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Review Article

Dental Ceramics - A Descriptive Review on its Evolution

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Abstract

Dental ceramics have an undeniable position in strengthening the restorative facet of dentistry. Ceramic has a history which can be traced to even prehistoric periods but it was ushered in to the field of dentistry in the 18th century. Afterwards the material has evolved tremendously in its composition, processing and usage. This article is a travel through its evolution based on historic details.

Keywords: Ceramics; Porcelain; Dental Ceramic; History of Ceramics

Introduction

Marco Polo, the Venetian merchant who travelled through Asia in the last quarter of 13^{th} century coined the term porcelain from the word 'porcellana' the Italian name for cowrie shell. He described Chinese porcelain, comparing the shell's, hardness, strength. translucency and thinness. Presently, porcelain refers to a specific composition of materials made by mixing kaolin (hydrated aluminosilicate), quartz (silica), and feldspars (potassium and sodium aluminosilicates), and firing them at high temperature. The word ceramic is derived from the Greek word 'keramos' which means 'burnt stuff'. Presently it indicates a material produced by burning or firing. When inorganic materials are processed by firing at high temperatures desirable properties are obtained to the Ceramic. In dentistry, both porcelains and ceramics are used almost synonymously especially in relation to metal ceramics (Figure 1,2). [1].

History

Almost all the historians have agreed to one fact that the beginnings of ceramics can be traced back to the Chinese. They used mud/clay to make vessels and fired in kilns (900^0 C) available in those times. The particles were not completely fused and which resulted in making porous utensils which could not hold liquids (25000 BC). Thus started the era of earthenware. Many centuries later (100 BC), the Chinese have used higher temperature for sintering and which made the vessels harder and impervious to water. This class of vessels were identified as stoneware. As years passed by, they developed the porcelain technology(1000AD) and made containers with very thin walls and having considerable translucency. These materials have become synonymous with the Chinese and were designated as China or chinaware. European craftsmen, despite repeated attempts, were unsuccessful to unravel the se-

Figure 1: Cowrie shells.
http://redcamel1.blogspot.com/2017/10/cowrie-jewelry

Figure 2: Ancient Chinese porcelain jar.
https://www.theguardian.com/science/

crets of Chinese ceramic technology. However, the European ceramic products could only match with the stoneware and not with the oriental porcelains. In 1717, Francis Xavier d'Entrecolles, a Jesuit priest won the confidence of Chinese potters and learned the porcelain manufacturing process. A French scientist Réne-Antoine Ferchault de Réaumur, found out the composition of the Chinese porcelain - Clay (50%), Feldspar (30%) and Quartz (20%). Subsequently Europeans started making their own porcelain but it got the identity of a dental material only after six decades [2-4].

Dental porcelain

Dental porcelain was used first to fabricate complete dentures. In 1776, a French apothecary Alexis Duchateau who was edentulous and was troubled by the stained and odour creating Walrus ivory dentures. Duchateau had observed that the glazed ceramic utensils, he used for mixing and grinding various chemicals, resisted staining and abrasion. He decided to make complete dentures by himself with ceramic but his attempt ended up in a disaster. Later he teamed up with a dentist of Paris, Nicolas Dubois de Chemant, and together they could make the complete dentures which fitted reasonably well. The material they used was designated as a mineral paste. De Chemant further improved on the formulation of the mineral paste to enhance the colour and dimensional accuracy of the material. The material used was a mixture of potash feldspar ($K_2O.Al_2O_3.6SiO_2$ - 70-80%), quartz (SiO_2 - 10-30%) and kaolin ($Al_2O_3.Si0_2.2H_2O$ - 0-3%). De Chemant patented the formulation in 1788. The invention appeared in print in the year 1797 by name A *Dissertation on Artificial Teeth.* The artificial teeth made by the material developed by Duchateau and De Chemant were hygienic and known as 'incurruptibles'. However it could not claim the premier status if the 'baked enamel' developed by Pierre Fauchard is also considered. It was developed in the year 1723. His attempt was to cover the metallic denture bases with enamel. Does not seem to be made of feldspathic porcelain [4].

