EFFECT OF SINTERING TEMPERATURE ON MECHANICAL BEHAVIOUR AND BIOACTIVITY OF CALCIA-STABILIZED ZIRCONIA DERIVED COCKLE SHELLS BIOCERAMIC

NUR AIN ADILA BINTI ABD WAHAB

UNIVERSITI SAINS MALAYSIA

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by

NUR AIN ADILA BINTI ABD WAHAB

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LIST OF SYMBOLS

Ө	Angle
cm	Centimetre
°C	Degree Celcius
ρ	Density
g	Gram
GPa	Gigapascal
kV	Kilovolt
Kgf	Kilogram-Force
Kg	Kilogram
mm	Millimetre
M	Mass
mL	Millilitre
MPa	Megapascal
nm	Nanometer
%	Percentage
pH	Potential of Hydrogen
rpm	Revolutions per Minute
σ	Sigma
V	Volume
wt%	Weight Percent
ʎ	Wavelength

LIST OF ABBREVIATIONS

Al_2O_3	Aluminum Oxide
ASTM	American Society for Testing and Materials
Be	Berium
Ca-SZ	Calcia-Stabilized Zirconia
CaO	Calcium Oxide
$CaCO_3$	Calcium Carbonate
Co-Cr	Cobalt-Chromium
$CaCl_2$	Calcium Chloride
CAD/CAM	Computer-aided Design & Computer-aided Manufacturing
Ca-P	Calcium-Phosphate
FDPs	Fixed Dental Prostheses
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
HCl	Hydrochloric Acid
Hap	Hydroxyapatite
MgO	Magnesium Oxide
ISO	International Organization for Standardization
K_2CO_3	Potassium Carbonate
Ni-Cr	Nickel-Chromium
Y_2O_3	Yttrium Oxide
SiO_2	Silicon Dioxide
SBF	Simulated Body Fluid
TEM	Transmission Electron Microscopes
XRD	X-ray Diffraction
Y-TZP	Yttria-stabilized Tetragonal Zirconia Polycrystal
ZrO_2	Zirconium Dioxide

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KESAN SUHU PENSINTERAN TERHADAP SIFAT MEKANIKAL DAN BIOAKTIVITI BIOSERAMIK ZIRCONIA YANG DISTABILKAN OLEH CALCIA MENGGUNAKAN KULIT KERANG

ABSTRAK

Penyelidikan eksperimen asal yang dijalankan untuk kajian ini oleh penyelidik terdahulu adalah dengan mengkaji kalsium oksida yang disintesis yang diperoleh daripada kulit kerang untuk digunakan sebagai penstabil bagi bioseramik zirkonia pada suhu yang berbeza. Penyelidikan ini diteruskan oleh pasukan penyelidikan kami dengan menambah baik pengeluaran kalsium oksida yang diperoleh daripada kulit kerang menggunakan penambahbaikan dari segi protokol dan menentukan ketulenannya. Selanjutnya, penambahbaikan analisis data bagi bioseramik Ca-SZ pada suhu tersinter yang berbeza dibandingkan dengan bongkah pergigian CEREC Sirona yang telah dikomersialkan. Oleh itu, matlamat kajian ini adalah untuk menyiasat kesan suhu pensinteran ke atas sifat struktur, morfologi, mekanikal dan biologikal bioseramik Zirconia yang distabilkan oleh Calcia menggunakan kulit kerang. Bagi mencapai objektif ini, tiga suhu pensinteran pada 1200 ^{o}C, 1300 ^{o}C dan 1400 ^{o}C telah dipilih untuk memahami sifat struktur, morfologi dan mekanikal bioseramik Ca-SZ dengan menggunkan 8 wt% serbuk nano-CaO yang diperoleh daripada kulit kerang. Selain itu, untuk memberikan hasil perbandingan yang lebih baik, CEREC Sirona telah disinter pada suhu 1510^{o}C mengikut protokol yang disedikan oleh Sirona, The Dental Company. Sewaktu kerja eksperimen ini dijalankan, serbuk kulit kerang yang telah dicairkan dicampur dengan Kalsium Klorida ($CaCl_2$) dan kalium karbonat (KCO_3), menggunakan proses sintesis mekanokimia. Kemudian, serbuk nano-$CaCO_3$ menjalani proses pengkalsinan pada suhu dalam julat 300 ^{o}C – 550 ^{o}C untuk mendapatkan serbuk nano-

