REVIEW ARTICLE

Metal Free Ceramics in Dentistry: A Review

Anup Pathrabe[1], Krishnakumar Lahoti[2], Jaykumar R Gade[3]

1- Post Graduate Student, Department of Prosthodontics including removable, fixed, maxillofacial and implantology, Swargiya Dadasaheb Kalmegh Smruti Dental College and Hospital, Nagpur, India. 2- Reader and PG Guide, Department of Prosthodontics including removable, fixed, maxillofacial and implantology, Swargiya Dadasaheb Kalmegh Smruti Dental College and Hospital, Nagpur. 3- Professor and Head of Department, Department of Prosthodontics including removable, fixed, maxillofacial and implantology, Swargiya Dadasaheb Kalmegh Smruti Dental College and Hospital, Nagpur.

Correspondence to:
Dr. Anup Pathrabe, Post Graduate Student, Department of Prosthodontics, Swargiya Dadasaheb Kalmegh Smruti Dental College and Hospital, Nagpur, India.
Contact Us: www.ijohmr.com

ABSTRACT

The demand for metal free ceramics with highly biocompatible dental restorative material has increased during the past decade. The esthetic demands made on dental restorations has resulted in an increased use of dental ceramics. For meeting the requirements of dental materials with improved strength and toughness, various new ceramic materials as well as new techniques have been developed during the past decade. These recent developments have attempted to overcome the principal disadvantages of inherent brittleness and the potential to abrade the opposing dentition by either the use of increasingly complex technology or by the simplification of existing techniques and/ or materials. This review outlines the developments in the evolution of metal free ceramics over the last century and their classification.

KEYWORDS: Metal free ceramic, CAD CAM, porcelain

INTRODUCTION

Ceramics are the earliest group of inorganic material to be structurally modified by man. The word ceramic is derived from the Greek word "keramos" that translates to mean, "burnt earth." It originated from the traditional art of fabricating pottery where mostly clay was fired to create a hard, brittle object.

Dental Ceramics is defined as "An inorganic compound with non-metallic properties typically consisting of oxygen and one or more metallic or semi metallic elements that are formulated to produce the whole or part of a ceramic based dental prosthesis."[1]

Since the introduction of the first successful porcelain fused to metal system in the early 1960's (Weinstein M Katz PFM Patent September 1962), there has been increasing demand for ceramic restorative materials. During 1990s, more than 71% of the estimated 35 million crowns used by the private practicing dentists had porcelain as one of the components.[2] This popularity may be the result of porcelain aesthetics. Historically, strength concerns compromised some of the beauty of porcelain crowns. Porcelain is intermittently brittle & has relatively low tensile strength, it is therefore generally fused to a metal substrate to increase its resistance to fracture.[3] However, this metal base reduces light transmission through the porcelain & creates metal ion discolorations that may affect the aesthetics of the porcelain. In addition, some patients have allergic reactions or sensitivity to various metals. These drawbacks, together have prompted the development of new all-ceramic (metal free ceramic) systems that do not require metal.

The development of all-ceramic systems for dental restorations has been noteworthy in last three decades. New processing techniques such as heat-pressing, slip-casting, and Computer Aided Design-Computer Aided Machining (CAD-CAM) for dentistry have been developed. Concurrently, all-ceramic materials have been developed with higher performance from mechanical point of view to meet all the dental requirements.

HISTORY

Aesthetics and durability of materials in the oral environment has always been a foremost concern to the dentist. Dental technology existed in Etruria since 700 BC and through Roman 1st century BC but remained undeveloped until 18th century.

Artificial teeth were made from animal products such as ivory, teeth or bone. It was first prepared by Ambroise Pare in 1562. Their tendency to deteriorate and disintegrate in the mouth and absorb stains and odor makes them unsuitable for use.

Ceramics originally referred to as art of fabricating pottery. The word ceramic comes from the Greek term "KERAMOS", meaning "A POTTER" or "POTTERY."

