1. INTRODUCTION

Modern dentistry has evolved from curative to creative science. Ceramics represents one of the four classes of materials used for the reconstruction of decayed, damaged or missing teeth. Other classes include metals, polymers and composites.¹

Aesthetics has a major role in today's world. Aesthetic dentistry primarily focuses on improvement in dental aesthetics based on colour, contour, shape form and overall smile appearance. The most commonly used aesthetic materials are ceramics and composites.

. Ceramics were the last to move into the high-technology phase of development. During the past decade, the demand for non-metallic highly biocompatible dental restorative material has, however, markedly increased.

Dental ceramics allow regular and diffuse transmission, as well as diffuse and specular reflectance of light, and therefore have the potential to reproduce the depth of translucency, depth of color and texture of natural teeth^{2,3}. In addition, dental ceramics are resistant to degradation in the oral cavity, are biologically compatible and have a coefficient of thermal expansion that is similar to that of tooth structure.

Today's ceramic restoration application, despite its popularity gained through esthetical advantages and superior hygienically features, has a fragile structure due to its low tensile strength quality.

Modern techniques in restorative dentistry include the use of ceramic materials for jacket crowns, laminates, inlays and onlays. These restorations not only look natural but also have a very good periodontal response when placed properly.

The word Ceramic is derived from the Greek word "*keramos*", which literally means 'burnt stuff', but which has come to mean more specifically a material produced by burning or firing. A ceramic is an earthly material usually of silicate nature and may be defined as a combination of one or more metals with a non-metallic element usually oxygen¹.

The word porcelain is said to have been invented by Marco Polo in the 13th century from the Italian word *porcellana*, or cowrie shell. Polo used the cowrie shell to

describe Chinese porcelain because it was similarly strong and hard while remaining thin and translucent.

The American Ceramic Society has defined ceramics as inorganic, non-metallic materials, which are typically crystalline in nature, and are compounds formed between metallic and non-metallic elements such as aluminium & oxygen, calcium &oxygen, silicon & nitrogen⁴.

The term porcelain is referred to a specific compositional range of ceramic materials made by mixing kaolin, quartz and feldspar in proper proportioning and fired at high temperature. Porcelain is essentially a white, translucent ceramic that is fired to a glazed state.

Ceramics and glasses are brittle, which means that they display a high compressive strength but low tensile strength and may be fractured under very low strain (0.1%, 0.2%).

As restorative materials, dental ceramics have disadvantages mostly due to their inability to withstand functional forces that are present in the oral cavity. Hence, initially, they found limited application in the premolar and molar areas, although further development in these materials has enabled their use as a posterior long-span fixed partial prosthetic restorations and structures over dental implants. All dental ceramics display low fracture toughness when compared with other dental materials, such as metals.

Metal ceramic systems combine both the exceptional esthetic properties of ceramics and the extraordinary mechanical properties of metals. Some metals used as restorative materials in dentistry may constitute a problem for some patients. These problems may reveal themselves as allergies, gum staining and release of metallic ions into the gingival tissue and the gingival fluid. These drawbacks, as well as the search for more esthetic materials by patients and dentists, have stimulated research and development of metal-free ceramic systems.

In dentistry, ceramics are widely used for making artificial denture teeth, crowns, bridges, ceramic posts, abutments and implants and veneers over metal substructures.

The success of all ceramic crowns and patient demand for metal free, tooth coloured restorations has led to the development and introduction of restorative systems for all ceramic fixed partial dentures.⁵

Ceramic materials are best able to mimic the appearance of natural teeth however two obstacles have limited the use of ceramics in the fabrication of dental prostheses

- 1. Brittleness leading to a lack of mechanical reliability
- Greater effort and time required for processing in comparison with metal alloys and dental composites.⁶

The evolution of computerized systems for the production of dental restorations associated to the development of novel microstructures for ceramic materials has caused an important change in the clinical workflow for dentists and technicians, as well as in the treatment options offered to patients⁷. One of the most important changes in this scenario was the introduction of monolithic restorations produced from high-strength ceramics, like zirconia.

Recent advances in ceramic processing methods have simplified the work of the dental technician and have allowed greater quality control for ceramic materials, which has increased their mechanical reliability. The recent developments in dental ceramic technology can be categorized into three primary trends:

- There has been a rapid diversification of equipment and materials available for computer-aided design/computer-aided manufacturing (CAD-CAM) of ceramic prostheses.
- 2. The availability of CAD-CAM processing permitted the use of polycrystalline zirconia coping and framework materials. The relatively high stiffness and good mechanical reliability of partially stabilized zirconia allows thinner core layers, longer bridge spans, and the use of all-ceramic fixed partial dentures (FPDs) in posterior locations.
- 3. Basic science researchers are increasingly using clinically relevant specimen geometry, surface finish, and mechanical loading in their in vitro studies. This implies that in vitro results will more accurately predict clinical performance of ceramic prostheses, but clinicians still need to be cautious in extrapolating from the laboratory to the clinical case.

The purpose of the present literature is to review the new materials and processes available for dental ceramic restorations. The first part summarizes basic concepts on dental ceramics and methods for improving the fracture resistance. The second part covers the new materials and processing techniques used for making ceramic dental restorations and their mechanical properties.

2. REVIEW OF LITERATURE

Obrein W.J.⁸(1993) conducted a study on the strengthening of a magnesia core ceramic. Six batches of the magnesia core material were made by reacting magnesia with a silica glass with holding times ranging from 17 to 120min. the flexural strength and forsterite content was measured. A statistically significant correlation was found between the forsterite content and flexural strength.

The proposed mechanism for strengthening is the precipitation of fine forsterite crystals in the glass matrix surrounding unreacted magnesia. Longer reaction times produced more dissolution of magnesia and subsequent precipitation of forsterite.

H.Norbdoe⁹(1994) evaluated the performance of 135 porcelain laminate veneers placed on anterior teeth without incisal preparation. Only 0.3–0.5 mm of the facial enamel was removed using a tapered round-ended diamond bur. The veneers were fabricated from a sintered feldspathic porcelain, etched and silanized and then bonded with a light-cured composite lute.

The veneers were yearly examined clinically for debonding, chipping, marginal integrity and staining. After 3 years of service all veneers were retained. Incisal chipping occurred in seven veneered teeth. Wear and staining were negligible. It was concluded that this minimal porcelain veneer restoration with no incisal overlapping was conservative, predictable and successful.

Thurmond J.W.¹⁰(1994) evaluated the bond strength of composite resin bonded to porcelain surfaces by use of a variety of treatment regimens with the All-Bond 2 adhesive system. There were significant differences in the 24-hour bond strengths between several of the surface treatment methods. The mean shear bond strength after 24 hours of water storage ranged from 10.6 +/- 2.3 MPa to 25.0 +/- 4.4 MPa. Nine of the surface treatment methods showed a significant decrease (p < 0.05) in bond strengths after 3 months of water storage and thermocycling.

After 3 months, the bond strengths ranged 0.1 +/- 0.1 MPa to 17.4 +/- 2.0 MPa. Porcelain surface treatment with aluminum oxide air abrasion followed by hydrofluoric acid, a silane coupling agent, and an unfilled resin produced a bond strength after 3 months' water storage and thermocycling that was significantly greater (p < 0.05) than the other nine porcelain surface-treatment techniques.

Seghi¹¹(**1995**) evaluated the relative flexural strength of six new ceramic materials using a 3 point bend test. Conventional feldspathic porcelain and soda lime glass were used as controls. The alumina –based crystalline reinforced materials exhibited the highest breaking strengths.

Scanning electron microscopic analysis of the fractured surfaces indicated crack deflection appeared to be the principal strengthening mechanism in the highly crystalline material.

Giordano R.A.¹²(**1995**) determined the flexural strength of In Ceram system component and compared the core material with conventional feldspathic ceramics and with Dicor all ceramic restorative material.

Four point flexural strength values of bend bars of each ceramic were 18.39+/- 5.00 MPa for InCeram sintered alumina, 76.53+/- 15.23MPa for In Ceram infusion glass and 236.15+/- 21.94 MPa for In Ceram infused alumina core. Flexural strength of selfglazed feldspathic porcelain was 69.74+/-5.47MPa, as cast Dicor ceramic 71.48+/- 7.17 MPa and polished Dicor ceramic was 107.78+/-8.45MPa.

Sorensen J.A.¹³(1995) found the velocity and extent of ceramic inlay movement during polymerization of resin cements. Cylindrical ceramic inlays were placed in dentin cavities filled with one of four commercially available resin composite cements. An initial standardized 200-microns-thick cement film was created.

The movement of the ceramic inlay during polymerization of one of the resin cements was measured by a dial gauge. The velocity of the inlay movement decreased exponentially with time and with a velocity constant of 0.09 min-1. The majority of the movement occurred within the first 12 min after photopolymerization and probably continued for several days, reaching an estimated value of 5.8 microns.

After 1-2 d of water storage, 1-2-microns contraction gaps at the cavity floors were observed microscopically for every cement used. It is concluded that in cavities without support for the inlay, about 2/3 of the resin cement contraction results in movement of the inlay and about 1/3 results in formation of gaps at the cavity floors.

I.L.Denry¹⁴(1996) conducted a study on the effect of cubic leucite stabilization on the flexural strength of feldspathic dental porcelain. He prepared eight porcelain compositions by mixing increasing amounts of either leucite (KAlSi₂O₆) or pollucite

(CsAlSi₂O₆) with Optec HSP porcelain (Jeneric / Pentron Inc. Wallingford, CT). X –ray diffraction analyses showed that the amount of stabilised leucite increased with the amount of pollucite added.

The stabilization of cubic leucite reduced the flexural strength and the no. of crack deflections in the leucite reinforced porcelain. The development of tangential compressive stresses around the leucite crystals when cooled is responsible for the significant amount of strengthening of feldspathic dental porcelain.

J.R.Mackert¹⁵(1996) studied on microcracks in dental porcelain and their behaviour during multiple firing. The result of this study indicate that even for porcelains that exhibit a measurable change in microcrack density as a function of multiple firings, the magnitude of the increase or decrease in microcrack density after several firings is sufficiently small to cause only negligible shifts in porcelain bulk thermal expansion.

Sulaiman¹⁶(1997) compared the marginal fit of InCeram, IPS Empress and Porcera crowns. InCeram exhibited the greatest marginal discrepancy (161 microns), followed by Procera (83microns) and IPS Empress (63 microns). The facial and lingual margins exhibited significantly larger marginal discrepancies than the mesial and distal margins.

Chai. J.¹⁷(2000) studied the probability of fracture of all- ceramic crowns. The four all ceramic crown systems were:

- (i) A glass infiltrated, sintered alumina system (inceram) fabricated conventionally
- (ii) The same system with machine milled alumina cores(CEREC)
- (iii) A heat press (IPS Empress) leucite reinforced glass
- (iv) High purity, high density alumina system (Procera)

10 crown systems of each system were fabricated & compressed at 45 degrees at the palatal surface until fracture. The result of this study showed there were no significant differences in the probability of fracture among the 4 systems.

Doreau F.¹⁸(2000) suggested that among the different rapid prototyping technologies, solid free form fabrication (SFF) is the most suitable for ceramics. Here a stereolithographic technique is presented that allows the usage of pastes composed of ceramic particles dispersed in a photocurable resin for the fabrication of alumina pieces.

They exhibit a similar flexural strength than alumina parts made by classical techniques like pressing.

Antonson S.A.¹⁹(2001) conducted a study on the contrast ratio of veneering and core ceramics as a function of thickness. Four core ceramics were selected for the study. (i) tetrasilicic fluormica glass ceramic (ii) quadruple- chain silicate glass ceramic (iii) sintered alumina.

The four veneering ceramics included two feldspathic body porcelains (i) one fine grained veneering porcelain (ii) one ultra low fusing porcelain. The result of this study showed the most translucent group of core materials was tetrasilicic fluormica glass ceramic and the least was sintered alumina.

The most translucent group among veneering ceramics was one of the feldspathic crowns(Ceramco) and the least translucent material for all thickness was ultra low – fusing veneering ceramics.(Duceram LFC).

Luthard²⁰(2001) determined the accuracy of the manual mechanical digitizer of the Precident-DCS system. Gauge blocks were aligned to the coordinate planes of the digitizer to determine the point and length measurement uncertainty. The measurement uncertainty was given by 95th percentiles.

The mean one-dimensional point measurement uncertainty in the Y direction was 11 microm for the first, 8 microm for the second, and 37 microm for both operators. The three-dimensional point measurement uncertainty in the Y direction was 10 microm for the first, 33 microm for the second, and 60 microm for both operators. The point measurement uncertainty was significantly influenced by the pressure during sensing and by the operator as well.

There were significant differences between the first and second recordings. The length measurement uncertainty in the Y direction for a gauge block of 20 mm was 52 microm for both operations. The reliability of the manually guided Precident-DCS digitizer is limited because of the significant influence of the operator and the mode of sensing (one or three dimensional).

Cheng K.C.²¹ (2002) studied on the effect of temperature and time on appearance and porosity during sintering of porcelain. It was studied for five dental dentine porcelains two aluminous: i)alpha ii) vitadur N and three feldspathic : omega, VMK68 and Carmen.

Disc specimens were sintered for 0-1000min over $750 - 1100^{\circ}$ C in a systematic approach pattern to establish limits of acceptable appearance. Porosity was measured using an image analyser on specimens fired for sintering times of 24 and 30s; 1,3,6 and 30 min;1,5, 10,15 and 20h; with sintering temperatures from 750 – 950 degree Celsius for Carmen and 800- 1050 degree Celsius for the others, all with 50 degree Celsius increments.

The result showed that the boundaries of the acceptable appearance areas in maps of sintering temperature vs sintering time were clearly delineated, analysis showed that they may be related to the activation energy of the diffusive processes occurring during sintering. Porosity increased markedly in the feldspathic porcelains, particularly VMK68.

Fradeani ²²(2002) reported on 5years experience with In-Ceram Spinell all-ceramic crowns. A total of 40 anterior crowns were positioned in 13 patients from October 1995 to December 1998.

Only one failure was recorded, and the fractured crown needed to be replaced; according to Kaplan-Meier analysis, the estimated success rate was 97.5%. A thorough description of the clinical procedures through which anterior teeth can be successfully treated with all-ceramic Spinell crowns is described.

Bindl A.²³(2002) evaluated the clinical performance of posterior CAD/CAM-generated In-Ceram Alumina and In-Ceram Spinell core crowns. Nineteen In-Ceram Spinell core crowns (four premolars and 15 molars) and 24 In-Ceram Alumina core crowns (two premolars and 22 molars) in 21 patients were examined using modified USPHS criteria at baseline and after a mean service time of 39 +/- 11 months.

The crown copings were machined from Vitablocs In-Ceram Alumina and Vitablocs In-Ceram Spinell using the Cerec 2 CAD/CAM system. Two molar In-Ceram Alumina core crowns fractured after respective service times of 14 and 17 months in the same patient. The Kaplan-Meier survival rate regarding fracture of the ceramic was 92% for In-Ceram Alumina and 100% for In-Ceram Spinell. At the follow-up examination, 80% alpha ratings and 18% beta ratings for In-Ceram Alumina core crowns were recorded.

Despite the two fractures, the clinical quality of CAD/CAM-generated In-Ceram Alumina and In-Ceram Spinell posterior crowns was excellent. Within the limitations of this study, both types of crowns appeared to be feasible. **Guazzato**²⁴(**2004**) conducted a study on strength, fracture toughness and microstructure of a selection of zirconia based ceramic materials. An experimentally stabilized zirconia (DC Zircon), InCeram Zirconia slip and InCeram Zirconia dry pressed were compared.

Microscope investigation and x ray diffraction revealed the important role played by the tetragonal to monoclinic phase transformation and by the relationship between the glassy matrix and the crystalline phase in the strengthening and toughening mechanisms of these ceramics

White S.N.²⁵ (2005) investigated the strength of a wide variety of layered zirconia and porcelain beams to determine whether the inclusion of zirconia cores results in improved strength. Eight types of layered or simple zirconia and porcelain beams (n = 10), approximately fixed partial denture-size, were made of a tetragonal polycrystalline zirconium dioxide partially stabilized with yttria core (Lava System Frame) and a feldspathic dental porcelain (Lava Ceram veneer ceramic).

Elastic moduli of the materials were measured using an acoustic method. Maximum force and modulus of rupture were determined using 3-point flexural testing and a universal testing machine. Beams with porcelain tensile surfaces recorded mean tensile strengths or moduli of rupture from 77 to 85 MPa, whereas beams with zirconia tensile surfaces recorded moduli of rupture almost an order of magnitude higher, 636 to 786 MPa. The elastic moduli of the porcelain and zirconia materials were 71 and 224 GPa, respectively.

Crack propagation following initial tensile cracking often involved the porcelain-zirconia interface, as well as bulk porcelain and zirconia. The layered zirconia-porcelain system tested recorded substantially higher moduli of rupture than have been previously reported for other layered all-ceramic systems.

Reich²⁶(2005) evaluated the clinical fit of all ceramic three unit fixed partial dentures generated with three different CAD/CAM systems. Twenty four all ceramic fpds were fabricated and randomly subdivided into 3 equally sized groups. 8 frameworks were fabricated using Digident CAD/CAM, another 8 frameworks using the cerec in lab system.

Vita Inceram Zirconia blanks were used for both the groups. In a third group frameworks were milled from yttrium stabilized Zirconium blanks using the Lava system. The mediams of marginal gaps were 7 micron for digi, 65 micron for lava, and 54 micron for

the conventional fpds. Within the limits of this study, the results suggest that the accuracy of CAD/CAM generated three unit FPDs is satisfactory for clinical use.

Herrguth²⁷ (**2005**) examined whether crowns fabricated from machinable blocks would achieve acceptable aesthetics and whether these could compete with the aesthetics of restorations obtained by individual layering technique. Fourteen patients, who were to receive single anterior crown restorations, participated in this study.

For each person two kinds of crowns were provided: one crown was made with the Cergogold system. The second one was produced in a Cerec machine and was additionally stained. Three independent examiners assessed the aesthetic appearance of crowns fabricated to match each subject's anterior shade. A scale of 1-6 was used to assess the aesthetic adaptation of each crown, with 1 representing excellent characteristics and 3.5 marking the threshold for clinical acceptability.

