructions, a glass ceramic based on a SiO_2-Li_2O system has been developed (Empress II, Ivoclar-Vivadent, Schaan, Liechtenstein).[9] The glass ceramic is claimed to be highly translucent due to the optical compatibility between the glassy matrix and the crystalline phase, which minimizes internal scattering of the light as it passes through the material. The processing route is the same as the hot-pressing route described above, except that the processing temperature, at 920^0C, is lower than for the leucite glass ceramic.[5]

Fluoromica Glass Ceramics:-

Fluoromicas are products based on the composition $SiO_2.K_2O.Mg0.Al_2O_3.ZrO_2$, with the addition of some fluorides to impart fluorescence in the prostheses, in a way similar to that encountered in the natural dentition. Mechanical property measurements suggest the flexural strength is in the region of 120-150MPa, which, when combined with the adhesion to tooth tissues, may just be adequate for posterior crowns but is insufficient for the construction of all-ceramic bridges.

Castable Glass Ceramics:-

These products are supplied as solid ceramic ingots, which are used for fabrication of cores or full contour restorations using a lost-wax and centrifugal-casting technique. Generally, one shade of material is available, which is covered by conventional feldspathic porcelain or is stained to obtain proper shading and characterization of final restoration. E.g. Dicor, Cerapearl, CD-200.[10]

Dicor:-

Dicor is a castable glass ceramic which is a fluorine containing tetrasillicic fluoronica glass ceramic in the pyroceram family of ceramic. A full contour transparent glass crown is casted at 1350^0C, and then it is heat treated at 1075^0C for 10 hours. This heat treatment, which is known as “Ceramming”, causes partial crystallization (55%) of tetrasillicic mica like crystals. The crystals function is two ways, they create a relatively opaque material out of the initially transparent crown and they significantly increase the fracture resistance and strength of the ceramic. These crystals are also less abrasive to opposing tooth structure than the leucite crystals found in traditional feldspathic porcelains. To achieve the appropriate shade, the colorant stains are baked on the surface of the glass ceramic material.[4]

Cerapearl:-

Habo and Kyocera Bioceram group developed a new apatite ceramic in 1985, which is castable and forms apatite crystals after the reheating process. This material cerapearl has a translucency comparable to natural enamel. It is strong enough to resist occlusal forces. Wear of natural enamel and cerapearl is minimal if the occlusion is well balanced. The technique for producing cerapearl restoration is very similar in concept to the Dicor-glass-ceramic system. The calcium phosphate based glass is transformed to partially crystalline body by a controlled heat treatment and then tinted by the application of colored glazes. Formation of the crystalline phase was said to produce a three -fold increase in tensile strength from 50 MPa to 150 Mpa. Refractive index, density, hardness, thermal expansion and thermal conductivity were all found to be similar to natural enamel.

CD-200:-

It is a new glass ceramic, which has been presented as a castable glass ceramic material that is bioinert and has excellent flexural strength and chemical durability. It consists of 50% SiO_2, 10% Al_2O_3, 10% P_2O_5, 20% CaO, and 10 % MgO. To fabricate this material, a vacuum pressure casting machine and ceramic furnace was developed. The technique uses conventional lost wax process. A special investment material that does not react with the cast glass allows the glasses to be crystalized (cerammed) within the ring investment immediately after casting, simplifying the laboratory procedures. Fixed dental restorations fabricated by this material are weaker than Dicor.

Machinable Ceramics:-

CEREC is a dental CAD/CAM machine. This system enables the direct chair side placement of ceramic restoration without auxiliary laboratory support. The CELAY SYSTEM employs a copy-milling machine and uses manufactured porcelain blank's to mill out ceramic inlays, onlays, crowns and bridges. It is a fine-grained feldspathic porcelain that is said to reduce the wear of antagonist tooth structure.[4,5] CAD/CAM is an acronym for Computer Aided Design/ Computer Aided Manufacturing (or Milling). CAD/CAM milling uses digital information about the tooth preparation or a pattern of the restoration to provide a computer-aided design (CAD) on the video monitor for inspection and modification. The image is the reference for designing a restoration on the video monitor. Once the 3-D image for the restoration design is accepted, the computer translates the image into a set of instructions to guide a milling tool (CAM) in cutting the restoration from a block of material.