It's considered that this word is realized with a Sanskrit term meaning "BURNED EARTH," since the components were clay from the earth, which was heated to form pottery (Friedmann 1991).[4]

After decades of effort, Europeans mastered the art of manufacturing fine translucent porcelain, comparable to the porcelain of Chinese by 1720. This resulted in promulgation of data about the fundamental aspects of porcelain: Kaolin and Feldspar.[4]

In 1723, enameling of metal denture bases was formulated by Pierre Fauchard, who initiated research in

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porcelain that imitates color of the teeth and gingival tissue.

In 1774, a French pharmacist Alexis Duchateau with collaboration of a dentist named Nicholas Dubois De Chemant continually improved porcelain composition based on "green" traditional porcelain (50% Kaolin clay, 25% Feldspar and 25% Silica or Quartz).

In 1808, Giuseppangelo Fonzi, Italian dentist introduced individually formed porcelain teeth that contain embedded platinum pins known as TERROMETALLIC IN-CORRUPTIBLES.[4]

Improvement in translucency and color of dental porcelain was noticed via developments that ranged from preparations of Elias Wildman in 1838 to vacuum firing in 1949.

Glass inlays (not porcelain) were introduced by Herbst in 1882 with crushed glass frit fired molds made of plaster and asbestos.[5]

In 1885, Logan fixed the retention problem experienced between porcelain crown and post that were commonly made of wood by fusing the porcelain to platinum post (Richmond crown). These crowns represent the first innovative use of metal ceramic system.[5]

In 1886, combining burnished platinum foil like a substructure with the high controlled heat of a gas furnace. C.H.Land introduced first fused feldspathic porcelain crowns and inlay.[5]

Refinements in the metal ceramics systems dominated dental ceramic research during the past 35 years that resulted within enhanced alloys, porcelain metallic bonding, as well as porcelains.

In spite of aesthetic advantage, all porcelain crown systems did not get popularity because the main disadvantage of early restorations was their low strength. This necessitates use of ceramic restorations in low-stress situations such as anterior teeth. But still fractures of restorations were common, which led to the introduction of higher strength materials.

High strength ceramics are developed in two ways. In the first approach 2 ceramic materials were used to fabricate the restoration. Non-aesthetic high strength core material is veneered with a lower strength aesthetic material. The second approach is to develop a ceramic that combines good aesthetic with high strength.

The popularity of all ceramic systems increased after the introduction of alumina reinforced dental porcelain. McLean and HUGHES in 1965 were the first to introduce high strength porcelain into dentistry. They advocated the introduction of glass-alumina composites. By improving the fabrication technique of alumina core, the technique was further developed. In this technique, porous alumina was fused with a specially formulated glass by a process called slip casting. By this process material strength was increased by 3 to 4 times as compared to earlier alumina core material. This material was named as INCERAM (1988).

In 1980's, 'Shrink free' all ceramic crown systems were introduced. E.g. CERESTORE (1983: Cerestore injection – molded core by Sozio and Riley).[4,6,7]

CLASSIFICATION

Metal free ceramics can be broadly classified as:

Based on composition and fabrication:

1. Conventional (powder-slurry) ceramics;
2. Castable ceramics;
3. Machinable ceramics;
4. Pressable ceramics;
5. Infiltrated ceramics.

Based on the presence of specific attributes within their formulation:

1. Glass-matrix ceramics
2. Polycrystalline ceramics
3. Resin-matrix ceramics

Based on composition and fabrication:

1. Conventional (powder-slurry) ceramics: These products are available in powder form to which water is added by the technician to produce slurry. In order to form the contours of the restoration, slurry is built up in layers on a die. The powders supplied with characterizing stains and glazes are available in different shades and translucencies.

a. Duceram LFC[8]

It's a low fusing hydrothermal ceramic consists of an amorphous glass containing hydroxyl (-OH) ions. Based on the ideas and studies on industrial porcelain ceramic from the early 1960's, Duceram LFC was developed in mid-1980's and for the first time marketed in 1989 for use in all ceramic prostheses, ceramic/ metal-ceramic inlay, and partial crowns.