Porcelain teeth

Giusseppangelo Fonzi (an Italian) found out a method to produce porcelain denture teeth by 1808. Fonzi devised a technique to place platinum pins at the back of the teeth and this has helped in binding the teeth to the denture base. Fonzi named his teeth as 'ferro metallic incorruptibles' and their esthetic and mechanical versatility provided a major advancement in prosthetic dentistry. Antonio Plantou, a French dentist introduced porcelain teeth to America in 1817 but its commercial prospects were utilised by Samuel W Stockton, a jeweller who produced porcelain teeth in a massive scale. In the same period of time, an English gold smith, Claudius Ash also started manufacturing porcelain teeth. Ash is credited with producing the 'tube teeth' which could be fixed on a post (Figure 3).

Charles H Land

The technique of fusing porcelain to thin platinum foil which served as matrix is credited to Charles H. Land, a Detroit dentist, who patented the concept sometime between 1886 and 1889 (Figure 4). The porcelain jacket crown was formally introduced by Land through a publication in the year 1903. Two recognisable

Figure 3: Tube teeth.
https://collection.sciencemuseumgroup.org.uk/

techniques were practised in the time of Land. Teeth were prepared and a platinum matrix was adapted. Porcelain was baked on the matrix and then the foil was peeled to complete the fabrication of the all-ceramic crown. In the second technique, porcelain facing was prepared out of denture teeth and fused to platinum matrix using body porcelain. Possibly an alloy of platinum and iridium was used in the second technique. The second one can be considered as the precursor of metal ceramic crowns. He used low fusing porcelain in the former technique which was not adequately strong and deteriorated in the oral cavity. Land named the first one as 'enamelled caps' and the second one as 'enamelled metallic caps. In the later periods of time, Land was duly recognised as the 'father of porcelain dental art' [5,6].

Figure 4: Charles Henry Land.
https://en.wikipedia.org/wiki/Charles_H._Land

Metal ceramics

Though porcelain jacket crown was in the awareness of the dentists, majority of them opted metallic crowns. During the 1950s, porcelain was successfully paired with gold alloys by the addition of leucite to porcelain to increase the coefficient of thermal expansion and to improve retention to metal. In 1956, Charles Brecker published an article entitled 'Porcelain baked to gold-A new medium in prosthodontics' in the Journal of Prosthetic Dentistry which can be considered as an authentic source of information on metal ceramic technology. In his time iridium-platinum alloy, palladium alloy, and gold alloy were used for porcelain fused to metal restorations. Becker favoured gold alloy castings for the substructure because of the ease in casting and accuracy of fit. In fact, he casted a gold thimble over the adapted platinum foil. He recognised that without oxide formation, porcelain will not fuse to the metal and hence he painted red cadmium compound on the metallic surface and heated it before porcelain application. He described it as a refractory wetting agent. Even in those days, he used two layers of opaque, body porcelain and glaze. Brecker has illustrated cases in the article and the technique described are almost equivalent to contemporary practice.

In the 1962, vacuum firing of porcelain was introduced along with bonding of porcelain to gold alloys by Weinstein., *et al*. and they received patents on the technology. Alloys used in those days contained noble metals like gold, palladium and silver (more than 25% by weight). They contained tin, indium or iron which provided an oxide layer essential for porcelain bonding. Dentists belonging to western countries prefer gold alloys possibly to avoid medicolegal eventualities (Figure 5).

Figure 5: Porcelain fused to gold.

Base metal alloys

By 1970 base metal alloys were introduced and subsequently they were used in the field of metal ceramics. Most of them do not contain noble metals. Nickel chromium alloys are popular because they are stronger and harder than gold alloys. Thin, sag resistant, long span castings could be made and were comparatively affordable to patients. The possibility of nickel allergy cannot be ruled out. Itching, burning, dryness of mouth and redness are common oral manifestations of nickel allergy. Beryllium once used in the alloys are completely withdrawn because of the carcinogenic potential. Cobalt chromium alloys are popular with cast RPDs (Figure 6).

Figure 6: PFM prosthesis base metal alloys.
https://bestdentistaurora.com/

PFM technology can be considered as a remarkable breakthrough in dental aesthetics: Between 1985 and 1995, the Journal of Prosthetic Dentistry alone published nearly 25 articles on PFM technology per year indicating tremendous research in the field of PFM technology [7-10].

