# **Evolution of metal-free ceramics**

**Review Article** 

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# ABSTRACT

The focus of dentistry in the present times is not only on the prevention and treatment of disease but also on meeting the demands for better esthetics. Thus, dentistry has evolved from a curative to a creative science in a very short span and the evolution of ceramics has fastened this shift. This article presents a brief history of dental ceramics and an in-depth analysis of "all ceramic" systems.

KEY WORDS: CAD/CAM ceramics, feldspathic porcelain, glass ceramics

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# **INTRODUCTION**

It could be said that the ceramic material known as porcelain holds a special place in dentistry because it is still considered to produce esthetically the most pleasing result. Its color, translucency, and vitality cannot as yet be matched by any materials except other ceramics.

As people retain their teeth for much longer than in the past, the need for esthetically acceptable restorations is continuing to increase. This is reflected in the growing use by dentists of restorative procedures using ceramics. Its traditional use is in the construction of artificial teeth for dentures, crowns, and bridges. More recently, the use of ceramics has been extended to include veneers and inlays/onlays. The construction of such restoration is usually undertaken in dental laboratories by technicians skilled in the act of fusing ceramics.

Dental ceramics are the most suitable tooth colored restorative material. It is the most durable of the esthetic materials, impervious to oral fluids and biologically compatible. It is chemically indestructible in oral environment.<sup>[1]</sup>

Of all materials used in dentistry to restore the natural dentition, ceramics have by far the best optical

properties to mimic the tooth structure in appearance translucency; light transmission and biocompatibility give dental ceramics highly desirable esthetic properties.

# **HISTORY OF DENTAL CERAMICS**

Dental technology existed in Etruria as early as 700 BC and during Roman 1st century BC but remained undeveloped until the 18th century.<sup>[2]</sup>

Materials used for artificial teeth in the 18th century were:

- 1. human teeth;
- 2. animal teeth carved to the size and shape of human teeth;
- 3. ivory and
- 4. mineral or porcelain teeth.

The use of mineral teeth or porcelain dentures greatly accelerated an end to the use of human and animal teeth.

Feldspathic dental porcelain was adapted from European triaxial white ware formulations (clayquartz-feldspar).

After decades of effort, Europeans mastered the manufacture of translucent porcelain, comparable to

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the porcelain of Chinese by 1720. The use of feldspar to replace lime and high firing temperature are both critical developments.  $^{\left[2\right]}$ 

In 1723, enameling of denture metal bases was described by Pierre Fauchard in Le Chirur Gien Dentisle. He was credited with recognizing the potential of porcelain enamels and initiating research with porcelain to imitate color of teeth and gingival tissues.<sup>[3]</sup>

In 1774, a Parisian apothecary Alexis Duchateau with assistance of a Parisian dentist Nicholas Dudois De Chemant continually improved porcelain formulations. In England, Dudois De Chemant procured supplies in collaboration with Josiah Wedgwood.<sup>[2]</sup>

In 1808, Giuseppangelo Fonzi of Paris introduced individually formed porcelain teeth that contained embedded platinum pins known as "terro-metallic in-corruptibles" and their esthetic and mechanical versatility provided major advance in prosthetic dentistry.<sup>[2,4]</sup>

Improvement in translucency and color of dental porcelains was realized through developments that ranged from formulations of Elias Wildman in 1838 to vacuum firing in 1949.<sup>[2]</sup>

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

In 1885, Logan resolved the retention problem encountered between porcelain crowns and posts that were commonly made up of wood by fusing the porcelain to platinum post-Richmond crown. These crowns represent the first innovative use of the metal ceramic system.<sup>[5]</sup>

In 1886, combining the burnished platinum foil as a substructure with the high controlled heat of a gas furnace, Land introduced first fused feldspathic porcelain inlays and crowns.<sup>[5]</sup>

All porcelain crown systems despite their esthetic advantages failed to gain a widespread development until alumina was used as a reinforcing paste. A noteworthy development occurred in 1950 with an addition of leucite to porcelain formulation that elevated the coefficient of thermal expansion to allow fusion to certain gold alloys to form complete crowns and fixed partial dentures (FPD).<sup>[6]</sup>