CaO. Serbuk Nano-CaO yang diperolehi daripada kulit kerang telah menjalani pencirian menggunakan teknik belauan sinar-X (XRD), Pancaran Medan Mikroskopi Elektron Pengimbasan (FESEM) dan Pemetaan EDX (FESEM/EDX) dan TEM untuk memastikan ketulenan serbuk nano-CaO yang diperolehi bagi pembentukkan fabrikasi Zirconia yang distabilkan oleh Calcia. Analisis menggunakan FESEM dan TEM menunjukkan bahawa nano-$CaCO_3$ menghasilkan kristal bentuk heksagon manakala nano-CaO memaparkan bentuk sfera dengan struktur seperti kristal. Seterusnya, serbuk bioseramik Ca-SZ yang diperoleh pada suhu pensinteran yang berbeza kemudiannya dipadatkan dan dicirikan menggunakan FESEM dan XRD. Bioseramik Ca-SZ yang disinter pada 1400 ^{o}C menunjukkan sifat mekanikal yang paling memberi kesan yang baik dan juga menunjukan perbandingan yang lebih baik ketika diuji menggunakan larutan SBF 'in-vitro' berbanding spesimen tersinter lain kerana saiz liang berkurangan dalam kenaikan suhu. Bertentangan pula, Ca-SZ yang disinter pada 1400 ^{o}C menghasilkan kekuatan mekanikal yang lebih rendah jika dibandingkan dengan CEREC Sirona yang telah dikomersialkan. Oleh itu, penemuan ini mendedahkan bahawa dengan melaraskan protokol sebelumnya, penambahbaikan ketulenan nano-CaO boleh disintesis menggunakan sumber Ca semula jadi daripada kulit kerang. Selain itu, Ca-SZ yang difabrikasi mempunyai potensi dalam sifat biologi dan juga menunjukkan sifat mekanikal yang jauh lebih rendah berbanding dengan CEREC Sirona apabila disinter pada 1400 ^{o}C yang mungkin lebih mudah untuk pemesinan dan berpotensi untuk dikomersialkan tidak lama lagi yang membantu dalam kajian untuk rawatan pergigian.

EFFECT OF SINTERING TEMPERATURE ON MECHANICAL BEHAVIOUR AND BIOACTIVITY OF CALCIA-STABILIZED ZIRCONIA DERIVED COCKLE SHELLS BIOCERAMIC