Making of dental ceramics

Commonly used dental porcelain contains Silica, Kaolin and Feldspar (Figure 7-9). Kaolin (Clay) is used in limited quantity or not used. So dental porcelain if often called as dental glasses. These materials are mixed and heated to cause fusion and to form a frit. Feldspar which melts easily when compared to the other components, reacts with the surface of the particles of silica and kaolin. This frit is plunged into cold water to crack the mass into pieces. These pieces are finely ground and provided in bottles to the technician to be used in the fabrication of crowns and bridges (Figure 10). To obtain matching colours, metallic oxides are used. The powder is made of differently sized particles to ensure good quality compaction. Powder is mixed with a liquid and given the shape of the crown. Technicians use vibration for condensing the material and the expressed liquid is blotted out (Figure 11). This is fired in a furnace to make the hard mass (Figure 12).

Figure 7: Silica.
https://www.indiamart.com/proddetail/silica-quartz-stone

Figure 8: Kaolin.
https://www.yukami.co.id/

Figure 9: Feldspar.
http://www.kaverimine.com/potassium-feldspar.htm

Figure 10: Dental ceramic powder.
https://www.dentaltix.com/en/dental-ceramic-powderpaste

Figure 11: Dental Porcelain build up.
https://www.shofu.com/en/product/vintage-halo-porcelain/

Figure 12: Dental ceramic furnace (Ivoclar).
https://www.laboshop.com/index.

PFM restorations enjoyed very low failure (5% in five years) but metal framework caused aesthetic limitations because it hampered light transmission through the ceramic. Metal got reflected through the gingival tissues causing dark blue discolouration. Rarely allergic reactions were also reported. In 1970s, to overcome the problems, collarless preparations were introduced along with shoulder porcelain. Shoulder porcelains had high fusion temperature to prevent pyro plastic flow when subsequent veneer porcelain was applied (Figure 13). The system could not take off as expected because of the all ceramic entry [11-13].

Figure 13: Crown with and without metal collar.

McLean's contribution

In order to overcome the weakness of brittleness in ceramics, McLean and Hughes developed aluminous porcelains for the fabrication of crowns. One method they used was the fabrication of a core which was rich in Alumina. Over the core, veneer porcelain was applied which had matching expansion properties. Strength got increased but aesthetics suffered to an extent. In another method, pure alumina inserts were incorporated in the palatal region of the crown. In a third method, powdered alumina was incorporated in the composition of porcelain. Alumina particles incorporated were capable of stopping the propagation of cracks which caused the failure of crowns. In general, aluminous porcelain contains 40% alumina. Use of alumina is restricted to the inner core because of its opaqueness and the layering porcelains could compensate for that. It resisted cracks effectively because the cracks got initiated from the inner surface. Aluminous porcelain has a flexural strength of 120 - 180 MPa whereas unreinforced porcelain has a flexural strength of 70-120 MPa [14].

Slip process

Attempts to improve the strength of ceramics to suit the masticatory requirements, landed up in sintered alumina cores. These were prepared by 'Slip process'. In this method, the die is duplicated in porous gypsum and a slurry of ceramic is painted on its surface. The water will be absorbed by the die leaving a thin layer of alumina which will be fired at $1120^{o}C$. This produced a porous skeleton of alumina. The die shrinks at this temperature and the core could be removed easily. A slurry of lanthanum glass is painted on the external surface of the alumina core and fired at $1100^{0}C$. The glass infiltrates into the gaps between the sintered alumina particles (In-ceram alumina). This eliminated porosity, increased strength, and limited the potential sites of crack propagation. After removing the excesses, layers of feldspathic porcelain are added to complete the morphology of the crowns. The cores were opaque and to reduce the opacity magnesium was added to alumina (Inceram Spinell). Translucency increased but flexural strength was lowered. Both Inceram alumina and Inceram spinell were machinable (Figure 14,15). Further advancement to improve the strength was done by the addition of partially stabilized Zirconia (35%) and the flexural strength improved to 800MPa. It was opaque and was very difficult to mask. Hence its use was limited to the posterior teeth [14].