The different types of ceramic ingots used in the process are as follows:

Cerec Vitablocs Mark I:-

This is a feldspathic porcelain, which was the first composition used with the Cerec system (Siemens). It is similar in composition, strength and wear properties to feldspathic porcelain used for porcelain-fused-to metal restorations.[4]

Cerec Vitablocs Mark II:-

This is a feldspathic porcelain of increased strength and has a finer grain size than the Mark I compositions; this produces less abrasive wear of the opposing tooth structure.[4]

Dicor MGC (Dentsply, L.D. Caulk Division):-

This is a machinable glass ceramic composed of fluorosilicic mica crystals in a glass matrix. It has greater flexural strength than the castable Dicor and the Cerec compositions. This material is softer than conventional feldspathic porcelain and produces less abrasive wear of the opposing tooth structure than Cerec Mark I and more wear than Cerec Mark II.[4]

COMET System (Coordinate Measuring Technique):-

This system allows the generation of a 3-dimensional data record for each superstructure with or without the use of a wax-pattern. For imaging, 2-dimensional line grids are projected onto an object, which allows mathematical reproduction of the tooth surfaces. It uses a pattern digitization and surface feedback technique, which accelerates and simplifies the 3-dimensional representation of tooth shapes while allowing, individual customization and correction in the visualized monitor image.

CICERO System:-
Computer Integrated Crown Reconstruction (Elephant industries). This Dutch system was marketed with the Duret (French) system, Sopha Bioconcept and the Minnesota system (Denti CAD) as the only three systems capable of producing complete crowns and FPDs. The CICERO CAD/ CAM system developed for the production of ceramic fused to metal restorations, makes use of: optical scanning, nearly net-shaped metal and ceramic sintering, computer-aided crown fabrication techniques.

PROCERA System:-
The Procera System is based on the concept of CAD/ CAM to fabricate dental restorations. It consists of a computer controlled design station in the dental laboratory that is joined through a modern communication link to Procera Sandvik AB, where the coping is manufactured with advanced powder technology and CAD/ CAM technique.

Zirconia Based Ceramics:-
Zirconia is a polymorphic material, which is a crystalline dioxide of zirconium that occurs in 3 forms: monoclinic (M), cubic (C), and tetragonal (T). At its melting point of 2680^0C, the cubic structure exists and transforms into the tetragonal phase below 2370 ^{0}C. The tetragonal-to-monoclinic phase transformation occurs below 1170^0C and is accompanied by a 3-5% volume expansion which causes high internal stresses.

Yttrium-oxide (Y 3% mol) is added to pure zirconia to control the volume expansion and to stabilize it in the tetragonal phase at room temperature. This partially stabilized zirconia has high initial flexural strength and fracture toughness. Tensile stresses at a crack tip will cause the tetragonal phase to transform into the monoclinic phase with a localized expansion. The volume increase creates compressive stresses at the crack tip that counteract the external tensile stresses. This phenomenon is known as *transformation toughening* and retards crack propagation. In the presence of higher stress, a crack can still propagate. The toughening mechanism does not prevent the progression of a crack, it just makes it harder for the crack to propagate. Ytrium-oxide partially stabilized zirconia (Y-TZP) has mechanical properties that are attractive for restorative dentistry; namely, its chemical and dimensional stability, high mechanical strength, and fracture-toughness.[5]

Summary:-
As dental ceramic technology is one of the fastest growing areas of dental material research and development, we have discussed all-ceramic systems regarding their processing techniques, strength and wear characteristics. These systems are currently in use by dental laboratories for the fabrication of restorations. Each system has its own merits and demerits. The choice of the most appropriate all-ceramic system depends on the particular clinical situation. The stronger materials should be used in stress bearing situations, and the softer materials should be used in situations in which tooth abrasion may be critical. However, the clinical success will also depend on the further developments in resin-composite luting cements and dentine-bonding agents.

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