ABSTRACT

The original experimental research carried out for this study by previous researcher was to investigate the synthesized of calcium oxide derived from cockle shells to be used as stabilizer for zirconia bioceramic at different temperatures. However, this research was continued by improved the production of calcium oxide derived from cockle shells using an improved protocol and determine its purity. Further, the improved data analysis of Ca-SZ bioceramic at different sintering temperatures were compared to the commercialized CEREC Sirona dental block. Hence, the aim of this study is to investigate the effect of sintering temperature on structural, morphological, mechanical, and biological properties of calcia-stabilized zirconia derived cockle shells bioceramic. To achieve this objective, three sintering temperatures at 1200 ^{o}C, 1300 ^{o}C and 1400 ^{o}C were selected in order to understand the structural, morphological and mechanical properties of Ca-SZ bioceramic after incorporation of 8 wt% of nano-CaO powders derived from cockle shells. Moreover, to give better comparative results, CEREC Sirona was sintered at temperature 1510 ^{o}C followed the protocol provided by Sirona, The Dental Company. In this experimental work, the diluted cockle shells powder was mixed with calcium chloride ($CaCl_2$) and potassium carbonate (KCO_3), using mechanochemical synthesis process. Then, nano-$CaCO_3$ powder underwent calcination process at a temperature range of 300 ^{o}C – 550 ^{o}C to obtain nano-CaO powders. Nano-CaO powder derived from cockle shells were characterized using X-Ray Diffraction (XRD) analysis, Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscope (TEM) to ensure high purity of nano-CaO powder was obtained in fabricating Calcia-Stabilized Zirconia (Ca-SZ). FESEM and TEM analyses show that nano-$CaCO_3$ produced hexagonal shape crystals while nano-CaO display spherical shape with crystal-like structure. Next, Ca-SZ bioceramic derived cockle shell powder obtained at different sintering temperature were then compacted and characterized using FESEM and XRD. Ca-SZ sintered at 1400 ^{o}C showed the highest mechanical properties and better in in-vitro test using SBF solution compared to other sintered specimens due to the pore size reduced within temperature rise. However, Ca-SZ sintered at 1400 ^{o}C produced lower mechanical strengths when compared to commercialized CEREC Sirona. Therefore, these findings revealed that by adjusting the previous protocol, improved, pure nano-CaO may be synthesized using natural Ca source from cockle shells. Additionally, the fabricated Ca-SZ has a potential in biological properties and also showed a significantly lower mechanical properties compared with CEREC Sirona when sintered at 1400 ^{o}C which may be easier for machining and has a potential to be commercialized soon which helps in study for dental treatment.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Zirconia has been used in dentistry for fixed prosthodontics (Laumbacher, *et al.*, 2021) and also for dental implants (Chopra, *et al.*, 2022). Calcia-stabilized zirconia (Ca-SZ) bioceramic has a potential to be used in dentistry as an alternative zirconia. In a previous study, Ca-SZ bioceramic has been fabricated using calcium oxide (CaO) derived from cockle shells as stabiliser (Hussein *et al*, 2020B). The CaO was synthesised in-house by Hussein *et al*. in 2020, however, the yield product of CaO in the previous study was very limited (Hussein *et al*, 2020A). This current study was carried out to investigate the effectiveness of a new synthesis method to produce calcium oxide (CaO) derived from cockle shells to be used as stabiliser for zirconia. This study provides new insights on improving the yield product of CaO from previous method done by Hussein *et al.* in 2020. In addition, this study also investigated the mechanical and biological properties of Ca-SZ bioceramic it was sintered at different sintering temperatures of 1200 ^{o}C, 1300 ^{o}C, 1400 ^{o}C and compared it with commercial dental block (CEREC Sirona).

Recent evidence suggests that the usage of CaO for medical and clinical applications due to its excellent biocompatibility towards human cells (Louwakul *et al*., 2017; Ranjbar *et al.*, 2019; Fernando *et al.*, 2018; Hussein *et al.*, 2020B). The usage of CaO as a stabilizing agent for zirconia (ZrO_2) for clinical applications have been known before such as for hip replacement (Arun *et al*., 2021). However, CaO stabilised zirconia has not been used in dentistry. The current zirconia ceramics available in the market for single crowns and partial fixed prostheses (FDPs) include yttrium-oxide tetragonal zirconia polycrystals (Y-TZP).

ZrO_2 has been known as an important material oxide due to its excellent properties such as good chemical and dimensional stability, high mechanical strength and toughness (Piconi *et al*., 1999). Besides, it is considered to be inert in body cells and can exhibit minimal ion release compared to the metallic implants such as titanium and titanium alloys (Özkurt *et al*., 2011). Hence, it can prevent the galvanic side effects after contact with saliva. Pure zirconia stabilized with oxides such as yttrium-oxide tetragonal zirconia polycrystals (Y-TZP) has been used in medical application such as ball heads for total hip replacements at early stage in implant for surgery. Hence, many researchers are determined to expand the potential of this materials to be used in clinical and manufacturing applications (Basu *et al.*, 2004; Pittayachawan *et al.*, 2009).

In recent years, Y-TZP has been used in dental applications as a commercial dental block due to its high toughness in the tetragonal to monoclinic (t-m) transformation toughening mechanism, which can prevent crack propagation in the situation of crack pressure area. However, due of its high fracture and superior hardness strengths, Y-TZP has been limited to the constraints of micro crack formation when milled using a computer-aided-design and computer-aided-manufacturing (CAD/CAM) technique (Luthardt *et al.*, 2004; Pihlaja *et al*., 2014). The impact of milled technique can induce micro crack on Y-TZP matrix, which can affect the final strength of the final restoration and could provide chipping at marginal area (Kelly *et al*., 2008; Brenes, 2017; Øilo *et al.*, 2018).