Refinements in metal ceramic systems dominated dental ceramic research during the 35 years that

resulted in improved alloys, porcelain metal bonding, and porcelain.  $\ensuremath{^{[2]}}$ 

In 1965, McLean and Hughes developed a Porcelain Jacket Crown (PJC) with an inner core of aluminous porcelain containing 40–50% alumina crystals to block the propagation of cracks. The inner core is layered with conventional porcelain resulting in a restoration approximately twice as strong as a traditional PJC. But the structure is still insufficient for anything but anterior crowns. Fracture resistance of the aluminous PJC was improved by a technique in which the platinum matrix is left in completed restoration. The platinum foil decreased the amount of light transmitted which diminishes the somewhat esthetic advantage of all ceramics.<sup>[2,3]</sup>

The introduction of a "shrink-free" all-ceramic crown system (Cerestore, Coors Biomedical) and a castable glass ceramic crown system (Dicor, Dentsply) in 1980s provided additional flexibility for achieving esthetic results.<sup>[2]</sup>

The introduction of an aluminous porcelain crown in early 1900s and the methods to produce a durable metal ceramic in the 1960s, and improvements in both the composition of ceramics and methods forming the ceramic core of ceramic crowns have greatly enhanced our ability to produce more accurate and fracture-resistant crowns made entirely of ceramic materials. In 1984, Adair and Grossman demonstrated an improvement in all-ceramic systems developed by a controlled crystallization of a glass (Dicor). In early 1990s, a pressable glass ceramic (IPS Empress) containing approximately 34 vol% leucite was introduced that provided a strength and marginal adaptation. In late 1990s, a more fracture-resistant, pressable glass ceramic (IPS Empress 2) containing approximately 70 vol% of lithium disilicate crystals was introduced. The CEREC 1 system was introduced in the mid-1980s, and improvements in software led to the CEREC 2 and CEREC 3 systems for the production of ceramic inlays, onlays, and veneers.<sup>[3]</sup>

Advanced ceramic systems introduced with innovative processing methods stimulated renewed interest in all ceramic prostheses.

# **ADVANCES IN CERAMICS**

The first colored, full-coverage restoration of teeth was invented by Charles Land in the early 1900s. Prior to this, most of the teeth were restored with amalgam or an adhesive gold foil. Neither method resulted in an especially good-looking tooth. The idea was to cut the remaining tooth back and then rebuild the stump using porcelain, which was called a "jacket." The porcelain jacket was made from feldspathic porcelain clay. It was fabricated by burnishing a piece of a thin platinum foil over a die, and adding layers of porcelain over it using a small, wet paint brush. The foil, along with each successive layer, was fired in a kiln, and the process was continued until the porcelain overlying the platinum foil resembled a tooth. Since platinum is a noble metal, the lack of an oxidized layer meant that the porcelain would not bond to it. After all the firings had been completed, platinum was removed and the porcelain "jacket" was luted to the tooth using the zinc phosphate cement.

The porcelain jacket crowns eventually became a popular restoration in spite of the fact that they had some drawbacks. The strength of the porcelain crown was inadequate and the removal of the platinum foil after the crown was fired meant that there was a gap at the margin from where the cement would be exposed to the oral environment leading to its breakdown and an eventual accumulation of food debris would take place. Finally, the porcelain tended to be too opaque to match the surrounding teeth.

## **Dental Feldspathic Porcelain**

The feldspathic porcelain consists of three major constituents namely fluxes (potash and soda), stabilizer (aluminium oxide), and glass former (silica).

Porcelain is glass with a refractory internal structure. All ceramics contain a refractory skeletal structure made up of particles of metallic oxides. Most frequently, they are particles of aluminum oxide in the form of alumina (kaolin), and silicone dioxide in the form of silica.

Kaolin is opaque due to the fact that much of it remains in a crystalline form throughout the ceramic body. The opacity is the result of the internal scattering of light by refractory alumina in the form of kaolinite crystals. This was the reason that Land's porcelain jackets were not very esthetic, and this opacity remained a recurring problem in early dental porcelains. In light of this problem, ceramic technologists began to formulate feldspathic porcelains with less and less kaolin and by 1938, kaolin was omitted entirely.