The examiners' scores were averaged, and the mean values were analysed with the Wilcoxon signed rank test (P<or=0.05). Regardless of the fabrication method the crowns were aesthetically acceptable in all 14 patients. The mean values for the layering technique and for the machined restorations did not differ significantly. Within the limits of this study it was documented, that machinable blocks could attain aesthetically satisfying results.

Curtis A.R.²⁸(2006) studied on the influence of surface modification techniques on the performance of a Y-TZP dental ceramic. The result showed no significant difference in the biaxial flexural strength of 25, 50 and 110 micrometre alumina abraded and the control specimens stored in dry and wet for 24hrs.significant increase in moduli was identified for alumina abraded specimens stored dry.

Alumina abraded specimens reduced surface roughness with the controls. The surface modification techniques initiated a phase transformation mechanism and resulted in the formation of a layer of compressive stresses on the surface of the disc shaped specimens.

Sailer .I.²⁹ (2007) determined the success rate of 3- to 5-unit zirconia frameworks for posterior fixed partial dentures (FPDs) after 5 years of clinical observations.Forty-five patients who needed at least 1 FPD to replace 1 to 3 posterior teeth were included in the study.

Fifty-seven 3- to 5-unit FPDs with zirconia frameworks were cemented with 1 of 2 resin cements (Variolink or Panavia TC). The following parameters were evaluated at baseline, after 6 months, and 1 to 5 years after cementation at test (abutments) and control (contralateral) teeth: probing pocket depth, probing attachment level, Plaque Index, bleeding on probing, and tooth vitality. Intraoral radiographs of the FPDs were taken. Twenty-seven patients with 33 zirconia FPDs were examined after a mean observation period of 53.4 +/- 13 months. Eleven patients with 17 FPDs were lost to follow-up.

After the 3-year recall visit, 7 FPDs in 7 patients were replaced because they were not clinically acceptable due to biologic or technical complications. After 5 years of clinical observation, 12 FPDs in 12 patients had to be replaced. One 5-unit FPD fractured as a result of trauma after 38 months.

The success rate of the zirconia frameworks was 97.8%; however, the survival rate was 73.9% due to other complications. Secondary caries was found in 21.7% of the FPDs, and chipping of the veneering ceramic in 15.2%. There were no significant differences between the periodontal parameters of the test and control teeth. Zirconia offers sufficient stability as a framework material for 3- and 4-unit posterior FPDs. The fit of the frameworks and veneering ceramics, however, should be improved.

Jun Zhou³⁰(2008) conducted a study using water quenching-induced cracked-glass was used as to prepare glass-ceramics. The cracked-glass panel was first heat-treated through two-step method, i.e. sintering for 1 h at 860 °C and subsequent crystallization for 1.5 h at 1080 °C, and then naturally cooled down to room temperature to be transformed into glass-ceramics.

XRD and SEM observations confirm that the cracked-glass can be used as parent glass to deposit β -wollastonite crystals depending on crack crystallization mechanism. The volume densities, porosities and bending strengths of the glass-ceramics are respectively around 2.7 g/cm3, 0.5% and 40 MPa. As compared with glass-ceramics prepared by conventional glass grain sintering process, the new type of glass-ceramics produced by CGC process shows pseudo-bioclastic texture and has less gas pore flaws, and may therefore become an alternative for materials of architectural decoration

Ebert .J.³¹ (2009) suggested a novel generative manufacturing technique, direct inkjet printing to improve the accuracy and to limit the possible microcracks and waste of material through substractive process. A tailored zirconia-based ceramic suspension with

27 vol% solid content was synthesized. The suspension was printed on a conventional, but modified, drop-on-demand inkjet printer. A cleaning unit and a drying device allowed for the build-up of dense components of the size of a posterior crown.

A characteristic strength of 763 MPa and a mean fracture toughness of 6.7 MPam(0.5) were determined on 3D-printed and subsequently sintered specimens. The novel technique has great potential to produce, cost-efficiently, all-ceramic dental restorations at high accuracy and with a minimum of materials consumption.

Dana .M. Quiblawi³²(2010) evaluated the effect of mechanical surface treatment of yttria-partially stabilized zirconia on its flexural strength and the effect of mechanical and chemical surface treatments on its bond strength to a resin cement. For flexural strength evaluation, zirconia bars $(4 \times 5 \times 40 \text{ mm})$ were prepared from zirconia blocks, sintered, then assigned into 4 groups: (1) control (no treatment), (2) airborne-particle abrasion, (3) silica coating, and (4) wet hand grinding.

For shear bond strength evaluation, zirconia rods $(2.5 \times 3 \text{ mm})$ were prepared from zirconia blocks, sintered, and assigned into 16 groups. Each group underwent a combination of the following mechanical and chemical treatments. Mechanical treatment included: (1) control (no treatment), (2) airborne-particle abrasion, (3) silicoating, or (4) wet hand grinding. Chemical treatment included: (1) control (no treatment), (2) acid etching followed by silanation, (3) silanation only, or (4) application of zirconia primer.

Dentin specimens were prepared from extracted molars stored in 0.5% chloramine-T. Zirconia rods were bonded to dentin using a resin cement (Multilink Automix), then light polymerized. After storage, the specimens were loaded to failure with the notched shear bond test method in a universal loading apparatus. Airborne-particle abrasion and hand grinding significantly increased flexural strength.

The highest shear bond strength values were achieved for the following groups: silicoated + silanated > hand ground + zirconia primer > airborne-particle abraded + silanated > zirconia primer > airborne-particle abraded + zirconia primer. Artificial aging resulted in significantly lower shear bond strength for the silicoated/silanated and the zirconia primer groups. Mechanical modification of the surface increased the flexural strength of Y-TZP. The resin bond to Y-TZP was improved by surface treatment. A combination of mechanical and chemical conditioning of the zirconia surface was essential to develop a durable resin bond to zirconia.

Osvaldo D.Moráguez³³(**2010**) found that polytetrafluoroethylene (PTFE) tape is used to seal the screw access channel to protect the screw head of the abutment and crown screw in implant-supported restorations. The material can be sterilized, is easy to manipulate, radiopaque, and less associated with malodor when retrieved. Malodor is primarily associated with the implant-abutment interface configuration and the suprastructure component design of a given implant system.

This technique enables fast removal of the filling material in a single piece, preventing unpredictable and time-consuming manipulations when removal of the screw-retained crown or abutment is required

Makarouna³⁴(2011) evaluated the clinical performance of lithium disilicate FPDs. 18 patients received lithium disilicate FPDs (study group) and 19 patients received conventional fpds(control).

After 6 years, the survival probabilities were found to be 63% in the study group and 95% in the control group. The data suggest that strict conditions should be considered before the use of lithium disilicate glass ceramic for FPDs.

Flinn B.D.³⁵(**2012**) assesses the accelerated aging characteristics of 3 commercially available yttria stabilised tetragonal zirconia polycrystalline (Y-TZP)materials by exposing specimens to hydrothermal treatments at 134 °C, 0.2 MPa and 180°C,1MPa in steam. Thin bars of Y-TZP from 3 manufacturers – Lava, Zirkonzhan and Zirprime were used. After 200 hours at 134°C and 0.2MPa, flexural strength decreased significantly from 1156 MPa to 829.

After 200 hours at 134°C and 0.2 MPa, some tetragonal crystals transformed to the monoclinic phase. The relative XRD peak intensity of the monoclinic to tetragonal crystal phases increased from 0.07 to 1.82 for Lava, from 0.06 to 2.43 for Zirkonzahn, and from 0.05 to 0.53 for Zirprime. After 28 hours at 180°C and 1.0 MPa, all Lava and Zirkonzahn specimens spontaneously fractured during aging. The Noritake specimens were intact after 48 hours, and the flexural strength showed no significant change, 1156 (87.6) MPa to 1122 (108) MPa.

The flexural strength decreased with an increase in the monoclinic phase. SEM micrographs revealed a transformed layer on the fracture surfaces. Hydrothermal aging of Y-TZP can cause significant transformation from tetragonal to monoclinic crystal structure, which results in a statistically significant decrease in the flexural strength of

thin bars. Although the strengths of all 3 Y-TZP materials are higher than other materials used for ceramic restorations, there are notable differences among them.

Cecilia Persson³⁶(**2012**) conducted a study where a sol–gel method was optimized to produce nano grain-sized zirconia–silica glass ceramics with properties adequate for dental applications. The material properties were compared to those of IPS e.max® CAD, a commercially available lithium disilicate.

The zirconia–silica glass ceramic was found to be translucent, with a transmittance of over 70%, and possessed excellent corrosion resistance. It also presented a somewhat lower elastic modulus but higher hardness than the lithium disilicate, and with the proper heat treatment a higher fracture toughness was achieved for the zirconia–silica glass ceramic.

In conclusion, the material produced in this study showed promising results for use in dental applications, but the production method is sensitive and large specimen sizes may be difficult to achieve.

Akihiro Fukabori³⁷(**2012**) studied the correlation between crystal grain sizes of transparent ceramics and scintillation light yields. Light yields of Y_2O_3 ceramics are different from specimen to specimen.

Nature of this phenomenon is not clear yet. Furthermore, origin of emission peaks for Y_2O_3 is not well understood. The results reported suggest that the emission derived from trapped excitons originates from the defects accumulated in the grain boundaries of the ceramics.

Xiang-Rong³⁸(2012) studied on the phase development, microstructural evolution and dielectric properties of manganese-doped barium strontium titanate glass ceramics. The specimens with (Ba,Sr)TiO₃ (BST) as the major crystalline phase were prepared by bulk crystallization process.

The results show that the dielectric constant and the dielectric loss measured at room temperature pass through a maximum with increasing MnO₂ concentration. This MnO₂ concentration dependence of dielectric properties was also investigated by impedance analyses. The evidence of impedance spectroscopy indicates that the activation energy values of grain and grain boundary coincide with the change in dielectric properties.

P.K.Maiti³⁹(2012) investigated the influence of barium oxide, heat treatment time and temperature on the crystallization, microstructure and mechanical behavior of the system in order to develop novel, high strength and machinable glass–ceramics. Three glasses were prepared and characterized by differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscope (SEM) techniques and some mechanical testing methods.

The crystallization kinetics of glass–ceramics was also studied. Activation energy and Avrami exponent calculated for the crystallization peak temperature (Tp) of three different glass batches. The Vickers hardness decreased slightly on formation of the potassium fluorophlogopite and barium fluorophlogopite phases, but decreased significantly on formation of an interconnected 'house of cards' microstructure.

Setsuaki Murakami⁴⁰(**2012**) reported that porous hydroxyapatite (HA) ceramics composed of rod-shaped particles exhibited high functional ability to be integrated in natural bone quickly compared to sintered HA ceramics. In addition to improved biological properties, rod-shaped particles might also provide unique mechanical properties to the HA porous ceramics. In this study, porous HA ceramics composed of rod-shaped HA particles with different aspect ratios were synthesized by a hydrothermal process, and their fracture behavior was examined by a flexural test.

As the reaction temperature in the hydrothermal process decreased, the aspect ratio of the resultant particles increased and was successfully controlled from 13 to 37. Porous HA ceramics composed of rod-shaped particles with large aspect ratios exhibited non-elastic deformation in the flexural test. As the aspect ratio of the particles increased, the flexural strength and strain at fracture increased. Furthermore, the flexural strength and strain at fracture of the porous HA ceramics composed of rod-shaped particles with large aspect ratios was higher than that of sintered porous HA ceramics with a similar.

Schmitter⁴¹(**2012**)studied on the ultimate load to failure of zirconia based crowns veneered with CAD/CAM manufactured ceramic. Thirty two identical, anatoform zirconia (Sirona inCoris ZI, mono L F1) frameworks (thickness 0.6 mm) were constructed (Sirona inLab 3.80). Afterwards, 16 crowns were completed using a CAD/CAM manufactured lithium disilicate ceramic veneer (IPS e.max CAD, Ivoclar Vivadent). The remaining 16 frames were veneered using conventional manual layering technique. For

the CAD/CAM manufactured veneers, the connection between framework and veneer was accomplished via a glass fusion ceramics.

Before fracture tests, half of the specimens underwent thermocycling and chewing simulation (1.2 million chewing cycles, force magnitude Fmax = 108 N).Nearly all (87.5%) conventionally veneered crowns failed already during chewing simulation, whereas crowns with CAD/CAM manufactured veneers were non-sensitive to artificial ageing.

Crowns veneered with lithium disilicate ceramic displayed ultimate loads to failure of about 1600N.The CAD/CAM production of veneers for restorations with zirconia framework is a promising way to reduce failures originating from material fatigue.

Fu Wang⁴²(**2013**) investigated the relationship between translucency and the thickness of different dental ceramics. Six disk-shaped specimens of 8 glass ceramics (IPS e.max Press HO, MO, LT, HT, IPS e.max CAD LT, MO, AvanteZ Dentin, and Trans) and 5 specimens of 5 zirconia ceramics (Cercon Base, ZenotecZr Bridge, Lava Standard, Lava Standard FS3, and Lava Plus High Translucency) were prepared following the manufacturers' instructions and ground to a predetermined thickness with a grinding machine.

A spectrophotometer was used to measure the translucency parameters (TP) of the glass ceramics, which ranged from 2.0 to 0.6 mm, and of the zirconia ceramics, which ranged from 1.0 to 0.4 mm. The TP values of the glass ceramics ranged from 2.2 to 25.3 and the zirconia ceramics from 5.5 to 15.1. There was an increase in the TP with a decrease in thickness, but the amount of change was material dependent. The translucency of dental ceramics was significantly influenced by both material and thickness. The translucency of all materials increased exponentially as the thickness decreased.

All of the zirconia ceramics evaluated in the present study showed some degree of translucency, which was less sensitive to thickness compared to that of the glass ceramics.

Jing Zhao⁴³(2013) studied to process and evaluate bi-colored zirconia ceramics as a pilot dental material by using well-established techniques. Two commercially available partially stabilized zirconia granules, one undoped and one doped with 0.202 wt% Fe₂O₃, resulted in white and yellow colors after sintering, respectively.

Bi-colored zirconia was fabricated by two-step dry pressing of both zirconia granules one above the other to form green bodies, followed by cold isostatic pressing (CIP) and, a two-step pressureless sintering finally at 1450 °C. The dilatometer results showed that the Fe2O3 doped zirconia sintered slightly rapid, but the difference of shrinkage between two powders was <1%. Sintered bars achieved full density, 6.018 g/cm3 (~99%TD), without cracks in the ~1 mm color gradient zone.

The microstructures were characterized by scanning electron microscopy (SEM) and careful observation of both surface and interior provided no obvious structural difference of either grains or pores among the three distinct regions, comprising white, yellow and color gradient zone. Vickers hardness of bi-colored zirconia was \sim 13.1 GPa, with no obvious difference in the three regions.

The four-point bending strength of the bi-colored zirconia bars was 745.5 ± 159.6 MPa, which appeared noticeably lower than that of the single-colored references being above 1000 MPa. Fractographic analysis revealed that in most of the cases (60%) the fracture was initiated at the color gradient zone, where large voids with high coordination numbers, agglomerates with critical size and concentration of irregular grains with porous surfaces were observed.

Above all, bi-colored zirconia ceramics prepared by the improved technique could meet the basic requirements of dental materials. The ways of minimizing the defects within bicolored blocks should be developed for the production of esthetic zirconia ceramics of high strength and reliability.

Burcu Kanat⁴⁴(**2014**) assesses the fracture resistance (FR), flexural strength (FS), and shear bond strength (SBS) of zirconia framework material veneered with different methods and to assess the stress distributions using finite element analysis (FEA). Zirconia frameworks were fabricated in the forms of crowns for FR, bars for FS, and disks for SBS (N = 90, n = 10) were veneered with either (a) file splitting (CAD-on) (CD), (b) layering (L), or (c) overpressing (P) methods.

Crowns were then cemented to the metal dies. Mechanical tests were performed, and data were statistically analyzed. Stereomicroscopy and scanning electron microscopy (SEM) were used to evaluate the failure modes and surface structure. FEA modeling of the crowns was obtained. Results were verified and the file splitting technique showed higher bonding values in all mechanical tests, whereas a layering technique increased the FR

when an anatomical core design was employed. File splitting (CAD-on) or layering veneering ceramic on zirconia with a reduced framework design may reduce ceramic chipping.

Park J.H.⁴⁵(2014) conducted a study to evaluate the 2-body wear of antagonists for 3 computer-aided design and computer-aided manufacturing (CAD/CAM) anatomic contour zirconia ceramics and veneering porcelain when opposing natural human enamel. Zirkonzahn Y-TZP (polished zirconia, zirconia with staining, zirconia with staining and glazing), Acucera Y-TZP, Wieland Y-TZP, and Noritake feldspathic ceramic were tested (6 groups).

Eight disk-shaped specimens 15 mm in diameter and 5 mm thick were prepared for each group. Forty-eight specimens were fabricated for a wear test against maxillary premolars without caries or previous restorations with 240 000 masticatory cycles in a masticatory simulator. The SEM observations of each group revealed fine bubbles and porous surfaces in the Noritake feldspathic ceramic group, whereas the polished Zirkonzahn Y-TZP group, Acucera Y-TZP group, and Wieland Y-TZP group had smooth surfaces. The surface roughness of Zirkonzahn Y-TZP after staining and glazing was significantly greater than that of any other groups (P<.01).

The tooth opposing the polished Zirkonzahn Y-TZP group demonstrated the least wear $(1.11 \pm 0.51 \text{ mm}^3)$, while Zirkonzahn Y-TZP with staining and glazing produced the greatest enamel wear $(3.07 \pm 0.98 \text{ mm}^3)$ among the zirconia groups. The Noritake feldspathic ceramic group showed significantly more antagonistic tooth wear than other groups (P<.05).

Hirokazu Masai⁴⁶(2015) investigated the nano-structure of TiO₂-precipitated CaO-B₂O₃-Bi₂O₃-Al₂O₃-TiO₂(CaBBAT) glass–ceramics, and discussed the effect of the addition of SnO. Sn Mössbauer spectra of the Sn-doped glass suggest that most of the SnO was oxidized during melting. Selective crystallization of TiO₂ occurred independently of SnO addition in the homogeneous glass.

However, EDX analysis of the glass–ceramics revealed that the Ti cation is partially localized and that the addition of SnO promotes the nano-phase separation. It can be concluded, therefore, that the addition of SnO influenced the formation of secondary particles of TiO₂ nano-crystallites and thereby improved the photocatalytic activity.