It has greater density, higher flexural strength, greater fracture resistance and lower abrasion than feldspathic porcelain. The restoration is made in two layers. The base layer is Duceram MC (Duceram Metal Ceramic); containing Leucite, followed by the veneer - Duceram LFC (Duceram Low Fusing Ceramic). Duceram MC is condensed on a refractory die using conventional powder slurry technique and sintered at 930^{o}C. Duceram LFC is condensed with this base layer and sintered at 660^{o}C. Being highly polishable they do not require glazing.

b. Optec HSP[9]

It is a leucite reinforced feldspathic porcelain which is condensed and sintered like aluminous and traditional feldspathic porcelain over a refractory die rather than platinum foil. Its moderate strength is derived from the nucleation and growth of fine dispersion of a higher volume fraction of leucite crystals. In spite of the rise in crystallization, the material retains its translucency apparently as a result of closeness of the refractive index of leucite with that from the glass matrix.

2. Castable ceramics: These products are supplied as solid ceramic ingots, which are used for fabrication of cores or full-contour restorations using a lostwax and centrifugal casting technique. The material is generally available in single shade which is either covered by conventional feldspathic porcelain or stained for achieving proper shading and characterization of the final restoration.

a. Dicor
The first commercially available castable glass-ceramic material for dental use was developed by 'The Corning Glass Works' (Corning N.Y.) and marketed by Dentsply International (Yord, PA, U.S.A). The term "DICOR" is derived from the combination of manufacturer's names: Dentsply International & Corning glass.

Dicor will be castable polycrystalline fluorine containing tetrasilic mica glass-ceramic material, initially cast as a glass by a lost-wax technique and subsequently heat - treated resulting in a controlled crystallization to produce a glass - ceramic material.

b. Cerapearl
It contains a glass powder distributed in a vitreous or non-crystalline state. The wax pattern of the proposed restoration is invested in exclusively developed phosphate-bonded high heat investment (CTE to match Cera Pearl's casting shrinkage of 0.53%). Following burnout, the investment is transferred to an especially designed automatic casting machine. The Cera Pearl crystals (8-10gms) are placed in the ceramic crucible, melted under vacuum (1460^{o}C) and casted (1510^{o}C) in the mold. Annealing is done after one hour in an automatic furnace to release the inner stresses of the cast structure. The investment material around the cast structure is removed by sandblasting (25-30um Al_2O_3 beads) and ultrasonically washed. Properties of cerapearl are similar to natural enamel in composition, density, refractive index, thermal conductivity, coefficient of thermal expansion and hardness.

3. Machinable ceramics: These products are supplied as ceramic ingots in various shades and are used in computer aided design - computer aided manufacturing, or CAD-CAM, procedures. The machined restoration can be stained and glazed to obtain the desired characterization.

a. **Digital Systems (CAD/ CAM):**
To automate the fabrication of the equivalent of cast restorations, Computer aided design and computer aided manufacturing (CAD/ CAM) technologies have been combined into a whole system. By using digital information about the tooth preparation or a pattern of the restoration a computer-aided design (CAD) is created on the video monitor for inspection and modification. The image acts as reference for designing a restoration on the video monitor. After acceptance of 3-D image for the restoration design, the computer translates the image into a set of instructions to guide a milling tool (computer-assisted manufacturing [CAM]) in cutting the restoration from a ceramic block.

i. Direct:
Cerec System[10,11]
The CEREC (Ceramic Reconstruction) system (Siemen/sirna corp.) was originally formulated by **Brains A.G.** in Switzerland and first demonstrated in 1986 but have been repeatedly described since 1980. Defined as *CEREC* CAD/CAM *system*, it had been produced in West Germany and marketed by the Siemens group (Fig 1).

Figure 1: Cerec System

ii. Indirect:
The Duret System (Hanson International)[10,12]
The Duret CAD-CAM system was formulated by **Francois Duret** and produced by **Sopha (Lyon, France)**.

CICERO System
The computer integrated crown reconstruction (Elephant industries) was only marketed with the three systems resourceful of producing finished crowns and FPDs, namely Duret (French) system, Sopha Bioconcept and the Minnesota system (Denti CAD).