The interest in using CaO as a stabiliser for zirconia to be used in dentistry as a bioceramic material in fixed prosthodontic through CAD/CAM systems grew as a result of the limitations of Y-TZP. CaO acting as a stabilizing oxide for zirconia is proposed to allow a more stable tetragonal structure at room temperature and reduce the crack propagation during t → m transformation catastrophic failure upon cooling (Homaei *et al.*, 2016; Gionea *et al.*, 2016). Zirconia has three phases that change with the change in temperature. These phases are monoclinic (M) at 1170 ^{o}C, tetragonal (T) at 2370 ^{o}C and cubic (C) at 2680 ^{o}C. The attractiveness of pure zirconia as a base material over all the ceramic prosthetic materials are due to a unique toughening function which help transformation of t → m phase when heated up to 1170 ^{o}C (Lughi *et al.*, 2010; Grech *et al.*, 2019).

In addition, this current study was expected to produce Ca-SZ bioceramic which has a lower hardness compared to the commercial dental block (Y-TZP) so that the new Ca-SZ bioceramic will not wear the milling machine for the construction of single crowns and partial fixed protheses (FDPs) through CAD/CAM system (Fischer *et al.*, 2008; Nakamura *et al.*, 2012).

Synthesized CaO powders derived from cockle shells was used in this study to reduce the reliance on manufactured CaO in dental applications. Cockle shells are readily available, harmless, and cheap potential sources of calcium carbonate. They exist in three polymorphs in nature such as calcite, aragonite and vaterite (Rashidi *et al.*, 2011; Mohamed *et al.*, 2012; Shafiu Kamba *et al.*, 2013; Habte *et al.*, 2019).

In view of the aforementioned recent development, the use of CaO as a zirconia stabilizing oxide has shown promising results in medical and clinical applications applications (Ranjbar *et al.*, 2019; Ab Ghani *et al.*, 2020). The comparison with CEREC Sirona dental block was done because this dental block has been established and accepted globally in fixed prosthodontic treatments since 1985 (Mörmann, 2006). It is also due to the elemental content in CEREC block include zirconia which is almost similar to the elements in Ca-SZ bioceramic.

1.2 Problem Statement

An in-house freeze-dry method has been done in a previous study by Hussein *et al.* in 2020A to synthesize CaO derived from cockle shells which was then used as a stabilizing oxide for zirconia (Ca-SZ) Hussein *et al.* (2020B). The yield product from previous study was considered a succes since the final product was yielded with the smallest average particle size of CaO after calcined. However the amount of CaO produced was very limited in about 0.2 g per cycle (Hussein *et al.*, 2020A). Therefore, this study was conducted to upscale the yield of CaO derived from cockle shell using a different synthesis method, using the oven-dry method. The pH value of nano-$CaCO_3$ (pH 9.0) per cycle was checked before the calcination process. Since the fabricated Ca-SZ bioceramic has shown promising physical and mechanical properties for dental applications by previous study, therefore, this study was conducted to investigate the upscaling yield product of nano-CaO as stabilizer for zircona and to investigate its new mechanical properties.

Furthermore, the Ca-SZ has not been compared to the commercial dental zirconia. The biological properties were also investigated as an added value for Ca-SZ specimens to be used in clinical study. The ability of Ca-SZ bioceramic to bond to biological hydroxyapatite (HA) in a simulated body fluid (SBF) solution with ion concentrations approximately equal to those of human blood plasma has yet to be investigated. This is very important as Ca-SZ bioceramic derived from cockle shells may be used as dental implant.

1.3 Justification of Research Study

If the up scaling of CaO derived from cockle shells was achieved, then the dependency of manufactured CaO for dental applications will be minimized. Efforts have been made to incorporate waste products from cockle shells into the production of calcium oxide. Based on the latest trend and study, recent attention has focused on the provision on using cockle shells as a raw material in the production of calcium carbonate ($CaCO_3$), which can be relevant for environmental safety and be used in biomedical and clinical applications. Since $CaCO_3$ has potential sources of calcium and has three polymorphs in nature, such as calcite, aragonite, and vaterite, it can therefore supply a safer and more economical of high content of calcium sources in nature compared to commercialized synthesized CaO available in the market. In this study, the synthesized CaO was used to stabilize zirconia which may have a potential to be an alternative material for dental crown and bridgework, and also as dental implant if the Ca-SZ was proven to have mechanical and biological properties suitable for dental applications.