Xiaojun Hao⁴⁷(**2015**) studied the preparation and properties of transparent cordieritebased glass-ceramics with high crystallinity. The crystallization kinetics of parent glass was deeply investigated by differential scanning calorimetry (DSC). After heat-treatment at 1030 °C for 6 h, a large amount of α -cordierite (indialite) crystals devitrified from the parent glass, which was confirmed by the X-ray diffraction and TEM results.

The crystallinity of the obtained transparent glass-ceramics reached up to 87.5%, which can be ascribed to the composition and heat treatment of parent glass. In addition, these transparent glass-ceramics possessed low density (2.477 g/cm³), low thermal expansion coefficient ($1.435 \times 10^{-6} \text{ °C}^{-1}$) and high Vickers hardness (8.1 GPa).

The combination of excellent physical, thermal and optical properties makes this new family of transparent glass-ceramics exhibiting potential applications in the fields of base materials for rare-earth ions.

Xianglong Han⁴⁸(2015) investigated the characterization and synthesis of ZTA nanopowders and ceramics by rotating packed bed(RPB). The nanopowders in those reactors were characterized by XRD, SEM, TEM, EDS, and XPS. The results showed that ZTA nanopowders prepared by RPB had the lowest extent of agglomeration, the most homogeneous microstructure and the narrowest particle size distribution concentrating on 28–53 nm with an average sphere diameter of 41 nm.

RPB could also dramatically decrease the reaction time and then decrease the energy consumption and production costs in preparation process. All the results indicated that the presented novel reactor (RPB) may provide a new way to the production of nanopowders and ceramics in the industrial application

Camillo D' Arcangelo⁴⁹(2016) conducted a study to compare the 2-body wear resistance of human enamel, gold alloy, and 5 different dental ceramics, including a recently introduced zirconia-reinforced lithium silicate ceramic (Celtra Duo)Cylindrical specimens were fabricated from a Type III gold alloy (Aurocast8), 2 hot pressed ceramics (Imagine PressX, IPS e.max Press), 2 CAD/CAM ceramics (IPS e.max CAD, Celtra Duo), and a CAD/CAM feldspathic porcelain (Vitablocs Mark II) (n=10). Celtra Duo was tested both soon after grinding and after a subsequent glaze firing cycle. Ten flat human enamel specimens were used as the control group.

All specimens were subjected to a 2-body wear test in a dual axis mastication simulator for 120 000 loading cycles against yttria stabilized tetragonal zirconia polycrystal cusps.

The wear resistance was analyzed by measuring the vertical substance loss (mm) and the volume loss (mm3). Antagonist wear (mm) was also recorded. Data were statistically analyzed with 1-way ANOVA tests (α =.05). The wear depth (0.223 mm) of gold alloy was the closest to that of human enamel (0.217 mm), with no significant difference (P>.05).

The greatest wear was recorded on the milled Celtra Duo (wear depth=0.320 mm), which appeared significantly less wear resistant than gold alloy or human enamel (P<.05) The milled and not glazed Celtra Duo showed a small but significantly increased wear depth compared with Aurocast8 and human enamel. Wear depth and volumetric loss for the glaze-fired Celtra Duo and for the other tested ceramics did not statistically differ in comparison with the human enamel.

Xiaokai Li⁵⁰(2016) investigated the optical properties of vacuum-sintered and airannealed ceramics where were characterized using transmittance spectra and a Commission International de l'Eclairage (CIE) diagram. The corresponding defects are investigated by electron paramagnetic resonance (EPR) spectra. The band gap of the vacuum-sintered samples is 2.72 eV, which is much smaller than that of the annealed sample.

The results reveal that the Vo⁺ (F⁺ center) and Zr³⁺ defects form transition energy levels near the top of the valence band and at the bottom of the conduction band, respectively. The color-related absorption is mainly attributed to the electronic transfer from the Zr³⁺ level to the conduction band and from the F⁺ center to the Zr³⁺ level.

Stephanie Pfeifer⁵¹(**2016**) conducted a study where polycrystalline zirconia toughened alumina (ZTA) fibers were prepared from aqueous solutions of aluminum hydroxide chloride 2.5-hydrate and zirconium oxychloride octahydrate. Fiber processing was accomplished via dry spinning. Poly(vinylpyrrolidone) (PVP) was used as spinning aid. Polycrystalline ZTA fibers were obtained by calcination of the green fibers followed by sintering at defined temperatures in air.

Ceramic fibers were 10 μ m in diameter and had an average tensile strength of 1010 (±363) MPa with peak values reaching 1535 MPa. Differential scanning calorimetry/thermogravimetric analysis coupled with mass spectrometry (DSC/TGA-MS) showed an exothermic peak at 1156 °C assigned to the crystallization of α-Al2O3 and tetragonal ZrO2 and an overall ceramic yield of 41.7% at 1400 °C. X-ray diffraction

(XRD) analysis showed that tetragonal ZrO2 can be obtained at 1350 °C directly from the amorphous precursor whereas pure-phase α -

Iman Abd-Elwahab Radi⁵²(2016) introduced a straightforward and cost-effective technique for accessing the abutment screw channel and unscrewing the abutment and cement-retained prosthesis as 1 unit is described. The technique does not jeopardize the integrity of the restoration, screw, abutment, or implant.

A guiding acrylic resin index is fabricated for locating and guiding the access to the screw channel of the abutment, provided that the patient's cast with the implant analog is available. The procedure could be extrapolated to computer-aided designed and computer-aided manufactured (CAD-CAM) implant prostheses, whereby a CAD-CAM index could be fabricated on the digital modelAl2O3 is formed stepwise via transition alumina phases.

Hamza T.A.⁵³(**2017**) conducted a study to evaluate the marginal fit of 5 different monolithic zirconia restorations milled with different CAD-CAM systems. Thirty monolithic zirconia crowns were fabricated on a custom-designed stainless steel die and were divided into 5 groups according to the type of monolithic zirconia crown and the CAD-CAM system used: group TZ, milled with an MCXL milling machine; group CZ, translucent zirconia milled with a motion milling machine; group ZZ, zirconia milled with a dental milling unit; group PZ, translucent zirconia milled with a zirconia milling unit; and group BZ, solid zirconia milled using an S1 VHF milling machine.

The type of CAD-CAM used affected the marginal fit of the monolithic restoration. The mean (\pm SD) highest marginal discrepancy was recorded in group TZI at 39.3 \pm 2.3 µm, while the least mean marginal discrepancy was recorded in group IZ (22.8 \pm 8.9 µm). The Bonferroni post hoc test showed that group TZI was significantly different from all other groups tested (P<.05)

Within the limitation of this in vitro study, all tested CAD-CAM systems produced monolithic zirconia restorations with clinically acceptable marginal discrepancies; however, the CAD-CAM system with the 5-axis milling unit produced the best marginal fit.

Danko Ćorić⁵⁴(2017) investigated and analysed the fracture toughness of yttriastabilized tetragonal zirconia polycrystal (Y-TZP) dental ceramics by means of the Vickers indentation technique. Nine different fracture toughness equations are considered and the results are compared with the literature value obtained by a conventional method, single edge V-notched beam (SEVNB) test. The influence of the applied indentation load on fracture toughness was also observed.

Tests were conducted under four different loading conditions (29.42 N, 49.03 N, 196.13 N, and 294.20 N). Obtained results indicate that the fracture toughness of Y-TZP dental ceramics depends on the indentation load, morphology of indentation cracking as well as on the applied model of fracture resistance.

Hongyu Xing⁵⁵(**2017**) studied on zirconia (ZrO2) ceramic bars with three different printing sizes which were fabricated by a stereolithographic (SLA) 3D-printing process and subsequent sintering. An anisotropic character of the ceramics surface quality was observed. The surface roughness of the horizontal surface was below 0.41 μ m, whereas it reached 1.07 μ m along the fabrication direction on the vertical surface.

The warpage and flatness were utilized to measure the dimensional accuracy of the 3D printed ZrO2. Furthermore, it was evaluated that the warpage and flatness were below 40 μ m and 27 μ m, respectively, even if the printed size of ceramic bar reached 3 mm × 4 mm × 80 mm. In addition, the flexural strength, the fracture toughness, the hardness and the density of ZrO2 ceramics can reach to 1154 ± 182 MPa, 6.37 ± 0.25 MPa m1/2, 13.90 ± 0.62 GPa and up to 99.3%, respectively.

Moreover, the effects of scanning paths and printing size on properties of the sintered ZrO2 samples were analyzed. The anisotropic character of surface quality was related to the various scanning paths. The warpage and flatness of 3D printed ZrO2 bars were apparently affected by the various printed sizes. Also, the effects of special microstructure on the mechanical properties of sintered ZrO2 samples were investigated.

Melis Kaplan⁵⁶(2018) proposed a study to evaluate the production and different properties of yttria stabilised zirconia for dental applications. Dense zirconia stabilized with 3 mol% yttria ceramics were produced in disc shape by first cold isostatically pressing at 100 MPa and then sintering at 1450 °C at ambient laboratory conditions. Coloring was accomplished by immersion the discs in NiCl₂, MoCl₃, and NiCl₂ + MoCl₃ solutions for 5, 30, and 60s. Different concentrations (0.1, 0.25, and 0.5 wt%) were applied to get the color of natural tooth.

The density, color, microhardness, fracture toughness, compressive strength, and wear rate of the discs were measured to evaluate the suitability of the colored discs for dental applications. Color assessments were made by measuring CIE Lab L*, a*, b*, and ΔE^* values. Low temperature degradation of the samples was evaluated by aging sensitivity tests in autoclave for 2, 4, and 6 h.

Results have shown that color produced depends on the kind and concentration of the colorant solution while time of immersion has no significant effect on coloring process. Coloring solutions containing 0.1 and 0.25 wt% MoCl₃ provided clinically acceptable color with the ΔE^* value ranging from 5.16 to 6.42 for dental applications.

Pouya Takav⁵⁷(**2018**) aims to highlight the role of TiO2 (titanium dioxide) on concurrent densification-crystallization behavior, microstructure as well as mechanical and chemical properties of fluorcanasite glass-ceramics.

According to the obtained results, the addition of TiO2 to the base composition (stoichiometric fluorcanasite) and an increase of its content, decreased crystallinity of the relevant glass-ceramics; but improved their sinterability. Fully densified glass-ceramics were obtained from TiO2 containing compositions after sintering at 900–950 °C. Calcium fluoride and fluorcanasite crystallized in all fabricated glass-ceramics during sintering; while goetzenite crystallized as the dominant crystalline phase in those glass-ceramics contained more than 6 weight ratios of TiO2.

On the basis of microstructural observation, the interlocking status between the precipitated crystals was remarkably diminished by an increase of TiO2 content. Measurement of mechanical properties confirmed the rise of Vickers micro-hardness and simultaneous decrease of flexural strength and fracture toughness by enhancing of TiO2 content in the examined glass-ceramics.

3. HISTORY OF CERAMICS

The earliest traces of the origins of ceramics were porous fragments of mud and clay fired at low temperature. These rudimentary products described as earthenware were estimated to date back to approximately 23,000 BC in China. Firing in primitive kilns at temperatures upto 900°C allowed the clay particles to fuse at points of contact, which yielded a rather porous final result.⁵⁸

Thousands of years later in 100BC, the Chinese discovered how to produce more refined pieces at higher temperatures. The resultant stoneware was more stronger and less porous than earthenware. Subsequent development of porcelain occurs in early 1000 AD. These refined material was called as China stone or China ware that strong, functional, transparent containers were produced with walls only a few millimetres thick.

Ceramic like tools have been used by humans since the end of the Old Stone Age around 10,000 BC. Dental technology existed in Etrucia since 700 BC and through Roman 1st century BC but remained undeveloped until 18th century.⁵⁹

Ceramics originally referred to as art of fabricating pottery. The word Ceramics comes from Greek term KERAMOS, meaning A POTTER. In Sanskrit, this word means BURNED EARTH, since the components were clay from the earth, which was heated to form pottery.⁶⁰ Ceramics were probably the first material, to be significantly made by human beings. The Greek word 'Keramos'. Pottery or burnt stuff of fire has been known to man for about 4,00,000 years. The earliest glassing technique was a Sumerian invention made famous about 4,000 B.C. Historically 3 basic type of ceramic materials were developed.

1. Earthern ware:

It fired at low temperature and is relatively porous.

2. Stone ware:

Which appeared in China in about 100 B.C. and is fired at a higher temperature than earthern ware, which results in both higher strength and renders the material impervious to water.

3. Porcelain:

Which was obtained by fluxing white China clay with "China stone" to produce a white translucent stone ware. This was developed in King-te-tehing in China in about 1,000 A.D.This material was strongest than the stone ware and earthern ware. The development of the art and science of dental ceramic in many way parallels the historical development of industrial revolution.

In 700 BC, Etruscans made artificial teeth of ivory and bone, human teeth and animal teeth that were held in place by gold wires, or flat bands and rivets.

John Greenwood carved teeth from hippopotamus ivory for 1 of 4 sets of complete dentures. One of the first set of dentures made for US President George Washington contained extracted teeth but later his dentures were made of hippopotamus ivory.⁶¹

The first porcelain tooth material was patented in 1789 by Nicolas Dubois de Chemant, a French dentist in collaboration with Alexis Duchateau, a French pharmacist. An important version of the mineral paste teeth produced in 1774 by Duchateau.^{58,59}

In 1808, Giusseppangelo Fonzi, an Italian dentist, invented a terrometallic porcelain tooth held in place by a platinum pin or frame.^{59,61}

Planteau, a French dentist, introduced porcelain teeth to the US in 1817. Peale, an artist developed a baking process in Philadelphia for these teeth in 1822. Commercial production of these teeth by Stockton began in 1825.⁶²

In England, Ash developed an improved version of the porcelain teeth in 1837.Improvement in translucency and colour of dental porcelain was noticed by Elias Wildman in 1838.^{58,61}

In 1839, invention of vulcanized rubber allowed porcelain denture teeth to be used effectively in denture base.

In 1903, Charles Land introduced one of the first ceramic crowns to dentistry. This crown was made by combining burnished platinum foil like a substructure with the high controlled heat of a gas furnace.⁵⁸

1910: Mechanic props. Published.

1918: Chemical analysis of porcelain.

1923: First casting of dental porcelain.

1940: Vacuum firing of dental porcelain.

1942: Fluoroscent porcelains.

1956: Porcelain fused to gold systems to improve strength.

1962: Development of much improved gold alloys as a porcelain fused to metal system

Improvements in metal ceramics happened during the past 35 years that resulted with enhanced alloys, porcelain metallic bonding as well as porcelains.

In spite of aesthetic advantage, all porcelain crowns did not get popularity due to its low strength. In 1960, feldspathic porcelains with reliable chemical bonding have been used in metal ceramic restorations.

In 1962, Weinstein and Weinstein et al , described two important breakthroughs responsible for the long standing superb esthetic performance and clinical survival rates of metal ceramic restorations.

- 1. Identified the formulations of feldspathic porcelain that enabled the systemic control of the sintering temperature and coefficient of thermal expansion.
- ^{2.} Described the components that could be used to produce alloys that bond chemically to and that are thermally compatible with feldspathic porcelain.⁶¹

In 1963, first commercial porcelain by Vita Zahnfabrik was produced.⁶²

In 1965, McLean and Hughes developed a Porcelain Jacket Crown with an inner core of aluminous porcelain containing 40-50% alumina crystals to block the propagation of cracks. The inner core is layered with porcelain resulting in restoration approximately twice as strong as traditional PJC. The platinum matrix is left in complete restoration to improve the fracture resistance.^{59,63}

1967: Restriction of uranium to 1% by Wt.

1968: First use of a glass ceramic by McCulloch.

1970: Development of porcelain fused to base metals.

1974: Porcelain fused to noble metals.

1980: Development of "non-shrink" aluminous direct moulding core for crowns.

1983: Development of high expansion core material by O'Brien (DCNA).

1984: Introduction of glass-ceramic system. First international standard published.

1984: for dental ceramic powders by Corning Glass Company. ISO 6872-1984 (E).

1985: Organic liquid binder instead of H₂O was developed by Sanderson.

1991: Repair of porcelain by Ralph using hydrofluoric acid etching silane.

1993: Monsenego Burdaicon studied the effect of fluorescence in ceramics and showed the effect of cementing media on fluorescence of ceramics.

In 1980s, the introduction of shrink free all ceramic crown system(Cerestone) provided additional flexibility for achieving esthetic results. In 1984, Adair and Grossman demonstrated an improvement in all ceramic systems developed by a controlled crystalisation of a glass(Dicor).⁵⁹

In 1990s, a pressable glass ceramic (IPS EMPRESS) containing approximately 34 vol% leucite was introduced that provided a strength and marginal adaptation.in late 1990s, an improved version of IPS EMPRESS 2 containing 70vol% lithium disilicate crystals was introduced.⁶⁴

Advancement in the field of CAD/CAM led to the development of CAD/CAM ceramics. In 1980s, Dr. Werner H Mormann and Dr. Marco Brandsteini developed a basic concept of the in office CAD/CAM which had a two dimensional software capability to fabricate inlays.

In 1985, CEREC 1 unit was introduced. The first chair side inaly was fabricated on September 19, 1985. It was later extended to provide for onlays and veneers.

In 1994, CEREC 2 was introduced at Seimens(Munich, Germany). Partial and full crowns and copings could be fabricated.

In 2000, CEREC 3 was introduced. This system helps to fabricate a three unit bridge.⁶⁵

Zirconia was introduced to ceramic dentistry in 20th century. The zirconia used in dentistry is zirconium oxide which is stabilised by the addition of yttria.⁶⁶

4. TERMINOLOGY

A **ceramic** is an earthly material usually of silicate nature and may be defined as a combination of one or more metals with a non-metallic element usually oxygen. (GPT 9)

The American Ceramic Society had defined ceramics as inorganic, non-metallic materials, which are typically crystalline in nature, and are compounds formed between metallic and nonmetallic elements such as aluminum & oxygen (alumina – Al_2O_3), calcium & oxygen (calcia - CaO), silicon & nitrogen (nitride- Si_3N_4).