But, as the proportion of aluminous kaolin decreased, the strength of the glass declined. Thus feldspathic dental porcelains slowly began to be formulated with only a weak refractory skeleton composed of quartz particles and became more prone to failure as a result. On the other hand, they were (and still are) highly esthetic materials for building tooth-like structures.

The most serious drawback with the feldspathic

porcelain when used without a core is its inherent lack of strength and toughness. In order to further strengthen crowns made from the esthetic feldspathic porcelain so that it can stand up to the stresses encountered in the mouth, it is necessary to reinforce it by layering it over an unbreakable core. There are three ways in which this can be done:

## Metal cores—porcelain fused to metal (PFM)

In the 1950s, researchers were looking for further improvements in crown and bridge prosthodontics. Their main concern was to improve esthetics. The credit is usually given to Dr. Abraham Weinstein, who was the first to produce a commercially successful dental gold alloy and porcelain composite.<sup>[7]</sup>The metal alloy could be precisely formed to fit the tooth via the lost wax technique. This effectively solved the dilemma of a poor marginal fit, which had always been a problem with traditionally built porcelain jacket crowns.

## **Reinforced ceramic cores**

The idea of replacing the metal substructure of a PFM restoration with an opaque white porcelain substructure came about in the 1960s with the invention of the aluminous core. At the time when these were invented, they were simply a stronger version of the older feldspathic porcelain jacket crowns. They were cemented to the tooth using zinc phosphate cement, but the cement could form no bond to the porcelain crown. Aluminous cores were an improvement. Unfortunately, the use of alumina porcelains

was restricted to individual units or crowns because they are contraindicated for use in the posterior region due to their decreased strength.<sup>[8]</sup>

## **Resin-bonded ceramics**

It was not until the 1970s that the concept of "bonding" became accepted by the dental profession. The idea of actually bonding a porcelain jacket crown directly to the tooth structure did not become practical until the 1980s when it became possible to bond both porcelain and dentin with an intervening resin cement. In the 1990s, new forms of ceramic crowns that could also be bonded directly to the tooth structure and which were stronger and better looking than aluminous core crowns were invented.

#### **Glass Ceramics**

The older feldspathic dental porcelains started out as a form of domestic porcelain in which a refractory ceramic structure supported a vitrified feldspathic glass. Later, due to esthetic considerations, the refractory structure was removed producing a more esthetic, but a weaker glass structure. Finally, in the 1960s, the clinical failures experienced with porcelain jacket crowns drove the technology toward replacing the missing refractory structure by adding up to 50% by volume of fine aluminum oxide crystals to the glass recipe before fusing. This produced the aluminous glass core.

Glass ceramics also contain a substantial refractory crystalline core. However, they are not like the aluminous glass since they start out as a pure glass in which finely dispersed crystalline structures are stimulated to "grow" within the solidified glass matrix by a process of controlled devitrification known as "ceramming."

When feldspar is subjected to the process of ceramming, it undergoes incongruent melting to form crystals in a liquid glass. Incongruent melting is the process by which one material melts to form a liquid plus a different crystalline phase. Different feldspathic formulations and different firing schedules will yield different cerammed crystals. A few examples of different crystalline phases obtained are leucite (Empress, Optec OPS), fluoromica glass ceramic (Dicor), lithium disilicate (Empress II, Optec OPS 3G), and apatite glass ceramics.