1.4 Research Objectives

The objectives of this study are:

i. To up-scale the production of nano-CaO derived from cockle shells by adjusting the previous methodology.

ii. To fabricate and characterize Ca-SZ stabilized nano-CaO bioceramic derived from cockle shells.

iii. To investigate the effect of different sintering temperature on mechanical (flexural, compressive and hardness strengths) and biological (in-vitro test using SBF) properties of Ca-SZ stabilized nano-CaO bioceramic and compare it with commercial CEREC Sirona dental block.

1.5 Research Questions

i. Is it possible to up-scale the production of nano-CaO derived from cockle shells by adjusting the previous methodology?

ii. Is it possible to fabricate and characterize Ca-SZ bioceramic stabilized by improvising the methodology of nano-CaO derived from cockle shells?

ii. Are there any differences in mechanical and biological properties of Ca-SZ bioceramic derived from cockle shells when compared to Y-TZP commercial zirconia CEREC, Sirona?

1.6 Research Hypotheses

There are no differences in the mechanical and biological properties of Ca-SZ bioceramic derived from cockle shells when compared to Y-TZP commercial zirconia CEREC Sirona.

1.7 Scope of Study

This study was conducted to study the effectiveness of nano-CaO derived from cockle shells stabilized zirconia. The study was also carried out to investigate the effect of different sintering temperatures on structural, morphological, mechanical and biological properties of Ca-SZ bioceramic derived cockle shells when compared with commercial CEREC Sirona dental block. In order to implement objective stated in 1.4 (i), cockle shells powder was diluted using distilled water and titrated with 50 wt% of hydrochloric acid (HCl) to obtain $CaCl_2$ solution. Next, the solution was mixed with 6.0 wt% of potassium carbonate (K_2CO_3) to produce $CaCO_3$ solution. The solution was centrifuged to obtain solid form of $CaCO_3$. Then, the $CaCO_3$ precipitate was oven dried to produce approximately 5.00 g of $CaCO_3$ powders which was then calcined to get the purified CaO. The increased amount of CaO powders produced derived from cockle shells was achieved. For further investigation of objectives stated in 1.4(ii) and 1.4(iii), Ca-SZ bioceramic and commercial CEREC Sirona dental block were formed in the same pellet size (n=5) followed ASTM tests standard for specimen's sizes. The Ca-SZ powder was milled using lab mini roll ball mill machine, with the mix of 92 wt% commercialized ZrO_2 nano-powder stabilized and 8 wt% nano-CaO derived from cockle shells.

For the characterization for each specimen analysis, X-ray diffractometer (XRD) was used to evaluate the changes of calcite phases for the synthesis and calcined powders, and also to analyse the phases changes, elements presence for bioceramic specimen and its crystallite sizes. The surfaces morphologies of specimen were analysed using Field Emission Scanning Electron Microscopy (FESEM), while the crystal structure and morphologies of CaO before and after calcination was analysed using Transmission Electron Microscope (TEM). The mechanical tests involved in this study were microhardness, compressive and flexural strengths in evaluating the hardness and strengths between Ca-SZ bioceramic with commercial CEREC Sirona. Bioacitivity test was also performed following the protocol by Kokubo et al. (2006) for Ca-SZ bioceramic sintered at different temperatures and compared with commercial CEREC Sirona. The results from Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (FESEM/EDX) showed the ability of hydroxyapatite (HA) formation on specimen's surfaces with detection of emerging elements.

1.8 Thesis Outline

This thesis outline is broken down into five sections:

i. The first chapter discusses the research study's history, problem statement, justification, research objectives, and scope.

ii. In the second chapter, the literature review discusses the use of zirconia-based ceramics in fixed prosthodontic therapy and past studies on materials used in this treatment, as well as understanding of the CAD/CAM system. A review of the literature on the extraction of CaO from cockle shells for use in clinical studies, as well as an introduction to material equipment and testing, as well as the clinical benefits. In addition, the results of a bioactivity investigation on the development of hydroxyapatite in zirconia-based ceramics and their use in dental applications were included.

iii. The third chapter describes the materials and equipment utilised in the experimental technique, which is divided into three stages, as well as the characterisation of all tested specimens.

iv. In chapter four, the outcomes of all specimens that were tested are presented and discussed.