Ceramics are man-made, inorganic materials formed by heating raw minerals at high temperatures.⁶⁷

Dental porcelain (also known as dental ceramic) is a dental material used by dental technicians to create biocompatible lifelike dental restorations, such as crowns, bridges, and veneers. Evidence suggests they are an effective material as they are biocompatible, aesthetic, insoluble and have a hardness of 7 on the Mohs scale. For certain dental prostheses, such as three-unit molars porcelain fused to metal or in complete porcelain group, zirconia-based restorations are recommended.⁶⁸

Ceramics are characterized by their refractory nature, hardness, chemical inertness, biocompatibility and susceptibility to brittle fracture.

The word **porcelain** is said to have been invented by Marco Polo in the 13th century from the Italian word *porcellana*, or cowrie shell. Polo used the cowrie shell to describe Chinese porcelain because it was similarly strong and hard while remaining thin and translucent.⁶⁹

The term porcelain is referred to a specific compositional range of ceramic materials made by mixing kaolin, quartz and feldspar in proper proportioning and fired at high temperature.

Porcelain is essentially a white, translucent ceramic that is fired to a glazed state. All porcelains are ceramics, but not all ceramics are porcelains.

Porcelain veneers are thin pieces of porcelain used to recreate the natural look of teeth, while also providing strength and resilience comparable to natural tooth enamel. It is often the material of choice for those looking to make slight position alterations, or to change tooth shape, size, and/or color.⁵⁸

Metal ceramic restoration: an artificial crown or fixed complete or partial denture that uses a metal substructure and porcelain veneer (GPT 9)

5. CLASSIFICATION OF CERAMICS

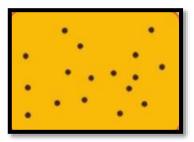
Dental ceramics can be classified in a number of different ways, including by their composition, processing method, fusing temperature, microstructure, translucency, fracture resistance and abrasiveness.

5.1. Classification by Composition:

Ceramics can be divided into three categories by composition^{70,71}:

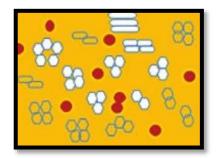
a) Predominantly composed of glass

Ceramics that are composed mostly of glass have the highest esthetics. Manufacturers sometimes add small amounts of filler particles to control the optical effects that mimic natural enamel and dentin. Generally, the more filler particles that are added to a ceramic, the greater the increase in the mechanical properties but the greater the decrease in its esthetic properties.



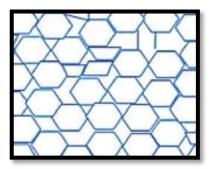
b) Particle filled glass

Polycrystalline ceramics contain no glass at all. As noted earlier, these are not porcelains. The crystalline arrangement lends these ceramic materials the highest strength, but they are generally less esthetic. The principle is similar to tooth-colored filling material (composite resins). By definition, any material that comprises different materials is a composite; therefore, a ceramic is also a composite. With composite resins, filler particles are added to a resin matrix; greater filler content means greater mechanical properties, but results in lower translucency. With ceramics, the glass is the matrix and the fillers are crystalline particles that melt at high temperatures.



c) **Polycrystalline ceramics**

Non glass-containing polycrystalline ceramics comprise an aluminium oxide or zirconium oxide matrix and fillers that are not particles but elements that alter optical properties. These added elements are referred to as dopants. Conventional dental ceramics are based on a silica (SiO₂) network and potash feldspar(K₂O-Al₂O₃-6SiO₂), soda feldspar (Na₂O-Al₂O₃-6SiO₂), or both.⁷² To control the coefficient of thermal expansion, solubility, and fusing and sintering temperatures, different elements are added, such as pigments (to produce the different hues), opacifiers (white-colored oxide to decrease translucency), and glasses.



5.2. Classification by Processing Method

Another approach to classifying ceramics is by the method by which they are processed. This includes:

a) Powder/Liquid Building

Mixing ceramic powder and liquid (ie, deionized water or the manufacturer's modeling liquid) is a conventional processing method. This condensation method incorporates building on a ceramic or metal core with a powder/liquid ceramic slurry with a brush or spatula by hand. The slurry is condensed by vibration to remove excess liquid, which rises to the surface and is blotted away by an absorbent tissue. It is important to remove any voids during the application, but this does not always occur.⁷³ Depending on

the skill of the technician, some voids may remain, decreasing the overall strength of the restoration. At certain steps in the fabrication, the ceramic buildup is vacuum fired at a selected temperature, which removes the moisture and further condenses the ceramic through a process called "sintering."

During the sintering process, fusion occurs at the particles' points of contact, which results in densification by viscous flow when the ceramic or glass particles reach their firing temperature.⁵⁸ Typically, a restoration is overcontoured by 25% to allow for densification or shrinkage during the firing cycle.⁷⁴

b) Slip Casting

The slip-casting fabrication method was introduced in the 1990s. This processing technique involves the creation of a porous core by slip casting, which is sintered and then infiltrated with a lanthanum-based glass, producing two interpenetrating continuous networks: a glassy phase and a crystalline infrastructure. The crystalline infrastructure could be alumina(Al₂O₃), spinel (MgAl₂O₄), or zirconia-alumina (12 Ce-TZP- Al₂O₃). Restorations produced through this method tend to have fewer defects from processing and have greater strength than conventional feldspathic porcelain.⁷⁵

c) Hot-Pressed Ceramic

The hot-pressed ceramic fabrication technique was introduced in the late 1980s and allowed the dental technician to create the restoration in wax. Then, using the lostwax technique, the technician was able to press a plasticized ceramic ingot into a heated investment mold. Ceramics containing high amounts of leucite glass or optimal pressable ceramics were initially used for this process.

In 2006, lithium disilicate became the second generation of materials to use this method. A commonly used technique involves waxing the restoration to full contour and then hot pressing to yield a restoration .The incisal area is then cut back to create mamelons ⁷⁶.This is followed by the application of various incisal porcelains. To account for shrinkage (densification) during the firing cycle, the layering porcelain is overcontoured.⁷⁷

d) <u>CAD/CAM</u>

In the mid 1990s, Nobel Biocare introduced the first all-ceramic product with a CAD/CAM substructure. The core consisted of 99.9% alumina on which a feldspathic ceramic was layered.

The use of CAD/CAM technology expanded machinable ceramic fabrication by allowing scanning, designing, and milling of either a full-contoured restoration or a single- or multiple-unit framework by a computer.

Two different CAD/CAM methods are used. The first method is an additive version in which an electrodeposition of powdered material is applied layer by layer to a conductive die through an electrical current. This technique is also referred to as rapid prototyping. The other (and more common) method is a subtractive method in which a substructure or full-contour restoration is milled from a solid block of ceramic material.

The available materials for the subtractive CAD/CAM processing include silicabased ceramics, infiltration ceramics, lithium-disilicate ceramics, and oxide highperformance ceramics. For example, lithium disilicate is actually milled as lithium metasilicate and then heated to 820°C in a two-stage oven. During this firing cycle, there is a controlled growth of the grain size($0.5 \mu m$ to $5 \mu m$) and a conversion of metasilicate crystals to disilicate crystals. This crystallization process not only changes the physical composition and strength but also causes the restoration to reach the indicated ceramic shade.⁷⁸

5.3. Classification by Fusing Temperature

On the basis of fusion temperature, ceramics are classified as:

- a) High Fusing (1300°C)
- b) Medium Fusing (1101-1300°C)
- c) Low Fusing (850-1000°C)
- d) Ultra Low Fusing (Below 850°C).

Denture teeth are an example of high-fusing porcelain. Crown and bridge porcelains can be either medium- or low-fusing, depending on the system, and ultra-lowfusing porcelain would be used for porcelains and glazes. To make it less complicated, some now refer to just two categories- high- or low-fusing porcelains-with the separation designated at 800°C.⁷⁹

5.4. Classification by Microstructure

As previously mentioned, porcelains have two different phases: the glass phase (responsible for the esthetics) and the crystalline phase (associated with mechanical strength).

In the case of feldspathic porcelain, a crystalline mineral called leucite (potassium-aluminum-silicate)forms when feldspar is melted. Between 1,150°C and 1,530°C, feldspar undergoes incongruent melting to form leucite crystals.⁸⁰Incongruent melting is a process in which one material does not uniformly melt and forms a different material.

The leucite crystalline phase has a diffraction index similar to the glassy matrix that, in this case, contributes to the overall esthetics of the porcelain. The leucite content of a porcelain is associated with the crack propagation strength. Greater leucite content means a greater decrease in the propagation of a crack. This type of porcelain is referred to as leucite-reinforced. During the sintering process of all-ceramic restorations, microporosities are formed on the surface that lead to crack initiation and propagation, ultimately resulting in failure.

Hot-pressed ceramics have high amounts of leucite crystals and are considered leucite reinforced glass ceramics. During the heated injection molding cycle, the sintering process is avoided and the leucite crystals act as barriers that counteract the increase in tensile stresses that can lead to the formation of microcracks. This type of ceramic can be used to press as an all-ceramic restoration or to a metal coping.⁸¹

As previously mentioned, McLean and Hughes developed an all-ceramic crown that had an inner core of aluminous porcelain that contained 40% to 50% alumina crystals. The principle behind this addition was the dispersion of a high-strength crystal with a high elastic modulus within the glassy matrix to increase the strength and hardness of the ceramic.⁸²Alumina increases the strength of feldspathic porcelain more than leucite, which increases the fracture resistance.

The particle size of the alumina may be responsible for the increase in the mechanical properties by decreasing agglomeration. When ceramics are sintered, the

particle size is critical. Finer powder yields a greater reduction in surface area. Fine powders tend to form clusters of irregular shape and uncontrolled size and are referred to as "agglomerates," which hinder flow properties.

Lithium disilicate was the second generation of hot-pressed ceramic materials. These ceramic restorations are referred to as lithium-disilicate—reinforced glass ceramics. This ceramic material contains 70% lithium-disilicate crystals, which results in an increased flexural strength of approximately 360 MPa (milled version) to 400 MPa (hot-pressed version). The increase in strength is found in the unique microstructure of lithium disilicate, which consists of any small interlocking plate like crystals that are randomly oriented. The lithium-disilicate crystals cause cracks to deflect, branch, or blunt, which arrests the propagation of cracks.

Zirconia as a pure oxide does not occur in nature. It has been given the nickname "ceramic steel," and the scientific term is zirconia dioxide. This biomaterial is widely used in medicine and dentistry because of its mechanical strength as well as its chemical and dimensional stability and elastic modulus similar to stainless steel. Zirconia has a normal density of 6 g/cm².

The theoretical density (ie, 100% dense) of zirconium oxide is 6.51g/cm². The closer these two density values are, the less space between the particles, resulting in greater strength and a smoother surface. A unique characteristic of zirconia is its ability to stop crack growth, which is termed "transformation toughening". An ensuing crack generates tensile stresses that induce a change from a tetragonal configuration to a monoclinic configuration and a localized volume increase of 3% to 5%. This volume increase results in a change of tensile stresses to compressive stresses generated around the tip of the crack.

The compressive forces counter the external tensile forces and stop the further advancement of the crack. This characteristic accounts for the material's low susceptibility to stress fatigue and high flexural strength of 900 MPa to 1200 MPa. Zirconia dioxide can be used as a monolithic restoration or a substructure with a veneering porcelain.⁸³

5.5. Classification by Translucency

Translucency is the relative amount of light transmitted through a material. A natural tooth derives most of its color as a result of the light reflectance from dentin that is altered by absorption and scattering by the enamel. The shade of a human tooth is determined by the shade of the dentin because the enamel is more translucent. This translucency becomes more apparent in the interproximal and incisal portions of the tooth because of the lack of underlying dentin.

There are several factors that affect the translucency of dental ceramics.⁸⁴ Thickness of the material has the greatest effect, but translucency can also be affected by the number of firings, the shade of the substrate, and the type of light source or illuminant. Because clinical settings can vary so widely, specimens should be compared at the recommended minimum thickness to be classified by translucency.

Porcelain translucency is usually measured with the translucency parameter, which is defined as the color difference between a uniform thickness of ceramic material over a black and a white background or the contrast ratio (CR), which is the ratio of illuminance of a ceramic material when it is placed over a black background compared with a white background.

The chemical nature, size, and number of crystals in a ceramic matrix will determine the amount of light that is absorbed, reflected, and transmitted compared with the wavelength of the source light.Therefore, the greater the number of crystals in the glassy matrix, the less translucent the ceramic.^{85,86,87}

5.6. Classification by Fracture Resistance

A quantitative way of expressing a ceramic's resistance to brittle fracture when a crack is present is referred to as the "fracture toughness,"which is the ability to resist crack growth.¹

If a material has a large value of fracture toughness, it will probably undergo ductile fracture.Brittle fracture is very characteristic of materials with a low fracture toughness value.⁸⁸

Flexural strength (modulus of rupture or bend strength) is defined as a material's ability to resist deformation under load. Flexural strength represents the highest stress experienced within the material at its moment of rupture and is measured in terms of stress.

Ceramic restorations have been known to cause wear of opposing enamel. The abrasiveness of a dental ceramic is mainly determined by the smoothness of the material. For wear to occur, there must be friction developed by mechanical interlocking between the two wear bodies. Low-fusing porcelains were developed to incorporate finer-sized leucite particles in lower concentrations with the idea of lowering the abrasiveness of the ceramic surface.

In their study, Elmaria and colleagues, compared the wear on opposing enamel by various restorative materials. These included gold, glazed, and polished or glazed-only Finesse (a low-leucite–containing ceramic),Procera AllCeram[™] (Nobel Biocare), and IPS Empress (Ivoclar Vivadent). They found that gold, glazed-and-polished Finesse, and glazed-and-polished All Ceram were the least abrasive, whereas glazed-only IPS Empress was the most abrasive.⁸⁹

Because there are two different scenarios, strictly classifying ceramics by their abrasiveness can present a problem when measuring surface roughness. One scenario is the surface roughness after fabrication and the type of finishing process (glazed only or glazed and polished). The other scenario is measuring the surface roughness after any adjustments are made intraorally.

5.7. Classification on Abrasiveness

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6. BASIC COMPOSITION OF CERAMICS

Dental ceramics are mainly composed with crystalline minerals and glass matrix. Crystalline minerals include feldspar, quartz, and alumina and perhaps kaolin as glass matrix.¹

Ingredient	Function
Feldspar	• It is the lowest fusing component which melts first and flows initiating these components into a solid mass.
Silica	 Strengthens the fired porcelain restoration Remains unchanged at the temperature normally used in firing porcelain and thus contribute stability to the mass during heating by providing frameworks to other components.
Kaolin	 Used as a binder Increases moldability of unfired porcelain Imparts opacity to the finished product
Glass modifiers	• They interrupt the integrity of silica framework and acts as flux.
Colour pigments	• To provide appropriate shade to the restoration
Zr/Se/Sn/ uranium oxides	• To develop the appropriate opacity.

Feldspar is responsible for forming the glass matrix. Feldspar is the lowest melting compound and melts first on firing, initiating these components into a solid mass. Feldspar is a naturally occurring mineral and composed of two alkali aluminium silicates such as potassium aluminum silicate (K₂O-Al₂O₃-6SiO₂); also called as potash feldspar or ortho case and soda aluminum silicate (Na₂O-Al₂O₃-6SiO₂); also called as soda feldspar or albite.

Most of the currently available porcelains contain potash feldspar as it imparts translucency to the fired restoration. Potash fuses with kaolin and quartz to form glass when heated from 1250°C to 1500°C. Soda feldspar lowers the fusion temperature of the porcelain that results in pyroplastic flow. This material did not attract the porcelain manufacturers as it does not influence the translucency of the porcelain.^{1,61}

Quartz has high fusion temperature and provides the framework as it remains same at the firing temperature of the porcelain. Quartz also acts as filler in the porcelain restoration.^{61,62}

Kaolin is a type of clay material which is usually obtained from igneous rock containing alumina. Kaolin acts as a binder and increases the moldability of the unfired porcelain. Kaolin also imparts opacity to the porcelain restoration so; dental porcelains are formulated with limited quantity of kaolin.^{1,61}

Glass modifiers are used as fluxes and they also lower the softening temperature and increase the fluidity. Color pigments or frits are added to provide the characteristic shade.

7. STRUCTURE

Ceramics can appear as either crystalline or amorphous solids (also called glasses). Thus, ceramics can be broadly classified as Non crystalline (Amorphous Solids or glasses) and Crystalline ceramics.

The mechanical and optical properties of dental ceramics mainly depend on the nature and the amount of crystalline phase present. More the glassy phase more the translucency of ceramics; however, it weakens the structure by decreasing the resistance to crack propagation. On the other hand, more the crystalline phase better will be the mechanical properties which in turn would alter the aesthetics.

Conventional or feldspathic porcelains are usually non-crystalline ceramics. These conventional porcelains are very weak and brittle in nature leading to fracture even under low stresses. Recent developments in the processing technology of dental ceramics have led to the development of crystalline porcelains with suitable fillers such as alumina, zirconia and hydroxy apatite. ^{1,61}

7.1. Non- Crystalline Ceramics

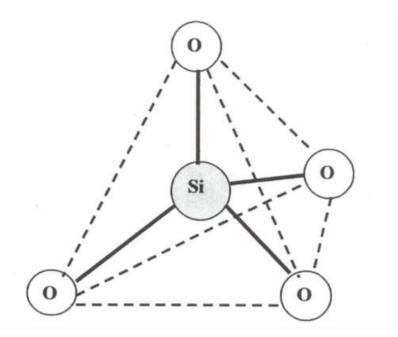


Figure 1. Tetrahedral configuration of Silica

These are a mixture of crystalline minerals (feldspar, silica and alumina) in an amorphous (non-crystalline matrix of glass) vitreous phase. The glass-forming matrix of dental porcelains uses the basic silicone oxygen (Si-O) network with the silicon atom combining with 4 oxygen atoms, forming a tetrahedral configuration [Figure 1] in which

the larger oxygen atoms serve as a matrix, with the smaller metal atoms such as silicone inserted into spaces between the oxygen atoms. Thus each silica unit consists of a single silicone atom (Si) surrounded by four oxygen atoms (O). The atomic bonds in this glass structure have both a covalent and ionic character thus making it stable and also make silica units to link with each other to form a chain configuration.

Several such linked silicate unit chains form the continuous SiO4 (tetrahedral network) in glass [Figure 2]. This stable structure, with strong atomic bonds and no free electrons imparts some important qualities like excellent thermal and optical insulating characteristics, inertness translucency to the glass matrix. However, these strong dual bonds may also impart brittleness to the glass matrix leading to the fracture even at low tensile stress applications.