COMET System[13,14]
This system generates a 3-dimensional data record for each superstructure with or without the use of a wax pattern. For creating images, 2-dimensional line grids are focused on the object to produce mathematical reproduction of the tooth surfaces. By using pattern digitization and surface feedback technique, it accelerates and simplifies the 3-dimensional representation of tooth shapes while allowing individual customization and correction in the visualized monitor image.

b. Analogous systems (Copying methods):
It is the mechanical shaping of an industrially prefabricated ceramic material, which has consistent quality and improved mechanical properties. In this method after taking the impression, model is prepared for fabrication of a prototype (pro-inlay or crown). Based on the model, a replica of inlay/ crown is made. It is then fixed in the copying device and transferred 1:1 into the selected material such as ceramic.

i. Sono erosion:[15]
It is based on ultrasonic methods. First, metallic negative moulds (so-called *sonotrodes*) of the desired restoration

are produced, both in the occlusal as well as basal direction. After connecting to an ultrasonic generator, both sonotrodes fitting exactly together in the equational plane of the selected restoration are guided under slight pressure onto a ceramic blank. This ceramic blank is surrounded by an abrasive suspension of hard particles, such as boron carbide, which are accelerated by ultrasonics thus erosion of the restoration takes place from the ceramic blank.

ii. Spark Erosion:[15,16]
It refers to *'Electrical Discharge Machining*' (EDM). During 1940's it was mostly used by tool and die industries and later on adapted into dentistry in 1982. In this process under carefully controlled conditions, by using a series of sparks, material is removed from a work place by erosion in a liquid medium. Generally the liquid medium is light oil called the '*dielectric fluid.'* It functions as an insulator, a conductor, and a coolant and flushes out all the particles of metal generated by the sparks.

4. Pressable ceramics: Also supplied as ceramic ingots, 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.

a. IPS EMPRESS
It's a pre-cerammed, pre-coloured leucite reinforced glass-ceramic formed in the leucite system (SiO_2-AI_2O_3-K_20) by controlled surface crystallization, subsequent process stages, as well as heat treatment. It was first described by **Wohlwend & Scharer**; and promoted by Ivoclar (Vivadent Schaan, Liechtensein). In this process, a crucible former is placed on the base of a specialized automated furnace (EP 500 Press furnace) provided with a alumina plunger & heated at 850°C. The ceramic ingot of the selected dentinal shade is placed under the plunger and preheated at 1,100^{0}C (temperature at which the ceramic plasticizes). When the temperature reaches 1150^{0}C, after holding for 20 minutes, the plunger presses the ceramic into the mold under a vacuum of 0.3-0.4 MPa. It is held under pneumatic pressure for 45 minutes to allow for complete and accurate filling of the mold. Then veneering is done by staining or layering technique.

b. OPTEC (Optimal Pressable Ceramic/OPC):[1,14]
Optec represents for Optimal Technology. It is a form of feldspathic porcelain with additional leucite content built to press restorations using leucite-reinforced ceramic in the pressing furnace that doubles compared to a conventional porcelain furnace. The manufacturer claims that the crystalline leucite particle size has been reduced with a more homogenous distribution without reducing the crystalline content, and the increased leucite content has resulted in an overall increase in flexural strength of OPC (over 23,000 psi and compressive strength upto 187,320 psi). However, due to its high leucite content, it could be expected that its abrasion against natural teeth will probably be higher compared to conventional feldspathic porcelain. Fabrication is however similar to IPS Empress.

c. IPS EMPRESS 2 (Ivoclar)[1]
It's a second generation of pressable materials for all-ceramic bridges. It is made of a lithium disilicate framework having an apatite layered ceramic. The glass-ceramic ingots are manufactured from lithium silicate glass crystals with crystal content greater than 60% by volume. The apatite crystals incorporated are mainly responsible for the improved optical properties (translucency, light scattering) which give rise to the unique chameleon effect of leucite glass-ceramic materials.