Figure 14: In-Ceram Alumina machinable blocks.
http://www.cerec.co.il/downloads/vita_in_ceram.pdf

Figure 15: In-Ceram Spinell machinable blocks.
http://www.cerec.co.il/downloads/vita_in_ceram.pdf

Zirconia

Zirconia (ZrO_2) in the pure form is a polymorphic material and which has three crystalline forms based on the temperature (Figure 16). These forms are 1. Monoclinic (room temperature to 1170^{0}C) 2. Tetragonal (1170 to 2370^{0}C) 3. Cubic (2370^{0}C to 2680^{0}C -melting point). When the material cools down from tetragonal to monoclinic phase, a volume expansion of 3 to 5% happens to cause high internal stresses and thereby generation of cracks. Yttrium-oxide (Y_2O) is added in small quantity (3% mol) to Zirconia to stabilize the tetragonal phase at room temperature and the expansion partially. This partially stabilised zirconia has high initial flexural strength and fracture toughness. During the cooling, tensile stresses are generated at the crack tip and will cause the tetragonal phase to transform into the monoclinic phase with an associated 3-5% localized expansion. This is an exclusively localised phenomenon happening in relation to cracks. The localised expansion causes compressive stresses at the tip of the crack and effectively counteracts external tensile stresses. This phenomenon is known as transformation toughening and retards the propagation of cracks.

Figure 16: Zirconium oxide.
https://wiki.aalto.fi/pages.

Yttrium oxide partially stabilised Tetragonal Zirconia Polycrystal (Y-TZP) provides a material better suited for dental restorations. It is a high strength ceramic material having a flexural strength of 900 to 1200 MPa. This material is available in partially sintered (green state) and fully sintered forms. It is easy to machine (CAD/CAM) partially sintered Y-TZP but it has to be subjected to sintering at 1350^{0}C to1550^{0}C for 2 to 6 hours. During this process, the material shrinks by 20% to 25%. A bigger sized designing has to be done and after machining when the sintering is done, the object shrinks to the correct size. Copings and multiple unit frame work of fixed prostheses are made with this process. Fully sintered Y-TZP can also be machined but microstructure alterations are expected. The material requires prolonged milling.

The zirconia ceramic characteristics are dense, thermal conductivity is negligible, biocompatible, radiologically and optically opaque and resistant to bacterial adhesion. Frame works are rarely fractured but the veneering porcelains cannot enjoy that status. Chipping of veneering porcelain is attributed mainly to fast cooling after firing the veneering porcelain. Slow cooling is recommended to prevent fracture of zirconia-based restorations. Some authors have observed low grade degradation of zirconia at mouth temperature. This is caused by auto catalytic changes happening during firing and the residual stresses. [11,15-19].

CAD/CAM

The concept of CAD/CAM in ceramics was introduced by Duret in the year 1971. A commercially viable system was introduced 15 years later by name CEREC which is a short form for Chairside Economical Restoration of Esthetic Ceramics (Figure 17). The system was subsequently upgraded in the later years [11,20-22].

In order to suit the requirements of CAD/CAM technology IPS e. max CAD was introduced as ceramic blocks which could be milled. These blocks are partially pre-crystallised, containing 40% metasilicates (Li_2SiO_3). It has a flexural strength of 130MPa only and hence milling is easily done. After milling, it is subjected to a heating cycle of 840 to 850^{0}C for 10 minutes and metasilicate is converted to disilicate. And this process improves the flexural strength to 262MPa. [11] Presently the IPS e. max CAD blocks are available in a wide variety of sizes, shades and translucency levels. Many other manufacturers have also entered in the recent past.

Figure 17: CAD-CAM milling- CEREC System. https://www.thewellingtonclinic.com/cerec-crowns-veneers

Figure 18: Zirconia discs after CAD-CAM milling. https://www.globenewswire.com/

Additive manufacturing (AM)

Conventional metal casting and subsequent veneering with ceramics ruled the dental laboratory technology until Computer Aided Manufacturing (CAM) was introduced to mill all ceramic restorations. The CAD/CAM process was based on Subtractive Manufacturing (SM). SM had a disadvantage of using blocks/discs of materials and left so much of unused material after milling (Figure 18). Milling tools were abraded fast (Figure 19). In this context the idea of additive manufacturing (AM) was brought in. ASTM international has defined AM as “a process of joining materials to make objects from 3D model data, usually layer upon layer”.

Charles Hull can be considered as the pioneer in the field of 3D printing who patented stereolithography (SLA) in 1986. In the later years many systems were created and most of them found wide applications in the industrial field. 3D printing has found variety of applications in the field of health sciences especially in surgical planning, in the preparation of custom surgical devices and to make effective communications with the patients. This has found applications in almost all the specialities of Dentistry especially in prosthodontics, implantology, orthodontics and maxillofacial surgery.