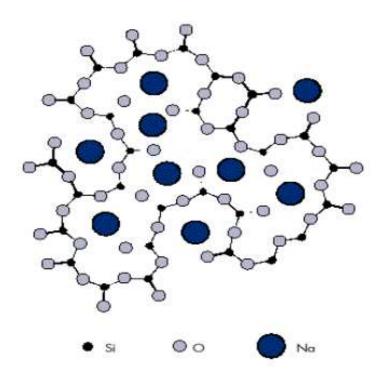


Figure 2. Glass structure with the presence of large alkali cations

7.2. Crystalline Ceramics

Ceramics are reinforced with crystalline inclusions such as alumina and leucite into the glass matrix to form crystal glass composites as a part of strengthening the material and improving its fracture resistance (dispersion strengthening). McLean and Hughes (1965) introduced the first generation of reinforced porcelains for porcelain

jacket crowns, which are generally referred to as "Aluminous porcelains". Covalent crystals are very hard and have a very high melting point, e.g. Silicone carbide.

Crystalline silica

8. PROPERTIES

Dental ceramics exhibit excellent biocompatibility with the oral soft tissues and are also chemically inert in oral cavity. They possess excellent aesthetics. Ceramics are good thermal insulators and their coefficient of thermal expansion is almost close to the natural tooth. The structure of porcelain restoration is probably the most important mechanical property.

The structure of porcelain depends upon its composition, surface integrity and presence of voids. The strength is also depends on the presence of surface ingredients. The nature, amount, particle size and coefficient of thermal expansion of crystalline phases influence the mechanical and optical properties of the materials.⁹⁰

Compressive strength	330 MPa
Diametral tensile strength	34 MPa
Transverse strength	62 - 90 MPa
Shear strength	110 MPa
MOE	69 GPa
Surface hardness	460 KHN
Specific gravity	2.2–2.3 gm/cm ³
Thermal conductivity	0.0030 Cal/Sec/cm ²
Thermal diffusivity	0.64 mm2/sec
Coefficient of Thermal expansion	12 × 10-6/°C

8.1. Physical and Mechanical Properties of Dental Ceramics

Dental ceramics possesses very good resistance to the compressive stresses, however, they are very poor under tensile and shear stresses. This imparts brittle nature to the ceramics and tend to fracture under tensile stresses.

Various modes of clinical fractures of ceramic structures include cracks initiating from the contact zone at the occlusal surface, from the cementation surface beneath the contact, and from the margins of crowns and connectors in fixed partial denture. Structural defects lead to the failure in dental ceramic prostheses. Defects may arise in the form of micro-cracks of sub-millimeter scale; during fabrication of ceramic prostheses and also from application of masticatory forces in the oral cavity

Fatigue strength plays an important role in the durability and longevity of dental ceramic restorations. Fatigue can be accounted for by chemically-enhanced, rate-dependent crack growth in the presence of moisture and cyclic application of stresses. Water enters incipient fissures and breaks down cohesive bonds holding the crack walls together and results in initiation of slow crack growth which progresses steadily over time, accelerating at higher stress levels and ultimately leading to failure.^{90,91}

Surface hardness of ceramics is very high hence they can abrade the opposing natural or artificial teeth. Ceramics are good thermal insulators and their co-efficient of thermal expansion is almost close to the natural tooth.

During firing any residual water is lost from the material accompanied by loss of any binders that results in volume shrinkage of about 30–40%, due to elimination of voids during sintering. Therefore, a precise control of the condensation and firing technique is required to compensate for such shrinkage value during the construction of porcelain restoration.

Adhesion of ceramic restoration to the natural tooth also plays a significant role in the durability of the restoration. The success of a fixed restoration depends on the use of the luting agent and cementation technique.

Glass ionomer cements and resin cements are most commonly used for luting of ceramic restorations. The ceramic surface must be altered to provide adequate bonding with the luting agent and also with orthodontic bracket either by mechanical or chemical or by combined approaches. Mechanical approaches include use of air abrasion/sand blasting, a diamond stone bur, sand paper disks and lasers. However, excessive roughening of the surface should be avoided since it may induce the crack initiation and propagation within ceramic that results in fracture of the ceramic restoration during service.

Chemical alteration of the ceramic surface can be introduced by either etching the surface to increase the mechanical retention of the adhesive or by changing the ceramic surface affinity to the adhesive materials. Studies have shown that chemical conditioning

methods such as silanation increases the adhesion of the composite resin bond to the ceramic. The silica of the dental ceramic is chemically united with the acrylic group of the composite resin through silanation. To improve the bond strength of adhesive resins to ceramics, combination of mechanical and chemical conditioning methods are recommended.⁹²

9. METHODS OF STRENGTHENING CERAMICS

The major drawbacks of ceramics are brittleness, low fracture toughness and low tensile strength. Methods used to overcome the deficiencies of ceramics fall into two categories including methods of strengthening brittle materials and methods of designing components to minimize stress concentration and tensile stress.

The approaches in strengthening ceramics are as follows;

- 1. Shot peening
- 2. Strengthen with a metal substructure
- 3. Dispersion strengthening of glasses
- 4. Enamelling of high strength crystalline ceramics
- 5. Controlled crystallization of glasses
- 6. Production of prestressed surface layers in dental porcelain via ion exchange, thermal tempering.
- 7. Optimum Restoration Design
- 8. Crack tip blunting
- 9. Transformation Saturation
- 10. Minimizing the number of firing cycles

9.1. Shot peening

Shot peening is a type of surface treatment used to strengthen ceramics. It is a cold working process that shoots balls (shot) of steel, ceramics or glass beads at the workpiece to mechanically pre-stress the material surface beyond its yielding point. The localized plastic deformation induces residual stresses into the surface region of the material. The surface residual stresses are compressive. The induced compressive residual stresses inhibit crack growth under both static and cyclic loading, increasing the material hardness, fatigue life and resistance to stress corrosion cracking.

9.2. Strengthen with a metal substructure

The restoration system which involves strengthening the ceramic material with metal was firstly invented by Weinstein in 1962. Metal ceramic systems were developed to reinforce the ceramics. They are:

- 1. Noble metal alloy systems (high gold, low gold, gold free).
- 2. Base metal alloy systems (NiCr,Ti)

In order to strengthen dental ceramic and to improve its strength against tension, shear and pressure forces, generally a metal substructure is used. In a ceramic that substructurally improved by metal, micro fractures spread if only this strong substructure gets deformed. The perimeter of thermal dilatation of substructure material should be higher than porcelain's.

During cooling process, metal substructure shrinks more and more and it supports porcelain with pressure generated. Earlier methods employed to enhance bonding with precious metals were coating with tin oxide. Platinum copings were electroplated with a layer of tin oxide to which aluminous porcelain was attached.^{1,61}

Twin foil technique involves laying down of two platinum foils in close opposition to each other foil provides a matrix for the bonding of the porcelain which is removed after baking. The outer foil forms an inner skin to the crown. It is tin plated and oxidized to achieve a strong chemical bond with the aluminous core porcelain.

Noble metal foils are adapted, swaged and brazed on to dies and then bonded to feldspathic porcelain. The advantages here include reduction of metal and labour cost, a porcelain butt fit, avoidance of metal collar, less stresses at the porcelain metal interface, reduction of internal micro cracks and subsurface porosity, so lesser sites of crack propagation.

9.3. Dispersion strengthening of glasses

Dental ceramics that contains glass phase can be strengthened by dispersion strengthening i.e. dispersing ceramic crystals of high strength and elasticity such as leucite, lithium disilicate, alumina, magnesia-alumina, spinel, zirconia in the glass matrix. When crystal materials are added in the glassy phase, a strong glass-crystal composition is obtained, thus durability and fracture resistance increases. Crystal particles prevent micro fractures to push on forward and it provides a strong structure.⁶¹

Limiting factors while choosing reinforcing crystals are fusion temperature, coefficient of thermal expansion, bonding properties with dental porcelain, mechanical strength and resistance to thermal shock during rapid firing cycles.

Quartz (10-15%) undergoes changes during heating and has a high coefficient of thermal expansion and the strengthening effect of quartz is poor.

Alumina reinforcement: When alumina crystals are dispersed in a glass matrix and heated and cooled, different stress patterns are observed due to the differences in thermal expansion between glass and alumina.

9.4. Enamelling of high strength crystalline ceramics

During firing some form of crystallization takes place in ceramics (sintered or high alumina), resulting in an interlocking crystalline system which is better able to withstand high stresses than feldspathic porcelain.

High alumina cores with aluminous porcelain veneers have been used in combination. These laminates are much stronger than regular porcelain, similar to metal ceramic systems. The bonding at the interface is chemical in nature and an ionic bond ensures no porosity as the wetting of the porcelain enamel on high alumina is good.⁹³

9.5. Controlled crystallization of glasses

Under normal conditions, when a glass is heated up to a determined degree and then get cooled down, it does not crystallize. In this method, ceramic structure is heated up to first softening temperature, made to crystallize by adding a nucleating agent like titanium dioxide, lithia, zinc oxide, silica or metal phosphates.

Though the glass is amber in colour and glassy it becomes translucent and tooth like after crystallization or ceramming for 1 hour at 600°C. Here high thermal shock resistance and improved strength property has been observed.

9.6. Ion exchange (chemical tempering)

In general, ceramic restorations fail because of larger and deeper micro fractures caused by tensile strength. Ion exchange method is to generate at low temperature a compressive layer on ceramic's surface in order to micro fractures becomes larger. This compressive layer on surface is created by exchange of some ions with bigger ions of glass matrix.

Dental ceramic material is plunged into melted potassium nitrate salt tank cooler than glass transition temperature and Na+ ions found on dental ceramic's surface change place with K+ ions of salt tank. By way of compressing on silicate system, Potassium ions which are bigger than sodium ions, generate a compression power. This surface compression gives an increase in strength on the surface of porcelain.

9.7. Thermal tempering

Rapid cooling or quenching of a surface of an object while it is still hot creates residual surface compressive stresses on the surface of the ceramics. As the core is hot and soft and still in its molten state it tends to shrink and tries to pull the outer surface which is rigid now. On solidification, residual tensile stresses are created on the inner core and residual compressive stresses on the outer surface. Hot glass phase ceramics are quenched in silicone oil or other special liquids.

9.8. Optimum restoration design

Before designing a ceramic restoration which will cope with every negative condition, ceramic's weakness against low tensile strength, its fragility and sensitivity to micro fractures should be considered. In this design, ceramic should be protected from high tension. Avoid sharp edges and apparent thicknesses from restorations. Best way to decrease the tensile strength on bridges is to design connector zones that have intense stress with an appropriate thickness and shape.

Minimizing stress concentrators and stress raisers: Stress raisers are discontinuities in ceramic restoration that can cause stress concentration. The design of the ceramic should avoid these stress concentrators. Abrupt changes in contour including any grooves, pits, notches can alter the stress flow lines. The internal angles in tooth preparation should not be sharp but rounded.⁹³

9.9. Crack tip blunting

Porcelains are solid materials that have a very small work of fracture. They will tolerate cracks much deeper than 0.025 mm but when the crack propagates its tip radius remains the same throughout the length and very little force is required to propagate the stress. Once porcelain is under tension, the crack propagates and a complete fracture occurs suddenly.

Crack tip blunting is a reinforcing mechanism. The principle is somewhat perplexing in that hollow spaces are actually used to strengthen ceramics. As the crack progresses it is dissipated into the void space. The stress is usually increased at the narrow tip of the crack which is reduced at the voids and this prevents crack propagation.

9.10. Transformation saturation

Transformation saturation is a phenomenon, based on a phase transformation principal caused by tension strength. In transformation saturation method mostly leucite and zirconium is used to strengthen the ceramic. In this method, changes of temperature in ceramic material play an important role.

During thermal changes, volumes of leucite and zirconium found in glassy phase increases in glassy matrix and it creates pressure stresses inside the structure. This pressure stresses both prevent micro fractures to push on and does decrease tension stresses situated at microfracture's peak.

Pure zirconia can exhibit a polymorphic phase transformation.

- 1. Monoclinic (P21/c)- from room temperature to heating to 1,170°C
- 2. Tetragonal (p42/nmc)- 1,170°C to 2,370°C
- 3. Cubic (fm^3/m) above 2,370°C till the melting point.

On cooling from 950°C there is an increase in volume leading to a catastrophic failure. Pure zirconia is alloyed with stabilizing oxides, such as CaO, MgO, Y_2O_3 or CeO₂ which allows the tetragonal structure to remain stable at room temperature, thus efficiently arresting the crack propagation and leading to high toughness.

Disadvantages of PSZ (Partially Stabilized Zircona):

Refractive index not same as that of glass matrix. Thus particle of PSZ scatter light producing an opacifying effect that may not be aesthetically pleasing.

b) Designs of dental restoration:

- Avoid exposure to increased T.S.
- Avoid stress concentration at sharp angles or marked changes in thickness.
- i) To minimize tensile stress:
 - Use of ductile metal coping.
 - Use of bonded pt foil PJC.
 - Use of swaged Au alloy foil technique.

ii) Reducing stress raisers:

- Stress raisers are discontinues in brittle materials (Sa ceramics) that cause stress concentration.
- Avoid abrupt changes in shape and thickness in ceramic contour.

Stress raisers in PJC:

- Creases / folds of pt foil substrate form notches.
- Sharp line angles.
- Large changes in porcelain thickness.
- Small particle of porcelain along internal porcelain margin of crown.
- Stray particle fused within internal porcelain.

PFM – occlusion adjusted properly.

- Decreased contact points.

9.11. Minimizing the number of firing cycles

The purpose of porcelain firing procedure is to densely sinter the particles of powder together and produce a relatively smooth, glassy layer on the surface. Several chemical reactions occur over time at porcelain firing temperature: of particular importance is increase in concentration of crystalline leucite. Changes in the leucite content caused by multiple firing can alter the co efficient of thermal contraction of some porcelain products and produce stresses during cooling, sufficient to cause crack propagation in the porcelain.

Other methods to improve strengthening are:

- Good condensation techniques (powder condensation), programmed firing schedules, high pressure compaction, vacuum fired porcelain and better condensation in the wet stage which are all very essential to minimize shrinkage and avoid excessive air bubbles.
- If the surface is undisturbed, the strength of the glazed surface specimen is found to be higher.

• Thermal stresses occurring during improper cooling can cause cracks and weaken the porcelain. Water (saliva) can act as a network modifier and weaken the structure.^{93,94}

10. ADVANTAGES & DISADVANTAGES : CERAMIC RESTORATIONS:

10.1. Advantages

- *Esthetics* :Ceramics are considered the best in mimicking the natural tooth appearance. This is the primary advantage over other materials.
- Wear resistance: Ceramics are more wear resistant than direct restorative materials.
- *Precise contact and contours*: Indirect fabrication of all ceramic restorations provided more precise contour and contacts than directly placed restorations.
- *Biocompatibility*: The allergic reaction by some to metal alloys is a weak point against metal ceramic restorations which increased the demand on the more biocompatible all ceramic restorations

10.2. Disadvantages

- *Cost and time*: All ceramic restorations are fabricated indirectly and require at least two appointments to be delivered. The additional laboratory fees make this type of restoration more expensive than other restorations.
- *Brittleness of ceramics* : Adequate thickness of ceramic should be provided to avoid fracture of the restoration.
- *Wear of opposing dentition and restoration*: Ceramics can cause wear of opposing restorations and dentition. This problem has been considered during the improvement of ceramic restorations.
- Low repair potential: If fracture occurs, repair is not considered as a definitive treatment
- *Difficult intraoral polishing*: Ceramic restorations are difficult to polish once they are cemented.

11. EARLIER DEVELOPMENTS OF DENTAL CERAMICS

PAST DEVELOPMENTS

1. <u>Air firing</u> : prior to early 1960s, porcelain powders used had large particles size, to avoid opacity but resulted in porosities (internal). But aesthetic of these materials was excellent (Mclean 1979).

2. <u>Vacuum firing</u>: The introduction of vacuum fired porcelains reduced the internal porosities and further increased the aesthetics

The earliest successful porcelain systems used conventional feldspathic porcelain, derived from the natural mineral feldspar. This material was used for producing allceramic jacket crowns, which were very esthetic. Dental feldspathic porcelain is predominantly a glass material with an amorphous (non-crystalline) structure.

Glass mainly consists of a three-dimensional network structure of silica (siliconoxygen) in which each silicon atom is bonded to four oxygen atoms in the form of a tetrahedron. These tetrahedral are linked together by sharing common oxygen atoms to form a continuous three dimensional network. Other oxides (such as aluminum), may be incorporated to a very limited extent as substitute network formers.⁶¹

The introduction of oxides of alkali metals (e.g. potassium, sodium and calcium) into a silica glass composition results in disruption of the three-dimensional structure formed by the oxygen-silica bonds. When the alkali metals in the ionic form disrupt the oxygen-silicon bonds (resulting in non-bridging oxygen) the three-dimensional network structure breaks down to some extent, resulting in a lower fusion temperature and a more fluid behaviour during heating.

While pure (100%) silica glass fuses at about 1700°C, the introduction of alkali ions disrupts some of the silicon-oxygen bonds causing a more open network structure. The more open network structure has less cross-linkages, causing a lowering of the fusion temperature, together with a reduction in strength and chemical inertness. Thus, fusion temperature, strength and chemical inertness depend on the amount of alkali (or nonbridging oxygen) present in the glass.

Porcelain fused to metal systems were introduced in the 1950s. A development in 1962 greatly improved these systems; that is, the incorporation of a high proportion of leucite crystals into the feldspathic porcelain composition which veneered the cast gold alloy substructure. The leucite crystals serve to increase the thermal expansion of the porcelain to bring it closer to that of the metal substrate. The leucite prevents stresses occurring, due to a thermal mismatch, which could lower the strength. Metals are between 10 and 100 times tougher than ceramics; the presence of a metal substrate can contribute to a very strong restoration.⁶²

The incorporation of a small trace of tin and/or iron into the gold alloy was necessary to allow formation of the necessary oxide on the surface to permit good wetting by the porcelain and subsequent bonding to the alloy surface.⁵⁸

Base metal alloys were introduced in competition to the gold alloys. These are more technique sensitive than gold, but are now well established. An opaque ceramic such as a titanium oxide glass frit has to be applied as the first layer of veneer, to mask the metallic hue in the porcelain fused to metal systems.