5. Infiltrated ceramics: These products are supplied as two components: a powder (aluminum oxide or spinel) fabricated into a porous substrate and a glass infiltrated into the porous substrate at high temperature. The infiltrated ceramic will then be veneered while using conventional feldspathic porcelain technique.

a. In–ceram Alumina
Aluminum oxide (Al_2O_3) is most widely known as corundum. As a result of the homogeneous framework structure made from ultrafine Al_2O_3 particles, whose cavities are filled up with a special glass, the degree of tensile bending strength is significantly higher compared to all other ceramic systems. Synthetically produced corundum having a grain sized 2–5 um is used for In-Ceram alumina. In the solid phase, it's sintered at 1100°C, well below the melting point of 2040°C, after which infiltrated with dentine-colored glass at 1120°C.

b. In-Ceram Spinell (Vita Zahnfabrik)[1,9,14]
Optical properties may be improved by modification of the slip. Introduction of magnesium aluminate ($Mg\ Al_20_4$) leads to the improved optical properties characterized by increased translucency about 25% decrease in flexural strength. Spinel or Magnesium aluminate ($Mg\ A1_2O_4$) is a composite containing Al_2O_3 and Mg_2O (a natural oxide of $Mg^{2+}\ AI^{3+}$).

c. In-Ceram Zirconia (VitaZahnfabrik)[1,9]
The In-Ceram technique was improved to include its modified form with zirconia. Using a combination of zirconium oxide/ aluminium oxide being a framework material, the physical properties were improved without sacrificing the proven working procedure. The In-Ceram Zirconia material has a high flexural strength (2 to 3 times the impact capacity and 1.4 times the stability as compared to ln-Ceram Alumina), excellent marginal accuracy and biocompatibility. According to the manufacturer, this system allows fabrication of all-ceramic bridges even in the posterior molar area.

Based on the presence of specific attributes within their formulation:

1. **Glass-matrix ceramics:** nonmetallic inorganic ceramic materials which contain a glass phase
2. **Polycrystalline ceramics:** nonmetallic inorganic ceramic materials that won't contain any glass phase.

3. **Resin-matrix ceramics:** polymer-matrices were containing predominantly inorganic refractory compounds that could include porcelains, glasses, ceramics, and glass-ceramics.

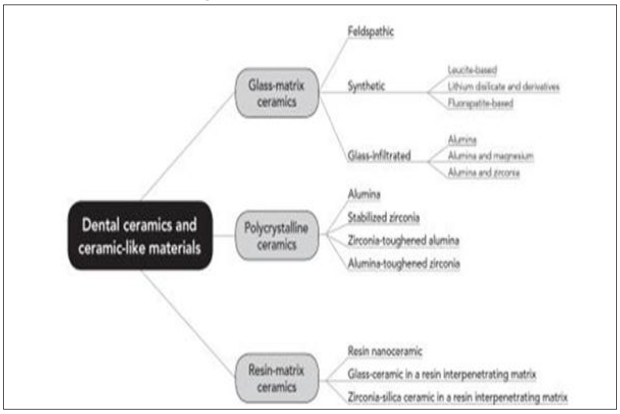

Figure 2: Classification based on the presence of specific attributes within their formulation

SUMMARY

For the past 200 years, ceramics have domain the field of dentistry. Their desirable features include their biocompatibility and their appearance. They can be customized to simulate the color, translucency and fluorescence of natural tooth. But their low fracture toughness is one of the major drawbacks. Furthermore, they exhibit large firing shrinkage.

Various metal free ceramic systems have been discussed. Stronger materials should be used in stress bearing circumstances, and the softer materials should be used where tooth abrasion is critical. The esthetic results of these crowns can be brought to the fullest in the hands of a trained and a skilled dentist. The merit of these systems over a long span is yet to be proven.

Advancement in the metal free ceramic systems like the IPS EMPRESS 2 has resulted in a functionally durable metal free ceramic restoration.

Finally, advancements in CAD-CAM has resulted in the restoration with esthetics, strength, and ease of fabrication done in a single visit. The only disadvantage with the CAD/CAM system is the occlusion with the opposing tooth, which requires manual refinement at present. But with the advent of newer software and advancement in systems, this minor hiccup is expected to be solved in the near future resulting in a restoration that is functionally durable, aesthetically excellent with accurate margins and low wear on the opposing teeth, more significantly, less technique sensitive with ease of fabrication and less time consuming.

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