Figure 19: Tools used for ceramic milling.
https://dental-concept-systems.com/

In 3D printing, mainly three different technologies are utilised Viz. *Powder Bed Fusion (PBF), Light curing and fused deposition modelling (FDM)*. PBF is further categorised into selective laser melting (SLM), selective laser sintering (SLS), electron beam melting (EBM) and direct metal laser sintering (DMLS). Titanium and Co-Cr based appliances and prostheses can be fabricated by PBF (Figure 20). Powdered metal of Cobalt Chromium/Titanium alloys with particle size of 3 to 14 microns, is spread in a layer of thickness of 20 to 100 micrometer, which is fused by Laser. Another layer is laid on this and fused. This process is continued till the three-dimensional object is built completely. Many prosthetic frame works were made like this in dentistry.

Figure 20: 3D printed metal crowns.
https://www.eos.info/en/all-3d-printing-applications/people-health/medical-3d-printing/dental.

In the light curing technology, 3D printing is undertaken using photo sensitive resins which are cured by light irradiation. This technology also has three variants viz. stereolithography (SLA), digital light processing (DLP) and photo jet (PJ). Ceramic printing is popularly done with SLA.

Fused Deposition Modeling (FDM) is a popular economy model of 3D printing which can be used in dentistry. Thermoplastic materials are heated and injected through a nozzle to build products layer by layer. Polylactic acid, poly carbonate and polyamides are some of the materials used with FDM. Polycarpic acid - tricalcium phosphate combinations are used for making tissue scaffolds with FDM.

AM technology was introduced in ceramics recently both in industry and dentistry. Slurry based ceramic content can be 3D printed by photo polymerization, inkjet or extrusion. Stereolithography (SL) is a commonly used 3D printing technology introduced in 1986. Dentistry started using SL by making splints, templates and surgical stents. For that purpose, resins are cured by light sources of ultraviolet range.

Stereo Lithography of ceramics is done by adding micro/nano sized fine ceramic particles into a photo curable liquid medium. The liquid forms a ceramic suspension which when subjected to light irradiation, only the liquid gets polymerized because ceramic particles are inert to light. Three dimensional objects are first formed by cross linked organic network through polymerization. This is further subjected to pyrolysis to remove the organic content. Subsequent sintering will make the ceramic particles dense (Figure 21).

Figure 21: 3D printed zirconia crowns.
http://denexpert.com/products/details/dmls-cadcam-8

There is an overwhelming interest in printing ceramic restorations with Lithium disilicate and Zirconia. Additive manufacturing has many advantages such as minimal material waste, the ability to form complex geometries, minimal residual stresses, elimination of tool wear and mass production. But there are certain limitations in the printed prostheses such as dimensional inaccuracy, long printing time and shrinkage between layers.

Manufacturers have developed lithography-based ceramic technology, which allows for the use of Lithium disilicate powders and furnaces which are commonly used with injection moulding or milling and ensuring comparable mechanical properties and surface quality. Laboratories claim that restorations can be printed with edges as thin as 0.1 mm. To compete with multi layer milling blanks, multi material printing is also tried to enhance aesthetic quality.

It is a proven fact that zirconia is a very stable and safe restorative material. The challenge in 3D printing zirconia restorations is in the sintering process. First-printed zirconia restorations took approximately two days to adequately sinter. A slow heating at the rate of 0.1 ºC per minute is recommended to sinter without cracks. The powder particle size is also of concern. If the powder is too coarse (0.3-0.6 μm) the desired accuracy may not be obtained. If the powder is too fine (40 nm) it becomes difficult to recoat after each layer.

Zirconia crowns made by additive and subtractive techniques have comparable internal fit and marginal adaptation. While 3D-printed crowns have better occlusal and axial trueness, milled crowns have better intaglio trueness. General assumption is that 3D printing produces more precise restorations than the milled ones. Printed zirconia is a comparatively recent entrant to the field of dental ceramics and it has to be subjected to optimization in mechanical and aesthetic properties [23-32].

Conclusions

Ceramic restorations were truly man made in its initial phases. Skill of the technician dictated the aesthetics and success of the restorations. But advancements in technology changed the profile of fabrication – from powder-liquid system to CAD-CAM milling to printing. This article tried to trace the evolution of dental ceramic technology.

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