#### **Castable/Machinable Glass Ceramics**

Dicor was released to the dental community in 1982. It was the first commercially available castable ceramic material for dental use. Dicor glass ceramic contains about 55 vol% of tetrasilicic fluormica crystals. Dicor MGC is a higher quality product that is crystallized by the manufacture and provided as CAD CAM blanks or ingots, which contain 70 vol% of tetrasilicic fluormica crystals.<sup>[8,9]</sup>

Dicor possesses compressive strength of 828MPa, modulus of rupture 152MPa, modulus of elasticity 70.3 GPa, and microhardness 362 kg/ mm2.<sup>[10]</sup>

It is processed by a combination of conventional lost wax investment techniques and glass casting. This ceramic was originally intended to be shaded with a thin surface layer (50–100  $\mu$ m) of a colorant glass. Because of the esthetic limitation of surface shading, practitioners began veneering cut back dicor copings with feldspathic porcelains used for all other ceramic systems. The main disadvantage was its inability to be colored internally.<sup>[8]</sup>

#### **Pressable Glass Ceramics**

Leucite was the first, and is still probably the most popular of the crystalline inclusions that form in a cerammed feldspathic glass. Examples for leucite reinforced glass-ceramics are IPS Empress and OPC (optimal pressable ceramic). These systems use the lost wax technique to press glass ceramic crowns. The glass ceramic is supplied in ingots in which the leucite particles (about 35% by volume) have been previously formed in a ceramming process done by the manufacturer. A wax pattern is made in the form of a crown and invested in a refractory die material. The wax is burnt out to create the space to be filled by the leucite-reinforced glass ceramic. A specially designed pressing furnace is then used to melt the glass ingot and *infuse* the mold with the glass ceramic melt. The main disadvantage is its low flexural strength and hence potential to fracture in posterior areas.<sup>[2,3]</sup>

The IPS Empress 2 and OPC 3G are similar to IPS Empress and OPC except that the core consists of litihium disilicate crystals in a glass matrix and the veneering ceramic contains apatite crystals. This improved the flexural strength of the core compared to the leucite-reinforced glass ceramic and hence could be used in posterior areas.<sup>[3]</sup>

#### **Apatite Glass Ceramic**

The IPS Empress 2 core ceramic has a coefficient of thermal expansion (10.6 ppm/°C) lesser than IPS Empress core ceramic (15.0 ppm/°C) and ordinary feldspathic glasses cannot be sintered over the lithium disilicate substructure. Therefore, a new esthetic glass ceramic with a thermal expansion of 9.7 ppm/C was invented to overlay the framework.<sup>[3]</sup> This new layering ceramic is an apatite glass ceramic. The crystals formed on ceramming have the composition  $Ca_{10}(PO_4)_6$ ·2OH. This is the same basic constituent in the natural tooth enamel. The very small apatite crystals cause light scattering in a way that resembles the scattering by the structure and components of tooth enamel.

## Glass infused ceramic core systems

Aluminous cores are made by adding alumina to the glass system before the frit-sintering stage. This method of manufacture limits the addition of alumina to no more than 40-50% by volume. On the other hand, glass infused ceramic cores are built using pure alumina, spinel or zirconia which is sintered prior to the introduction of the glass. Thus these cores achieve a much higher proportion of refractory crystalline filler than is possible with traditional aluminous core techniques.

In-Ceram by Vita was the first high-strength alumina core system, achieving approximately 85% by volume of sintered alumina in its core. It is fabricated using a slip casting process. A slip is simply a clay mixed with enough water to make it a creamy texture. In-Ceram uses a slip made up of water mixed with a suspension of finely ground alumina particles. The slip is used to coat a porous die in the shape of the final coping. In slip casting, the die is designed to absorb the water in the slip. This causes the suspended ceramic particles to condense tightly against the die. The "green" ceramic body is fired on the die at 1120°C for 10 h. This temperature is too low to completely fuse the silica, but it produces a sintered framework with a fairly dense structure and little or no shrinkage. The sintered body by itself is not especially strong, but it has a porous texture and when infused with a low-viscosity glass creates a thin coping with great strength. This coping is then overlain with the feldspathic dental ceramic to fill out the form of the tooth. This creates a somewhat opaque restoration that can be used on molars. The strength of this core material is not quite sufficient to be used as a framework for posterior bridges. This type of core is known as a glass-infused ceramic core. An In-Ceram all-alumina core's flexural strength is approximately 352 MPa.<sup>[11]</sup>

Vita has created other glass-infused core systems replacing the sintered alumina with other oxides and oxide mixtures. In-Ceram Spinel (ICS) uses spinel (MgAl<sub>2</sub>O<sub>4</sub>) in sintered form to produce a more translucent and esthetic version of its original In-Ceram at the cost of slightly reduced flexural strength (~ 350 MPa). ICS is indicated for anterior crowns. In-Ceram Zirconia (ICZ) uses a mixture of alumina and zirconium oxide crystals to produce a glass-infused ceramic that is even stronger than the original In-Ceram (~ 700 MPa). ICZ is used for posterior crowns and bridges, but not indicated for anterior testorations due to its opacity.