Porcelain-fused-to-metal (PFM) crowns have been considered the gold standard for the repair of damaged teeth. PFM crowns have good mechanical properties, satisfactory esthetic results, and an acceptable biological quality needed for periodontal health.

However, PFM crowns have some limitations that may limit their use. For example, the esthetic of PFM crowns is limited by the metal framework and the layer of opaque porcelain needed for masking the underlying metal grayish shade. The cost of precious metals has risen markedly making PFM relatively unattractive from an economic standpoint.

All-ceramic crowns have been used over the last four decades as an alternative for PFM crowns to overcome their esthetic limitations. All-ceramic crowns can be made from different types of ceramic, and not all ceramic types have the same physical and esthetic proprieties. Historically, resin-based crowns were the first metal-free crowns to be used, but they were abandoned because of their low fracture resistance.

Newer metal-free crowns are increasingly being used in dental practice; these crowns are made from different ceramic materials such as lithium disilicate, zirconia, leucite-reinforced glass, and glass-infiltrated alumina.⁶¹

11.1. SINTERED PORCELAIN

Leucite reinforced porcelain

Optec HSP material (leneric/Pentron, Inc.) is a feldspathic porcelain containing up to 45 vol% tetragonal leucite.⁹⁵ The greater leucite content of Optec HSP porcelain compared with conventional feldspathic porcelain for metal-ceramics leads to a higher modulus of rupture and compressive strength.

The large amount of leucite in the material contributes to a high thermal contraction coefficient⁹⁶. In addition, the large thermal contraction mismatch between leucite (22 to 25 x 10^{-6} /°C) and the glassy matrix (8 x 10^{-6} /°C) results in the development of tangential compressive stresses in the glass around the leucite crystals when cooled.

These stresses can act as crack deflectors and contribute to increase the resistance of the weaker glassy phase to crack propagation. After heat treatment of Optec HSP for one hour at temperatures ranging from 705 to 980°C, a second metastable phase identified as sanidine (KAlSi₃O₈) forms at the expense of the glassy matrix ⁹⁷.

The crystallization of sanidine is associated with a modification of the optical properties of the material from translucent to opaque. However, sanidine does not appear when the porcelain is heated to 980°C, since sanidine is metastable in the temperature range 500-925°C. The precipitation of sanidine has been reported as well upon isothermal heat treatment of conventional feldspathic porcelain for metal-ceramics⁹⁸.

An isothermal time temperature-transformation diagram that makes it possible to predict the amount of leucite and sanidine in samples subjected to different thermal histories has been established⁹⁹.

Alumina-based porcelain

Aluminous core porcelain is a typical example of strengthening by dispersion of a crystalline phase. Alumina has a high modulus of elasticity (350 GPa) and high fracture toughness (3.5 to 4 MPa.m05). Its dispersion in a glassy matrix of similar thermal expansion coefficient leads to significant strengthening of the core. ¹⁰⁰The first aluminous core porcelains contained 40 to 50% alumina by weight. The core was baked on a platinum foil and later veneered with matched-expansion porcelain.

Hi-Ceram (Vident, Baldwin Park, CA) is a more recent development of this technique. Aluminous core porcelain is now baked directly onto a refractory die.¹⁰¹

Magnesia-based core porcelain

Magnesia core ceramic was developed as an experimental material in 1985. Its high thermal expansion coefficient (14.5 x 10^{-6} /°C) closely matches that of body and incisal porcelains designed for bonding to metaL(13.5 x 10^{6} /°C). The flexural strength of unglazed magnesia core ceramic is twice as high (131 MPa) as that of conventional feldspathic porcelain (65 MPa). ¹⁰²

Indications:

Used with body porcelain normally used to veneer metallo-ceramic restorations
 → Magnesia reinforced material is thermally compatible with body porcelain because of its high thermal expansion coefficient.

Advantages:

- 1. Improved shade matching when used with veneers.
- Flexural strength is doubled this is due to treating of surface of magnesia core porcelain with a suitable glass.

Two mechanisms were suggested for improved strength:

- a) The glaze was thought to penetrate the open pores, effectively reducing the number of surface flaws.
- b) Glaze may have replaced the surface layer in compression.

Disadvantages:

 Due to high expansion magnesia core porcelain is more liable to thermal shock on cooling.

1. Bonded platinum foil coping:

This technique uses bonding of porcelain to metal by use of tin oxide coatings on platinum foil.

Objective:

 Improves aesthetic by replacing thicker metal coping with a thin platinum foil thus providing more space for porcelain.

Procedure: Aluminous porcelain is bonded to pt foil copings, attachment of porcelain in secured by electroplating the foil with a thin layer of tin and then it is oxidized in a furnace to provide a continuous film of tin oxide for porcelain bonding.

Rationale:

Bonded foil acts as an inner skin on the fit surfaces to reduce subsurface porosity and formation of microcracks in the porcelain thus increasing its fracture resistance of the unit.

RECENT PORCELAINS:

2. *All Ceramic System*: The evolution of porcelain materials has been a battle for the ideal strength-aesthetic combinations.

Due to the inherent drawbacks related to PFM, as stated earlier, all ceramic crowns were introduced into dentistry.

The first all-ceramic crowns were introduced by 'LAND' in 1903.

These materials were:

- a) Relatively weak.
- b) Had limited clinical use.

Thus, in 1965, Mclean and Hughes formulated aluminous porcelains composition which form the basic composition of these All-ceramic crowns.

- These aluminous porcelains had increased rate of fracture.
- More recently, newer types of all-ceramic restoration have been developed that may prove to have a lower incidence of clinical fracture:

This may be due to:

- a) All-ceramic restorations today consists of stronger materials and involve better fabricating techniques.
- b) These restorations can be etched and bonded to the underlying tooth structure with the new dentin adhesives.
- c) With greater tooth reduction than what was previously used for PJC's, clinicians now provide lab technicians with enough room to create thicker and stronger restoration.

The core material is made by reacting magnesia with a silica glass within the $1100-1150^{\circ}$ C temperature range. This treatment leads to the formation of forsterite (Mg₂SiO₄) in various amounts, depending on the holding time. The proposed strengthening mechanism is the precipitation of fine forsterite crystals ¹⁰³. The magnesia core material can be significantly strengthened by glazing, thereby placing the surface

under residual compressive stresses that have to be overcome before fracture can occur.

Zirconia-based porcelain

Mirage II (Myron International, Kansas City, KS) is a conventional feldspathic porcelain in which tetragonal zirconia fibers have been included. Zirconia undergoes a crystallographic transformation from monoclinic to tetragonal at 1173°C. Partial stabilization can be obtained by using various oxides such as CaO, MgO, Y₂O₃, and CeO, which allows the high-temperature tetragonal phase to be retained at room temperature.

The transformation of partially stabilized tetragonal zirconia into the stable monoclinic form can also occur under stress and is associated with a slight particle volume increase. The result of this transformation is that compressive stresses are established on the crack surface, thereby arresting its growth. This mechanism is called transformation toughening.⁶¹

The addition of yttria-stabilized zirconia to a conventional feldspathic porcelain has been shown to produce substantial improvements in fracture toughness, strength, and thermal shock resistance. ¹⁰⁵ However, other properties, such as translucency and fusion temperature, can be adversely affected. The modulus of rupture of commercially available zirconia-reinforced feldspathic dental porcelain (Mirage II) is not significantly different from that of conventional feldspathic porcelain.¹⁰⁶

11.2. GLASS-CERAMICS

Mica-based

As described earlier, glass-ceramics are obtained by controlled devitrification of glasses with a suitable composition including nucleating agents. Depending on the composition of the glass, various crystalline phases can nucleate and grow within the glass. The advantage of this process is that the dental restorations can be cast by means of the lost-wax technique, thus increasing the homogeneity of the final product compared with conventional sintered feldspathic porcelains.

Dicor (Dentsply Inc., York, PA) is a mica-based machinable glass-ceramic. The machinability of Dicor glass-ceramic is made possible by the presence of a tetrasilicic fluormica (KMg₂5Si₄O10F₂) as the major crystalline phase¹⁰⁷. Micas are classified as

layer-type silicates. Cleavage planes are situated along the layers, and this specific crystal structure dictates the mechanical properties of the mineral itself.

Crack propagation is not likely to occur across the mica crystals and is more probable along the cleavage planes of these layered silicates¹⁰⁸. In the glass-ceramic material, the mica crystals are usually highly interlocked within the glassy matrix, achieving a "house of cards" microstructure¹⁰⁹.

The interlocking of the crystals is a key factor in the fracture resistance of the glass-ceramic, and their random orientation makes fracture propagation equally difficult in all directions.

After being cast, the Dicor glass is converted into a glass-ceramic by means of a single-step heat treatment with a six-hour dwell at 1070°C. This treatment facilitates controlled nucleation and growth of the mica crystals.

However, it is critical to re-invest the cast glass restoration prior to the crystallization heat treatment, to prevent sagging or rounding of the edges at high temperature. The match in the thermal expansion coefficients of the glass and the investment is achieved by use of a leucite based gypsum-bonded investment.

The interaction of the glass-ceramic and the investment during the crystallization heat treatment leads to the formation of calcium magnesium silicate at the surface of the glass-ceramic.¹¹⁰

This crystalline phase could be formed by decomposition of the mica into magnesium silicate that later reacts with the gypsum-bonded investment. This surface layer, called the "ceram layer", has been reported to decrease the strength of glass ceramic crowns significantly.¹¹¹

The effects of alumina and zirconia additions on the bending strength of Dicor glass-ceramic have been investigated. It was found that alumina additions successfully increase the bending strength of Dicor glass-ceramic, whereas zirconia additions had no effect.¹¹²

Hydroxyapatite-based

Cerapearl (Kyocera, San Diego, CA) is a castable glass ceramic in which the main crystalline phase is oxyapatite, transformable into hydroxyapatite when exposed to moisture.¹¹³

Lithia-based

Glass-ceramics can be obtained from a wide variety of compositions, leading to a wide range of mechanical and optical properties, depending on the nature of the crystalline phase nucleating and growing within the glass.

Experimental glass-ceramics in the system Li2O-Al2O3- CaO-SiO2 are currently the object of extensive research work. The choice of adequate additives is critical in the development of tougher and higher-strength glass ceramics⁶¹.

Differential thermal analysis can be efficiently used to determine the heat treatment leading to the maximum lithium disilicate crystal population in the shortest amount of time, thereby optimizing the nucleation and crystallization heat treatment of this type of glass-ceramic.

11.3. MACHINABLE CERAMICS

Cerec system

The evolution of CAD-CAM systems for the production of machined inlays, onlays, and crowns led to the development of a new generation of machinable porcelains. There are two popular systems available for machining all-ceramic restorations. The best-known is the Cerec system (Siemens, Bensheim, Germany). It has been marketed for several years, and two materials can be used with this system: Vita Mark II (Vident, Baldwin Park, CA) and Dicor MGC (Dentsply International, Inc., York, PA).

Vita Mark II contains sanidine (KAlSi $_3O_8$) as a major crystalline phase within a glassy matrix. As explained earlier, the presence of sanidine could explain the lack of translucency of this material. Dicor MGC is a machinable glass-ceramic similar to Dicor, with the exception that the material is cast and cerammed by the manufacturer.

Colorants have been added to match tooth color. The glass-ceramic contains 70 vol% of the crystalline phase. Manufacturer's control over the processing of this material and the higher volume percent of the crystalline phase could explain the improved mechanical properties of Dicor MGC compared with conventional Dicor glass-ceramic.

The use of adhesive resinbased cements has been shown to improve the fracture resistance of all-ceramic crowns ^{114,11}. Other studies have shown that the overall fracture resistance of Dicor MGC was independent of cement film thickness. Presently, the main identified weakness of the Cerec system is the marginal fit of the restorations.

Celay system

The Celay system (Mikrona Technologie, Spreitenbach, Switzerland) uses a copymilling technique to manufacture ceramic inlays or onlays from resin analogs. The Celay system is a mechanical device based on pantographic tracing of a resin inlay or onlay fabricated directly onto the prepared tooth or onto the master die.¹¹⁵

As with the Cerec system, the starting material is a ceramic blank available in different shades. One ceramic material currently available for use with the Celay system is Vita-Celay (Vident, Baldwin Park, CA). This material contains sanidine as the major crystalline phase within a glassy matrix.

Recently, In-Ceram pre-sintered slip-cast alumina blocks (Vident, Baldwin Park, CA) have been machined with the Celay copy-milling system used to generate copings for crowns and fixed partial dentures¹¹⁶. The alumina copings were further infiltrated with glass following the conventional In-Ceram technique, resulting in a final marginal accuracy within 50 urn.

11.4. SLIP-CAST CERAMICS

Alumina-based (In Ceram)

In-Ceram (Vident, Baldwin Park, CA) 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. Two modified porcelain compositions for the Inceram technique have been recently introduced. In-Ceram Spinell contains a magnesium spinel (MgAl₂O₄) 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 glassinfiltration 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.¹¹⁷

11.5. HOT-PRESSED INJECTION-MOLDED CERAMICS

Leucite-based

IPS Empress (Ivoclar USA, Amherst, NY) is a leucite-containing porcelain. Ceramic ingots are pressed at 1150°C (under a pressure of 0.3 to 0.4 MPa) into the refractory mold made by the lost-wax technique. This temperature is held for 20 minutes in a specially designed automatic press furnace.

The ceramic ingots are available in different shades. They are produced by sintering at 1200°C and contain leucite crystals obtained by surface crystallization¹¹⁸. The leucite crystals are further dispersed by the hot-pressing step.

The final microstructure of IPS Empress exhibits 40% by volume of tetragonal leucite. The leucite crystals measure 1-5 um and are dispersed in a glassy matrix.

Two finishing techniques can be used with IPS Empress: a staining technique or a layering technique involving the application of veneering porcelain.

The two techniques lead to comparable mean flexure strength values for the resulting porcelain composite. The thermal expansion coefficient of the IPS Empress material for the veneering technique (14.9 x 10^{-6} /°C) is lower than that of the material for the staining technique (18 x 10^{-6} /°C) to be compatible with the thermal expansion coefficient of the veneering porcelain.

The flexural strength of IPS Empress material was significantly improved after additional firings¹¹⁹. The strength increase is attributed to a good dispersion of the fine leucite crystals as well as the tangential compressive stresses arising from the thermal contraction mismatch between the leucite crystals and the glassy matrix.

Spinel-based

Alceram (Innotek Dental Corp, Lakewood, CO) is a material for injection-molded technology and contains a magnesium spinel (MgAl₂O₄) as the major crystalline phase. This system was initially introduced as the "shrink-free" Cerestore system, which relied on the conversion of alumina and magnesium oxide to a magnesium aluminate spinel. One of the recognized advantages of this system was the excellent marginal fit of the restorations¹²⁰.

12. RECENT ADVANCES IN CERAMIC MATERIALS

Dental ceramics undergo tremendous modifications in the last few decades. Due to poor physical properties, conventional ceramics led to early catastrophic failures.

12.1. Monolithic zirconia restorations

Among polycrystalline ceramics, yttria stabilized tetragonal zirconia polycrystal (Y-TZP) for monolithic (full-contour) restorations has been developed more recently to overcome problems related to chipping of porcelain layers applied over zirconia.

Zirconia exists in three different crystallographic forms: cubic, tetragonal and monoclinic phases. Y-TZP shows superior performance among dental ceramics due the high strength level of more than 1000 MPa and its superior fracture toughness of 4 to 5 MPa.m0.5.

Especially the high fracture toughness is a consequence of a toughening mechanism related to the transformation of tetragonal grains into the monoclinic phase, which generates compression stresses around defects, hindering their catastrophic propagation.^{121,122} The microstructure of Y-TZPs for monolithic prostheses has been tailored to improve their translucency in comparison with conventional Y-TZP.

The better translucency of the new zirconia materials has been achieved by means of microstructural modifications, like decrease in alumina content, increase in density, decrease in grain size, addition of cubic zirconia and decrease in the amount of impurities and structural defects. The size of the crystalline grain is the microstructural feature that is more closely related to the adjustment of the translucency of polycrystalline ceramics. Larger grains lead to a smaller number of grain boundaries, therefore reducing light scattering.¹²³

For Y-TZP, it has been shown that larger grains are detrimental for both the mechanical properties and the stability of the tetragonal phase. Therefore, the translucency of zirconia cannot be achieved by means of increasing its grain size. Another approach to produce a more translucent Y-TZP is to decrease significantly the grain size.¹²⁴

However, the grain size needs to be decreased until reaching a critical value that results in mitigation of the so-called birefringence phenomenon. Birefringence occurs in Y-TZP due to the large amount of tetragonal crystal phase (> 90%), which is a crystal

that has different refractive indexes according to its crystallographic orientation in the microstructure. Such anisotropic behaviour related to the variation in the refractive index causes significant light scattering¹²⁴.

Another way to overcome these scattering effects is the use of cubic zirconia, which offers optical isotropic behaviour, increasing the translucency.

For clinicians and dental technicians, monolithic zirconia restorations have become a very promising alternative, since the processing methods are simplified in comparison to traditional multi-layered restorations, and therefore are less time consuming.

From the biological standpoint, monolithic restorations made with zirconia allow clinicians to make much less invasive preparations, since this ceramic material has relatively high mechanical properties, especially when compared to veneering porcelains. In fact, important microstructural mechanisms, such as transformation toughening, hinder crack propagation through the restorations, and therefore, thinner structures can be constructed, preserving tooth tissues.

Although novel zirconia microstructures have higher translucency, the color of the final restoration is still limited to a whitish shade. Therefore, an important technological development for these materials is the coloring process that allows for a larger range of aesthetic possibilities.

Laboratory studies indicated that the addition of coloring pigments to monolithic zirconia does not affect its flexural strength and translucency, however these results are related to specific coloring methodologies and cannot be generalized.¹²⁵

Different techniques can be used to add color to zirconia restorations. One of them involves immersion of the material (dip coating) when it is at the presintered state in a solution containing different types of coloring dyes. This method has the disadvantage of resulting in a non-homogeneous final shade, since the pigments may penetrate only to a certain depth.