v. In chapter five, the research study's final conclusions and recommendations for future study requirements are written.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of bioceramic materials in dental applications

Fixed prosthodontic treatment such as dental crowns and bridges, complete arch prostheses provide great satisfaction towards patient (Ce *et al.*, 2017). Prosthodontics is a specialised branch of dentistry that focuses on the design, manufacture, and fitting of these artificial replacements for teeth, as well as restorations of natural teeth. The fixed prosthesis can be in the form of single cast crown or multiple units of cast crowns joined together, commonly referred to as fixed partial denture or bridge. These treatments involved the use of several different types of materials to replace missing tooth structure. Traditionally, gold has been used as framework for dental crown and bridgework. Titanium (Ti) alloy is used as a standard material for tooth replacement in dental implantology (Özkurt *et al.,* 2011). They are used in dentistry because gold and Ti-alloy provide excellent biocompability. When titanium exposed is to air, titanium will immediately a stable oxide layer. These materials also provide favourable mechanical properties.

However, these materials are not aesthetic as they are not tooth coloured. Furthermore, gold is expensive (Wahi *et al.,* 2016). Ti-alloy shows dark greyish colour which are often visible through peri-implant mucosa, hence it does not produce an aesthetic outcome. Ti-alloy can affect the health of peri-implant and hard tissue by giving the long-term reaction corrosion reaction along with continuous corrosion which may lead to fracture of the abutments and implant body tends to undergo rapid oxidation (Noumbissi *et al.,* 2019). Therefore, ceramic materials have been widely used in dentistry. This is mainly due to the material's good properties and characteristics, biocompatibility, and aesthetics. All ceramic systems are used for small fixed partial dentures (FPD), single crowns, inlays, on lays, and veneers. All-ceramic systems are applied for the restoration of teeth and dental implants.

Additionally, developments of research work for fixed prosthodontic treatment have grown in using all ceramics materials which are porcelain veneered zirconia, with addition of stabilizing oxides such as magnesium oxide (MgO), aluminium oxide (Al_2O_3) and yttrium oxide (Y_2O_3) used as a competitive alternative to common metal–ceramics (cobalt-chromium, nickel-chromium). Despite metal-ceramics alloy frameworks has high strength, toughness, and wear resistance, however these materials have been less successful for digitally manufactured frameworks because of poor machinability, difficult to mill, costly and time-consuming. To ease the milling and cast ability, other element such as Beryllium (Be) needs to be added (Øilo *et al.*, 2018).

Zirconia has good biomechanical properties since it has the ability to withstand oral forces and provide many advantages in biomedical applications (Roehling *et al.*, 2019). Zirconia-based materials combinations used in fixed prosthodontic treatment with improved material strengths and provide high biocompatibility with white opaque material appearance which give this material advantages to be used for a wide range of promising in clinical applications (Abd El-Ghany *et al*., 2016; Heintze *et al*., 2011; Denry *et al*., 2008). It is also inert to the cell body and exhibit minimum ions release compared with metallic implants due to the presence of the addition of addition of stabilizing oxides such as magnesium oxide (MgO), aluminium oxide (Al_2O_3) and yttrium oxide (Y_2O_3) provide stabilization of zirconia phases (Özkurt *et al*., 2011). Table 2.1 shows the summary of the materials used in fixed prosthodontics dentistry.

Table 2.1 Summary of type of materials used in fixed prosthodontic treatment.

Denture types	Materials	Significance/deficiency	References
Full metals	Gold, titanium alloy	Gold and Ti-based alloy has high corrosive resistance and have good long terms in clinical results; however, they performed unnatural tooth colour and provide can led to side effect on galvanic reaction when contact with saliva.	(Wahi *et al.*, 2016; Noumbissi *et al.*, 2019)
Metal-ceramics	Cobalt-chromium (Co-Cr), Nickel-chromium (Ni-Cr)	Co gives hardness for prosthesis framework while Cr will prevent corrosion and improve the mechanical properties. Usually, Ni-Cr has good properties as Co-Cr, however Co-Cr chosen as an alternative for patients with allergies to Ni based alloy. Besides, other element such as Beryllium (Be) need to added in order to reduce the alloy's melting temperature and to improve cast ability.	(Srivastava *et al.*, 2020)
Zirconia based ceramics	Porcelain veneered zirconia	Zirconia provides tooth-alike, better mechanical properties and biocompatibility. Addition of porcelain veneered zirconia led to shining appearance of tooth-alike, however porcelain is brittle as its fracture resistance similar to tooth enamel and easily exposed to chipping. Large chipping cracks of porcelain veneered crowns may attach at core interface but generally do not enter the core itself.	(Agustín-Panadero *et al.*, 2014)