# **CAD/CAM CERAMICS**

#### Pure alumina cores

Pure alumina fuses between 1600°C and 1700°C, but sinters at a much lower temperature. Procera (Noble Biocare) All Ceram cores were the first CAD-CAM (computer-assisted design-computer-assisted manufactured) dental substructures made. A standard die made from an impression taken by a dentist is digitized using a specially designed mechanical scanning device and a computer that turns the shape of the die into digitized data. The data are then used to fabricate an oversized die by a factor of 0.2 (20%) to which 99.9% pure alumina is dry pressed.<sup>[12]</sup> The pressed, oversize green body is then removed from the die and sintered, thus shrinking to the correct size and creating a hard core to which a feldspathic porcelain veneer can be applied. Cores like these are about as strong as In-Ceram Zirconia (~700 MPa), but the coping is said to be more translucent and to give better esthetics. While they can be used for posterior crowns, posterior bridges are not advised. Procera Forte is a newer product in which the same mechanical technique is used to scan the model for fabrication of a milled, sintered zirconia product which is sufficiently strong to be used as a framework for posterior bridges.

#### Zirconia cores

Cercon (Dentsply), Lava (3M ESPE), Procera Forte (Noble Biocare) and Everest (Kavo) are a few systems which use zirconia for fabrication of cores. Three main types of zirconia are available for use in clinical dentistry. They are fully sintered or HIP type (hot isostatic pressing), partially sintered zirconia, and nonsintered or green state zirconia.<sup>[13]</sup> They can be used to fabricate an incredibly hard ceramic core in the range of 900–1100 MPa.<sup>[14]</sup> This material is strong enough to use as a framework for multiunit posterior bridges.

CEREC (computer-assisted CERamic REconstruction) Early in 1980s, Dr. Wernar H.Mörmann and Dr. Marco Brandestini developed a basic concept of the in-office CAD/CAM which had a two-dimensional software capability to fabricate inlays.

In 1985, the CEREC 1 unit was introduced. The first chair-side inlay was fabricated on September 19, 1985. In this arrangement, the ceramic block could turn on the block carrier with a spindle and feed it against the grinding wheel, which ground from the full ceramic a new contour with a different distance from the inlay axis at each feed step. This solution proved itself in a prototype arrangement. In 1988, CEREC 1 was extended to provide for onlays and veneers.

In 1994, a CEREC team at Seimens (Munich, Germany), equipped CEREC 2 with an additional cylinder diamond enabling the form-grinding of partial and full crowns. Partial and full crowns and copings could be fabricated.

In 2000, the two-dimensional CEREC 3 was introduced. This system skipped the wheel and introduced the two-bur system. A three-unit bridge frame could be fabricated.

The "step bur," which was introduced in 2005, reduced the diameter of the top one-third of the cylindrical bur to a small diameter tip enabling high-precision form-grinding with a reasonable bur life.<sup>[15]</sup>

The introduction of CEREC 3D in 2005 marked the three-dimensional virtual display of the prepared tooth. The tooth preparation is directly transferred from the mouth to the computer using an optical 3-D scanning The anatomy of the opposing tooth can also be virtually recorded along with the bite registration. This allows the dentist to create and seat a ceramic restoration in one appointment, all at the chair-side itself.

# CONCLUSION

The development of ceramics has been exponential over the past four centuries. This development of the

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from the yellowish metal ceramics to the wonderfully natural metal-free ceramics. This growth is limited only by one's imagination.

ceramics has changed the entire concept of esthetics

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