Another coloring technique allows for the production of pre-colored zirconia presintered blocks with a much more homogeneous shade. Pre-colored blocks of monolithic zirconia can be manufactured from a powder that is synthesized together with pigments or a powder which has been mixed with pigments.¹²⁶ One factor that affects the translucency of dental ceramics is the restoration thickness. In general, the lower the thickness, the higher the translucency of a ceramic restoration, therefore, it is mandatory that translucency data is always reported accompanied by the material thickness. Considering the thickness of 0.5 mm, traditional Y-TZP shows contrast ratio (CR) values that are higher (0.77) than those of monolithic Y-TZPs (0.57 to 0.62).

In addition to the mechanical and optical properties, another important characteristic for the long-term success of a restoration is the wear of the antagonist enamel and the marginal adaptation. Fortunately, laboratory studies have shown that monolithic zirconia usually causes a rather comparable wear of the antagonists in comparison to other restorative ceramics, and this wear rate is within the physiological range reported in the literature. Some of these studies compared different surface finishing techniques for monolithic zirconia restorations, such as polishing versus glazing, and found that polished surfaces resulted in less enamel wear of the antagonist.¹²⁷

The high surface hardness of zirconia has a major influence on the antagonist wear and a perfect polish of any monolithic zirconia restoration is therefore very important. A clinical study evaluated the occlusal surface wear of monolithic zirconia crowns placed in premolars and molars. Impressions of the restorations were taken at the beginning of the trial and then 24 months later. Epoxy replicas were produced and both a qualitative (scanning electron microscopy) and a quantitative (optical profilometry) surface analyses were performed.

The results showed that monolithic zirconia promoted an acceptable surface wear rate of the antagonist surface (natural enamel or ceramic material) after two years. Therefore, monolithic Y-TZP restorations with good surface finishing are not likely to wear significantly the antagonist element. However, following up these Y-TZP restorations is important because if there is a decrease in the surface quality, their wear potential will increase significantly.

The marginal adaptation of the monolithic restorations of Y-TZP improved over the years due to the evolution of CAD-CAM systems. Several of these systems and different materials had their adaptation evaluated: TZI, TZ Incoris (Dentsply-Sirona, Bensheim, Germany), CZ, Ceramill Zolid White (Amann Girrbach, Koblach, Austria), ZZ, Zenostar Zirconia (Wieland, Pforzheim, Germany), PZ, Prettau Zirconia (Zirkonzahn) and BZ, Bruxzir Solid Zirconia (Glidewell, Gais,Germany). Fortunately, all brands showed acceptable marginal discrepancy, with the most advanced five axis milling systems being superior to others.

Another important issue regarding the use of monolithic zirconia for dental restorations is the ageing phenomenon, since these restorations are loaded in direct contact with the oral environment. Laboratory studies have evaluated the formation of the monoclinic crystalline phase and the flexural strength of different monolithic zirconia after ageing.

Their results indicated that some brands are not susceptible to aging while others are more prone to tetragonal-to-monoclinic (t-m) transformation. However, more studies are needed to evaluate this ageing phenomenon, since to date there is no scientific evidence from clinical studies linking the clinical failure of dental Y-TZP with this type of ageing.

The higher translucency of monolithic Y-TZP expanded their indication for rehabilitations in aesthetic regions. However, extra caution is necessary before using this type of restoration indiscriminately, as there are only a few clinical follow-ups that evaluated monolithic zirconia crowns.

One of these studies showed that out of 82 monolithic zirconia crowns installed in 60 patients, 6 (7.3%) had complications after 3 years. The study showed that problems that affect this type of restoration are mostly related to loss of crown retention (2.4%) and endodontic complications (4.9%). Thus, this type of treatment is considered as promising, but clinical studies with longer follow-up times are still desirable.

Another study collected data over five years from two United States laboratories. The laboratories provided insurance for restorations of monolithic zirconia that had problems, making new restorations without additional costs to the clinicians. The study included 39,827 restorations (all cemented in the natural dentition), which were classified into: anterior single crown (1,952); posterior single crown (29,808); anterior fixed dental prostheses (1,779) and posterior fixed dental prostheses (6,288).

Only the restorations that returned to laboratories to be replaced due to catastrophic fracture were considered as failures. The fracture rate (%) was 0.97 for anterior single crowns; 0.71 for posterior single crowns; 3.26 for the anterior fixed dental prostheses and 2.42 for the posterior fixed dental prostheses. The study concluded that

restorations made with monolithic zirconia showed relatively low fracture rates. However, possibly some failed restorations may not have been counted, since the patient may have returned to another dentist or the dentist may have chosen another material to replace the restoration.¹²⁹

12.2. Multilayered dental prostheses

Traditionally, fixed partial dentures (FPDs) produced with a metallic infrastructure and a ceramic veneering layer have excellent clinical performance, with studies showing an annual failure rate around 1% and a survival rate of 94% after 5 years of clinical follow-ups. Although these metal/ceramic bilayers are still considered the gold standard for FPDs, many studies have been carried out in order to achieve the same level of excellence using all-ceramic systems.¹³⁰

The lower biocompatibility and lower translucency of metals, when compared to ceramic materials, are the factors responsible for the use of ceramics as infrastructure materials in multilayered restorations.¹³¹

On the other hand, the relatively low fracture toughness of ceramic materials is a major limitation for their unrestricted use for prosthodontics solutions. This problem led to the development of a series of ceramic materials with high crystalline content, which are able to withstand the mechanical stresses generated during the application of chewing forces. Examples of such materials are alumina-based zirconia-reinforced glass infiltrated ceramic, polycrystalline alumina and Y-TZP.

Among these ceramic materials, Y-TZP has gained remarkable popularity because of its excellent mechanical properties. However, materials with a high crystalline content still require a veneering layer constructed with a compatible porcelain in order to achieve a more favorable aesthetic result.

With respect to all-ceramic multilayered restorations, clinical follow-ups have reported little or no damage to the Y-TZP infrastructure during clinical use, however, chipping fractures of the veneering ceramic have been frequently reported. These failures compromise the restoration both functionally and aesthetically, requiring the replacement of the prosthetic piece when the fractured area is too large.

The fracture of the veneering layer applied over Y-TZP frameworks has been associated with different factors, such as:a) design of the Y-TZP infrastructure, which

should give support to the veneering layer; b) relation between the thicknesses of the restoration layers(infrastructure and veneering ceramic, anatomical design);c) thermal residual stresses within the restoration, which are generated either during the cooling step at the sintering furnace or due to a certain mismatch of the coefficients of thermal expansion (CTE) of both layers and d) mechanical properties of the veneering ceramic.

Several methodologies for the application of the veneering layer on the ceramic infrastructure are available in the market and all of them aim at optimizing the resistance of this layer and, in some cases, to reduce the generation of residual thermal stresses.

In the traditional or stratified processing technique, the manufacturer provides a ceramic powder and a modeling liquid (distilled water mixed with rheological modifiers). In order to produce the restoration, the Y-TZP framework receives the application of a mixture containing the veneering ceramic powder and the modeling liquid with the use of a brush.

Several layers need to be applied in order to construct the desired dental element anatomy. This technique generates veneering layers susceptible to processing porosities and a series of intrinsic defects that can act as stress concentration areas, favouring the fracture of the restoration during chewing.

Another technique for the application of the veering layer is the so-called presson method, in which the veneering material is applied on the ceramic infrastructure (made of Y-TZP) by means of a lost-wax in combination with a hot-pressing technique, resulting in a veneering layer with less pores and better mechanical behavior when compared to a veneering layer applied by the traditional technique.

In this case, the veneering ceramic is provided in the form of pellets which are injected into a refractory mold (generated from the lost wax technique) containing the previously sintered Y-TZP framework. Stawarczyk et al.¹³¹ evaluated the load-bearing capacity of bilayered all-ceramic crowns as a function of different techniques for application of the veneering layer (injection of the Y-TZP versus the stratified technique) and concluded that crowns produced by means of injection of the veneering layer exhibited comparable and under certain configurations even superior fracture loads when compared to those made with the stratified technique.

Advances in CAD-CAM systems (computer aided design-computer aided manufacturing) in addition to an attempt to decrease the generation of residual thermal

stresses in bilayered all-ceramic restorations have led to the development of new processing methods that involve milling of CAD-CAM blocks for both the framework and the veneering layer.

In a further step, these layers are bonded with a resin cement or a fusion glassceramic. One of these systems is called the Rapid Layer Technique (Vita) and involves milling of both the Y-TZP infrastructure and the veneering layer, including a posterior cementation step using dual-cure resin-based luting agents.

The other technique is called CAD-on (Ivoclar Vivadent, Schaan, Liechtenstein) and involves milling of the veneering layer from a lithium disilicate glass-ceramic CAD-CAM block. Lithium disilicate is a ceramic material that has much higher crystalline content compared to feldsphatic veneering ceramics and therefore presents higher mechanical properties. In the end of the process, both layers are bonded by means of a firing cycle that is carried out after the application of a fusion glass-ceramic (glass solder) between both layers.

One great advantage of restorations produced via CAD-CAM systems is the fact that the blocks used for production of the veneering layer are originated from optimized sintering procedures carried out by the manufacturer under ideal industrial conditions which results in mechanically stronger blocks with less defects when compared to the veneering layers obtained by the previously described methodologies.

In 2012,¹³² one study evaluated the load-bearing capacity of all-ceramic crowns composed of Y-TZP veneered using the traditional technique, and crowns produced with the Cad-on system. The fracture load values were significantly different between these two groups, with mean values of 1,575 N for the crowns produced by the CAD-on system and 1,166 N for the crowns that received the veneering layer by the traditional technique.

Another study used the CAD-on system to evaluate the effect of the bonding technique on the fracture resistance of molar crowns. In this study, specimens that had their layers bonded by a resin cement (Multilink Implant;Ivoclar Vivadent) showed a mean fracture resistance value lower than the value obtained for the group in which the components were bonded by means of the fusion glass-ceramic (IPS e.max Crystall Connect; Ivoclar Vivadent, Schaan, Liechtenstein). The mean values obtained in this study were $1,388 \pm 190$ N for the fusion glass ceramic group versus $1,211 \pm 158$ N of the cemented group; however, this difference was not statistically significant.

Another in vitro study¹³³ compared the fracture resistance of all-ceramic first molar crowns with Y-TZP infrastructures veneered with different techniques: layering (VM9; Vita, Bad Sachingen, Germany),press-on (IPS e.max ZirPress; Ivoclar vivadent, Schaan,Liechtenstein), and milling from CAD-CAM blocks (LavaTM DVS; 3M, Seefield, Germany) with posterior bonding using a fusion glass-ceramic.

Multilayered restorations made from CAD-CAM blocks showed significantly higher fracture strength values (6,242 N) when compared to crowns made with the layering (4,264 N) and press-on (5,071 N) techniques.

12.3. New glass-ceramics

Nowadays, glass-ceramics are broadly used in prosthetic dentistry due to the continuous improvements of their mechanical properties associated to better microstructures and new processing methods. The adequate mechanical properties of these materials reflect in the good longevity of such dental restorations.

The good aesthetic quality is another factor that greatly contributes to the attractiveness of glass-ceramics to clinicians. Since glass-ceramics started to be used in dentistry, materials with varied compositions have been developed; however, this class of materials gained popularity after the launching of lithium disilicate glass-ceramic in 1998 (IPS Empress® 2,Ivoclar Vivadent Ltda, Schaan, Liechtenstein, later on marketed as e.max®).

In comparison with leucite glass-ceramics, lithium disilicate-based materials have superior mechanical properties, what expands their indication to the production of all-ceramic fixed partial dentures up to 3 elements. The first lithium disilicate glass-ceramic (based on the system Li₂O:2SiO₂) was produced by melting a glass, which was then ground to form a powder that was used to make the so-called "blue" blocks or ingots with composition.

Depending on the type of piece produced, whether it was a "blue" block for CAD-CAM system or the ingot for hot-pressed technique, the crystallization technique of this glass-ceramic changed. However all the crystallization process were similar in all conditions.

Briefly, the crystallization of the lithium disilicate is controlled by a heating cycle, in which lithium metasilicate (Li2SiO₃) reacts with the glassy phase (SiO2) to originate lithium disilicate (Li2Si₂O₅). Lithium metasilicate is nucleated from the base glass (Li₃PO₄, amorphous) at the initial temperatures of the cycle. Later on, lithium disilicate glass-ceramics underwent some changes and gave rise to IPS e.max Lithium Disilicate (Ivoclar Vivadent Ltda., Barueri, Brazil), which has better mechanical properties, mostly due to the decrease in the size of the platelet shaped crystals (length varying from 2.0 to 3.0μ m) and the increase in interlocking among crystals.¹³⁴

Despite the great acceptance and broad use of lithium disilicate glass-ceramics, the evolution of dental materials has attempted to suppress the remaining disadvantages of this ceramic system by means of the development of glass-ceramics reinforced with polycrystalline ceramics.

These new glass-ceramics were designed to contain lithium silicate as the main crystalline phase in a vitreous matrix reinforced with zirconium dioxide crystals (~10%). When this material goes through the crystallization process, the nucleated lithium silicate crystals achieve a mean size (0.5 to 1 μ m) that is up to 6 times smaller than that observed for lithium disilicate crystals present in lithium disilicate glass-ceramics.

The formation of a smaller and finer crystalline phase occurs due to the presence of zirconia particles in the material, which acts as an additive influencing the crystallization by hindering crystal growth.¹³⁵ A microstructure containing smaller crystals guarantees to this material mechanical properties similar to those observed for lithium disilicate ceramics. Additionally, as observed for traditional glass-ceramics, these new zirconium-reinforced lithium silicate materials maintain good optical properties, are easily milled in CAD-CAM machines and attain good surface finishing, as they still have a high amount of glass matrix.¹³⁶

The two existing commercial examples of lithium silicate glass-ceramics are: a) Suprinity (Vita Zahnfabrik, Bad Sachingen, Germany), a material marketed in a partially crystallized state and that requires an additional thermal cycle in a furnace; and b) CELTRA.

Duo (Dentisply-Sirona, Bensheim, Germany), a material that is already in its final crystallization stage. Both materials have similar composition.¹³⁷

These novel zirconia-reinforced lithium silicate glass-ceramics have good mechanical properties associated with an excellent esthetic quality, thus being a valid alterative to lithium disilicate materials for prosthetic rehabilitations with high aesthetic demand. The main advantage of these materials is their timesaving ability for the production of dental restorations, since they are faster to be milled in CAD-CAM machines than lithium disilicate glass-ceramics and are already offered in their fully crystallized state (CELTRA Duo,Dentisply-Sirona, Bensheim, Germany) no furnace need) or need a very short crystallization cycle (Suprinity,Bad Sachingen, Germany). A particular advantage of the lithium silicate ceramic over the lithium disilicate version is the superior polishability due to the smaller crystal sizes in the microstructure.^{138,139}

12.4. Polymer infiltrated ceramic networks (PICNs)

In the last decades, the use of CAD-CAM systems in dentistry has increased exponentially, especially because of the general trends towards high productivity and aesthetics. Although CAD-CAM systems were developed initially for the production of ceramic restorations, pre-polymerized resin composites blocks have also been developed to be used with these systems. One of the first resin composites developed as a CAD-CAM block was ParadigmTM (3MTM, St Paul, USA), which was considered a fast-milling and wear-friendly alternative to the use of ceramics.

However, problems commonly related to resin composite systems still need to be overcome, such as the reduced mechanical properties and poor wear resistance. Recently, a new material has been developed by Vita(VITA Zahnfabrik, Bad Säckingen, Germany) which is marketed as a polymer infiltrated in a porous ceramic, generating an interpenetrating network (polymer infiltrated ceramic network, PICN). This new material was developed based on the glass infiltrated ceramic technology (In-Ceram System, Vita, Bad Sachingen,Germany), which was originally released by Vita in the 90's.

The infiltration of a resin into a porous ceramic preform is significantly different from the infiltration of a glass, since the final shrinkage of the polymer after infiltration is almost 5%, i.e., much greater than the shrinkage experienced upon cooling of the infiltration glass, which is in the order of 1%.¹⁴⁰

PICNs have the advantage of presenting an elastic modulus that is approximately 50% lower compared to feldspathic ceramics and hence closer to that of dentin, they are easier to mill and adjust, and also can be more easily repaired by composite resins. In comparison to dental porcelains, this new material has been proven to have lower elastic modulus and higher damage tolerance. In 2013,¹⁴¹ the product Enamic (Vita, Bad Sachingen,Germany) was introduced for dental restorations. This PICN is based on initial

sintering of a porcelain powder to approximately 70% of its full density, followed by infiltration with a monomer mixture.

The material is considered a resin-ceramic composite material, composed of two interconnected networks: a dominant ceramic and a polymer. Recent publications showed that the polymeric part of this material is composed of urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) crosslinked polymers. Compositional analyses of the dominant ceramic network revealed a major ceramic phase, composed (by weight) of SiO2 (58–63%), Al2O3 (20–23%), Na2O (9–11%), K2O (4–6%), B2O3 (0.5–2%), CaO (<1%) and TiO2(<1%). Although being marketed as a polymer infiltrated ceramic, scientific analysis has shown that the inorganic matrix is rather an amorphous glass.

A recent publication reported that Enamic showed elastic modulus values similar to that reported by the manufacturer (around 30 GPa), however, the fracture toughness values measured in this investigation (0.86 MPa.m1/2) were lower than that reported by the manufacturer (1.5 MPa.m1/2). The fracture toughness value obtained for PICN was similar to that of the feldspathic ceramic evaluated. Therefore, the authors rejected the hypothesis that the presence of a polymer network would create toughening mechanisms in the microstructure of the material. In addition, this study showed that PICN had increased susceptibility to SCG compared to a feldsphatic ceramic. This raised the question if the polymer is susceptible to water permeation and degradation.¹⁴²

PICNs have positive properties related to both the ceramic and composites, with an interesting balance between elasticity and strength, being indicated for single crowns, inlays, onlays and veneers. The polymeric part has a strength below 30 MPa and the ceramic network has a strength around 160 MPa, whereas the final PICN has strength of 135 MPa. As expected for a composite material, the properties are intermediate between those of ceramics and particle-filled resins.

The elastic modulus of these materials is in the range of 30 GPa, which is half of that reported for conventional veneering ceramics but closer to what is usually reported for dentin (15–20 GPa). Typical ceramic materials have a higher elastic modulus values than PICN. The Vickers hardness of human enamel (3.43 ± 0.16 GPa) and PICN (3.31 ± 0.11 GPa) are similar and both are higher than the hardness reported for resin composites (0.73 GPa to 1.60 GPa) and lower than the hardness of zirconia (13.94 GPa) and lithium

disilicate glass ceramics (10.0 GPa to 11.31 GPa). The flexural strength of Enamic (130 MPa) is lower than that of a reference lithium disilicate glass ceramic material, IPS e.max (342 MPa).