2.2 Zirconia in dentistry

In the past recent years, the use of ZrO_2 based ceramics as a biomaterial for implants and dental crowns in dentistry has risen significantly, due to the superior mechanical properties of ZrO_2, such as its high mechanical strength, biocompatibility, as well as its very high wear resistance and friction. It has also been widely used in dental restoration applications since 1998 due to its high strength for load bearing as dental crowns, fixed partial dentures (FPDs) and dental implants (Tinschert *et al.*, 2000; Guazzato *et al.,* 2004; Guazzato *et al.,* 2005). Zirconia implants were introduced as an alternative to other implant materials because of its outstanding characteristics such as high flexural strength (900 to 1,200 MPa) and Vickers hardness (1,200 Mpa). It is considered as biocompatible toward body implantation and exhibit minimal ion release compared with metallic implants.

2.3 Zirconia dental implant fixtures

A meta-review of clinical performance of zirconia implants by Afrashtehfar and Fabbro in 2020 stated that zirconia implant clinical outcomes were found to be similar or inferior to those for titanium implants. However, in spite of short-term promising results of zirconia implants, evidence with long term is lacking (Afrashtehfar *et al*., 2020). Another systematic review study suggested that the survival rate of titanium implants that support single crowns is ~97.2 and 95.2% over a period of 5 and 10 years, respectively which are relatively ideal for the clinical application of an implant material (Jung *et al.,* 2012). Qu and Liu stated that the outcomes of preclinical studies and clinical trials of zirconia as dental implants are sometimes controversial when compared with titanium, due to the lack of long-term follow-ups. Therefore, clinical trials are still needed to study the long-term performance of zirconia dental implants Qu and Liu, 2021).

2.4 Dental zirconia superstructures

A comprehensive review revealed that zirconia crowns are a promising valid alternative to metal crowns and show good clinical performance based on observation and *in vivo* investigations (Soleimani *et al.,* 2020). Another systematic review carried out by Svanborg revealed that the fit of zirconia single crowns and bridges may be regarded as clinically acceptable with the accuracy of~60 μm for marginal, internal, and total gap Svanborg, 2020). Alzanbaqi *et al.,* reported that zirconia crowns for primary teeth gave better gingival and periodontal health with good retention, high fracture resistance, color stability, high parental acceptance, good marginal adaptation, smooth cosmetic surface, and no recurrent caries. The author concluded that zirconia crowns are promising alternative to other restorative materials and crowns for paediatric patients with higher properties and performance in different clinical aspects (Alzanbaqi *et al.,* 2022).

2.5 Synthesis method used to obtain ZrO_2 stabilized ceramic oxides

Zirconia has unique characteristics unlike other ceramics, which the cracks formed under load are constricted and stopped and do not progress as transformation toughening of zirconia provide excellent strengths (Špehar and Jakovac, 2015). Hence, ZrO_2 takes a remarkable place amongst the various oxide ceramics due to its excellent mechanical as well as biocompatible properties suitable for dental applications.

There are various processing routes and synthesis methods used to obtain ZrO_2 stabilized ceramic oxides. Table 2.2 shows the summary of the processing route and synthesis method used to obtain ZrO_2 stabilized ceramic oxides.

Table 2.2 Synthesis method used to obtain ZrO_2 stabilized ceramic oxides.