PICN has a higher tolerance to diamond bur grinding damage than other CAD/CAM and pressed materials. A study evaluated the damage tolerance of different dental materials and showed that the damage tolerance of PICN was higher when compared to other ceramics for CAD-CAM, like veneering ceramic.

With respect to optical properties, the shrinkage of the curing resin results in interfacial stresses occurring between the ceramic framework and the polymer resulting in debonding and leading to a higher opacity because of the gaps developed at the interface. The selection of resin, the application of high pressure during the curing phase, and the silanization process enhanced bonding and helped overcoming the aesthetic problems by increasing the translucency of the material.

However, Enamic has been shown to be less translucent than IPS e.max orLava Ultimate (3M ESPE, St Paul, USA). Previous works have also shown that the surface of PICN is not as glossy as those obtained for IPS e.max or Lava Ultimate. Nevertheless, the stain resistance of PICN was superior than that measured for Lava Ultimate and inferior than that reported for IPS e.max.

Clinical simulations show promising lifetime results for PICN. A chewing simulation of five years demonstrated that none of the Enamic crowns failed, while six IPS e.max CAD had minor cracking and twelve Vita Mark II restorations revealed significant crack failures. In a cyclic fatigue experiment of 500,000 cycles, Enamic performed as well as a lithium disilicate glass-ceramic. Based on the reduced elastic modulus of Enamic, this material is especially indicated for prosthetic treatments on stiff implants.Due to the inferior optical properties, PICNs are more suitable in the molar than in the anterior region.

13. RECENT ADVANCES IN CERAMICS TECHNOLOGY

CAD-CAM refers to a computer system that is used to both design and manufacture a dental restoration. CAD technology uses a software to define the shape and dimensions of the restoration, while CAM technology takes the designed model to a computer numeric control (CNC) machine to manufacture the restoration, usually from a block made of a dental material (subtractive manufacturing). Currently, the production of metal-free restorations using polycrystalline ceramic infrastructures (e.g.,Y-TZP) depends on the use of the CAD-CAM systems.

The introduction of CAD-CAM milling systems for the production of restorations with these polycrystalline ceramics allowed their use in prosthetic restorations with greater reliability, since the only manufacturing technique available in the past was slipcasting, which resulted in a greater number of defects and cracks in the microstructure of the final restorations.

CAD-CAM systems have been used in Dentistry for almost 30 years, and during this period different machines have been launched, as these systems are constantly evolving and producing restorations with much better adaptation. Moreover, the evolution of CAD-CAM system have allowed their use to produce restorations with other materials such as veneering ceramics, resin composites and metal alloys.¹⁴³

Among dental CAD-CAM systems, there are two types of techniques for producing restorations. The first one is the machining of the prosthetic restoration from a block of the sintered material, while the second consists of machining a block in a partially sintered state with subsequent final sintering in a specific furnace. Both techniques are used in dentistry and each of them have their advantages and disadvantages.

Machining a block of sintered material provides the restoration with a greater precision of its contours and shape in addition to saving clinical time, since the restoration does not require an additional heat treatment. However, when machining a material with high strength like polycrystalline ceramics, both the wear of the machining unit tools and the machining time are very high. Also, machining brittle materials such as dental ceramics can lead to the formation of microcracks and surface defects.

On the other hand, when the restoration is produced from a partially sintered block, there is the advantage of promoting healing of machining microcracks during the subsequent sintering process. This processing technique is expected to have a shorter machining time for a less dense material, but one must keep in mind that the final sintering will promote dimensional changes due to shrinkage, which may lead to prosthetic restoration misfit¹⁴⁵.

Although the CAD-CAM systems described above are already well established in the dental market, they present a major drawback related to the great waste of material upon machining. The waste corresponds to approximately 90% of the prefabricated block for a typical restoration and left overs from these dental restorations are not reusable. Therefore, new technologies have been developed to overcome this problem. Some of them produce the restoration by means of adding layers instead of grinding pre-fabricated blocks (additive manufacturing).¹⁴⁶

13.1. CAD/CAM Components

There are 3 main sequences to CAD/CAD systems. The first sequence is to capture or record the intraoral condition to the computer. This sequence involves the use of a scanner or intraoral camera.

Once the data have been recorded to the computer, a software program (CAD) is used to complete the custom design of the final desired restoration, which may involve a full contour design of the restoration or just the internal coping or substructure of the final restoration.

The final sequence requires a milling device to fabricate the restoration from the design data in the CAD program. At present, the most common technique is a wet grinding subtractive milling process during which a preformed block of material is shaped by cutting instruments.

Results with in-office milling machines seem to be as good as those from laboratory milling machines. A systematic review of 16 articles that comprised 1957 restorations found no significant differences in 5-year survival rates between chairside CEREC(Chairside Economical Restoration of Esthetic Ceramics) restorations (90.2%– 93.8%) and Celay laboratory restorations (82.1%).

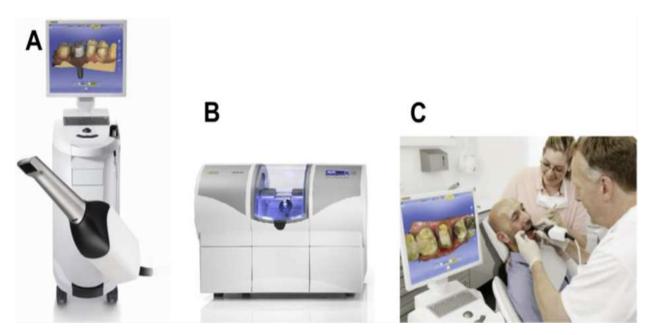


Fig. 1. (A) CEREC AC with Omnicam, (B) milling unit, and (C) data acquisition in CEREC system using Omnicam. (Courtesy of Sirona Dental Systems, Available at: www.sirona.com)

13.2. Scanner

There are 2 different scanning possibilities:

a) *Optical scanner*: This scanner uses the collection of 3D structures, for which the source of light and the receptor unit are in a definite angle in their relationship to one another.

Through this angle the computer can calculate a 3D data set from the image on the receptor unit. Either white light projections or a laser beam can serve as a source of illumination.

b) *Mechanical scanner*: In this scanner variant, the master cast is read mechanically line by line by means of a ruby ball and the 3D structure measured. The Procera Scanner from Nobel Biocare is one of the mechanical scanners in dentistry. This type of scanner is distinguished by a high scanning accuracy, whereby the diameter of the ruby ball is set to the smallest grinder in the milling system, with the result that all data collected by the system can also be milled.

The drawbacks of this data measurement technique are in the highly complicated mechanics, which make the apparatus expensive with long processing times compared with optical systems.

13.3. Design software

Special software is provided by the manufacturers for the design of various kinds of dental restorations. With such software, crown and fixed partial denture (FPD) frameworks can be constructed. Some systems also offer the opportunity to design full anatomic crowns, partial crowns, inlays, inlay retained FPDs, as well as adhesive FPDs and telescopic primary crowns.

The software of CAD/CAM systems presently available on the market is being continuously improved. The latest construction possibilities are continuously available to the user by means of updates. The data for the construction can be stored in various data formats. The basis is often standard transformation language (STL) data. However, many manufacturers use their own specific data formats, with the result that data for the construction programs are not compatible with each other.

13.4. CAD/CAM Development in Dentistry

The development of CAD/CAM is based around the data acquisition, data processing, and digital fabrication processes.

Digital data acquisition methods

The oral information for the patient can be directly extracted from a patient's mouth or indirectly by means of a stone model generated through making an impression.

The data acquisition techniques were originally developed for reverse engineering and intensively used in manufacturing industries. Their strengths were gradually recognized and these techniques are also applied in the medical field. The acquisition systems are divided into 2 basic categories: contact and non contact digitizers.

The digital data acquired through various techniques and instruments are converted into a standard format so that the data can be processed using the capabilities of a CAD/CAM system. This process is exemplified by the recent introduction of intraoral scanners, a number of which are now on the market: Lava COS (chairside oral scanner) from 3M, Trios from 3Shape and iTero from Cadent, and CEREC from Sirona.

A further development in the CAD/CAM technologies used in dentistry was the transition from closed to open access systems. Although in the past the digitizing, designing, and manufacturing came as a closed system (eg, CEREC), the technology is increasingly being opened up and the component parts of a CAD/CAM system can be purchased separately, which creates greater flexibility because data can be acquired from a range of sources (intraoral scanner, contact or laser model digitizer, computed tomography, magnetic resonance imaging).

Another important consequence of the transition from closed to open systems is that this opens up access to a wider range of manufacturing techniques such that the most appropriate manufacturing processes and associated materials can be selected. Thus, clinicians are no longer constrained by the computer numerically controlled machining technologies that are currently used in most dental CAD/CAM systems.

Data processing and remodelling

CAD software is often used to edit and manipulate the point cloud data generated by a digitizer. After the point cloud data are converted into a representation of a surface or solid, the next step involves a digital design process for the dental part.

The shape design of the 3D dental restoration is one of the core elements of successfully fabricating restorations. In these systems the basic models of teeth are available in their own libraries.

However, general forms of teeth geometry provided by these CAD/CAM systems can only give raw shapes. There are always some manual alterations and modifications required because every patient is unique and every tooth has its own topological features.

Digital fabrication processes

This is the last phase of the dental CAD/CAM process. It involves transforming a CAD model into a physical part that is later postprocessed and polished before being inserted into the patient's mouth.

Industrial 3D printers have existed since the early 1980s, and have been used extensively for rapid prototyping and research purposes. These printers are generally large machines that use proprietary powdered metals, casting media (ie, sand), plastics, or cartridges, and are used for many rapid prototyping uses by universities and commercial companies. Several methods can be used to fabricate the physical parts. These methods can be additive or subtractive.^{143, 144}

Subtractive manufacturing

Subtractive manufacturing removes material from a raw block to form an object of the desired shape and size, which can be done by conventional machining (eg, milling) and unconventional machining (eg, electrical discharge machining (EDM), laser machining).

CAD/CAM in dentistry is now primarily based around the process of subtractive manufacturing. The technology most people are familiar with is computer numerically controlled machining, which is based on processes in which power-driven machine tools, such as saws, lathes, milling machines, and drill presses, are used with a sharp cutting tool to mechanically cut the material to achieve the desired geometry, with all the steps controlled by a computer program. This method of manufacturing is wasteful because more material is removed than is used in the final product.

The main advantage of this type of manufacturing is the ability of the technique to create fine detail such as undercuts, voids, and complex internal geometries. Another limitation of the current dental CAD/CAM systems is that the process does not easily lend itself to mass production, such as crowns and bridges, because only 1 part can be machined at a time.

Additive manufacturing

Additive manufacturing describes technologies that can be used anywhere throughout the product life cycle from preproduction (ie, rapid prototyping) to full-scale production (also known as rapid manufacturing) and even for tooling applications or postproduction customization. 3D printing is achieved using additive processes, in which laying down successive layers of material creates an object.

The primary advantage of additive construction is its ability to create parts of almost any geometry, and the capability to spatially grade composition and/or microstructure (eg, porosity) to meet specific designs or needs, without requiring a previous mold. Also, this fabrication technology permits internal morphology, shape, distribution, and connectivity to be controlled more precisely. Another benefit from this system is the ability to print with multiple materials at one time as well as to create graded structures.

Modalities of Rapid Printing

The process of additive manufacturing is ideally suited to dentistry. Models are designed using data from a computed tomography scan or magnetic resonance imaging. The image is downloaded to a CAD machine and converted to an STLfile. Various rapid prototyping technologies can be used to produce anatomic models.

Addition CAD-CAM systems, also called "solid free-form fabrication",¹⁴⁶ are still a focus of research and development for polycrystalline ceramic materials and there are three techniques that have stood out recently. These techniques are:

- 1. Selective Laser Sintering or Melting
- 2. Direct 3D Printing and
- 3. Stereolithography.

The Selective Laser Sintering or Melting is an already well-established technique for metal alloys, but is still in development for polycrystalline ceramics. In this technique, the laser beam sinters thin layers of a ceramic from a container filled with powder to create a single coping or framework, in which each layer represents a cross section of the CAD model.

The possibility to directly use sintering products with no significant costs for post treatment as well as to synthesize new phases under non equilibrium conditions of high speed laser heating/cooling distinguishes the SLM method from other rapid prototyping techniques. Freedom from toxic binder also renders the SLM technique superior over other conventional techniques for fabricating implants for medical applications.

SLM is a powder-based process initially designed for 3-dimensional freeform fabrication of metallic component. In this process, powder particles are fully melted by the laser and fuse together instead of simply raising the temperature and allowing the particles to sinter together as in selective laser sintering (SLS). This results in a 3-D part with low porosity and good mechanical properties.

The process has been researched upon with a variety of metallic materials such as stainless steel, high speed steel, aluminium, gold and cobalt-chrome.¹⁴⁷

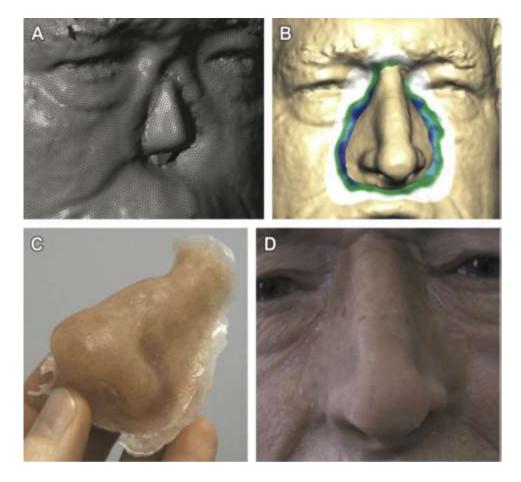
Stereolithography is frequently used nowadays, and has already evolved enough to allow production of more complex ceramic pieces, whereas the previously mentioned techniques are in the early development stage for dental applications. It is similar to 3D printing, however it makes use of a suspension containing ceramic particles mixed with a resin components (acrylates or epoxy monomers).

This resin part is polymerized during printing to shape the solid object and is subsequently removed during the ceramic sintering process. The great advantage associated with all additive techniques is that they provide minimal or no material waste. One still existing disadvantage of all additive methods to date is the rough surface quality and the poor fit or marginal precision.¹⁴⁸

Stereolithography, is a process whereby each layer is patterned by laser scanning on photopolymerizable medium to convert liquid monomer into solid resin. The method has been adapted to form ceramics by using a photopolymerizable suspension of ceramic powders in place of the liquid monomer.

To expand the term stereolithography to include all cases in which ceramics are made with multilayer photopolymerization, including cases involving layers patterned by laser scanning and by mask image projection.Photopolymerization is not a new ceramic process.

Photopolymerized tape casting systems were described in 1986 and photopolymerized dental ceramic composites are common place. Photoimageable tape cast products are commercial products. The technique was applied for additive manufacturing of ceramics using commercial laser scanning stereolithography machines or novel variants of laser scan devices. Patterning can also be done by mask image projection, typically with a spatial light modulator based on a digital mirror device (DMD). Applications are varied and include biomedical implants, ceramic prototypes, cellular ceramics, complex investment casting cores, and integrally cored investment casting molds. The process has been adapted for microscale ceramic forming as micro stereolithography for a variety of applications.^{148,149}



(A) The STL file polygon mesh data of the baseplate and surrounding anatomy. (B)The complete digital design with texture. (C) Completed prosthesis from the silicone wrapped direct RP-fabricated pattern. (D) Completed prosthesis from the RP-fabricated mold. (From Eggbeer D, Bibb R, Evans P, et al. Evaluation of direct and indirect additive manufacture of maxillofacial prostheses. Proc Inst Mech Eng H 2012.

Direct 3D Printing is similar to a traditional inkjet printer, performing the direct printing of a ceramic suspension, allowing the generation of dense green bodies with high resolution, and producing complex shapes.

It is the technique that stands out, as the equipment is relatively more accessible and allows for the production of a dense green body ready for sintering. In 2009, using a modified inkjet printer, a zirconia crown was manufactured with sufficient mechanical properties to be used in the oral cavity. The impression of the posterior dental crown was performed using a cartridge filled with a 27 vol% solid content of zirconia-based ceramic suspension.

Variations of the Direct 3D Printing technique have also been studied, the socalled "Robocasting".Both techniques are very similar, differing only in the way the deposition of the ceramic suspension is made.

Robocasting is a rapid prototyping (RP) that fabricates objects based on layering techniques. Robocasting uses computer-controlled extrusion of colloidal pastes (slurries, gels, or inks) onto a flat substrate without using molds or tooling.

Unlike milling, in which blocks are cut back to create a form, robocasting uses a computer generated scan from computed tomography of a SLA file to create a strategically printed 3D structure. This process has been used in orthopedics for bone and tissue engineering. Robocasting in the dental setting is a new development with limited information or practice.

The advantages of printing versus milling are the ability to make microstructure as needed for the prosthesis without requiring a previous mold; that it allows internal morphology, shape, distribution, and connectivity to be controlled more precisely; and a significant decrease in waste of materials.

To achieve its full potential as a dental restoration production process, robocasting must improve the use of support materials to produce better tolerance for occlusal surfaces. In addition, the digital nature of the layer printing process leads to a stair stepped surface that may need to be improved for commercial acceptance.

The step size is a function of the nozzle diameter used for printing. The issue of support materials/structures seems to be a tractable problem; however, the stair stepping may require some post processing (eg, a dip-coating process) before final sintering. Drying issues, such as cracks, sometimes occur produce the object.¹⁵⁰

14. CONCLUSION

Dental ceramics and processing technologies have evolved significantly in the past ten years, with most of the evolution being related to new microstructures and CAD-CAM methods. Also, a trend towards the use of monolithic restorations has changed the way clinicians produce all-ceramic dental prostheses, since the more aesthetic multilayered restorations unfortunately are more prone to chipping or delamination. Composite materials processed via CAD-CAM have become an interesting option, as they have intermediate properties between ceramics and polymers and are more easily milled and polished.

The future of ceramics for dentistry is clearly open to new technologies. the success of new all ceramic systems will depend as much on developmental analytical research.

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