Processing route	**Synthesis method**	**References**
Thermal decomposition	Heating (evaporation) Spray drying Vapor phase (CVD) Freeze drying Calcination	(Feng *et al.,* 2020; Lakusta *et al.,* 2016; Tholey *et al.,* 2011)
Precipitation of hydrolysis	Neutralization and precipitation Homogeneous precipitation Coprecipitation Salts solution Sol-gel	(Hajizadeh-Oghaz *et al.,* 2015; Huang *et al.,* 2019)
Hydrothermal	Precipitation (Co-precipitation) Crystallization Decomposition Oxidation Synthesis Electrochemical Mechanochemical	(Chaikina *et al.,* 2014)

2.6 Phase transformations of Zirconia

ZrO_2 is known as an oxide in a chemical term, and it is usually used as a ceramic material. It also shows its characteristic as non-water soluble but can be soluble in a strong acid such as sulfuric acid (H_2SO_4) and weak acid such as hydrofluoric acid (Hf). Hence, it can undergo phenomenon of allotropy behaviour, which provides similar chemical composition, but different atomic arrangement based on temperature heated on it. Zirconia can be classified into three crystallographic phases, which is the cubic phase (C) in the form of straight prism with square side, the tetragonal phase (T) with rectangular sides and the monoclinic phase (M) in the form of a deformed prism with parallel piped sides (Abd El-Ghany *et al.*, 2016). The cubic phase is stable above 2370 ^{o}C and with moderate mechanical properties. The tetragonal phase is stable between 1170 ^{o}C and 2370 ^{o}C with improved mechanical properties, and the monoclinic phase, which is stable at room temperature up to 1170 ^{o}C, with lower mechanical properties and may contribute to a reduction of the ceramic particles' cohesion.

Therefore, as temperature changes during cubic to tetragonal (c → t) transformation and from tetragonal to monoclinic (t → m) transformation, leading to diffusion less transformation. This transformation occurs when there is movement of homogenous motion of atoms that can cause a change in a crystal structure. In these cases, the volume of zirconia can expand during (t → m) transformation. It also can cause the thermal effect which leads to severe crack leading to catastrophic failure upon cooling. In order to prevent catastrophic failure of pure zirconia, the alloying method used as stated by Lughi *et al.* (2010). The following crystallographic structures is shown in Figure 2.1.

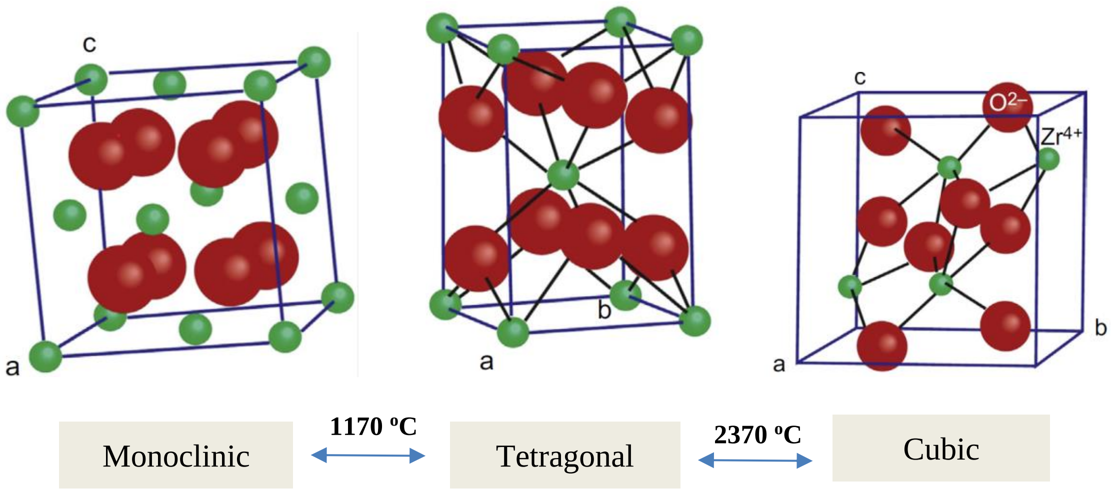

Figure 2.1 Crystallographic structures of ZrO_2 (Sergo *et al*., 2010) .

Additionally, in principle, any composition which is sintered in the cubic phase and retains a wholly cubic crystal structure on cooling is considered to be fully stabilized. The continued possession of the tetragonal phase at room temperature will also be feasible, provided that the tetragonal to monoclinic phase transformation is inhibited. This can be achieved by a combination of fine powders, matrix constraints and stabilizing additions of dopants. The amount of alloying oxide required to produce this respective stabilization is determined from the relevant phase diagram, which can be seen in Figure 2.2 for the zirconia–yttria system.

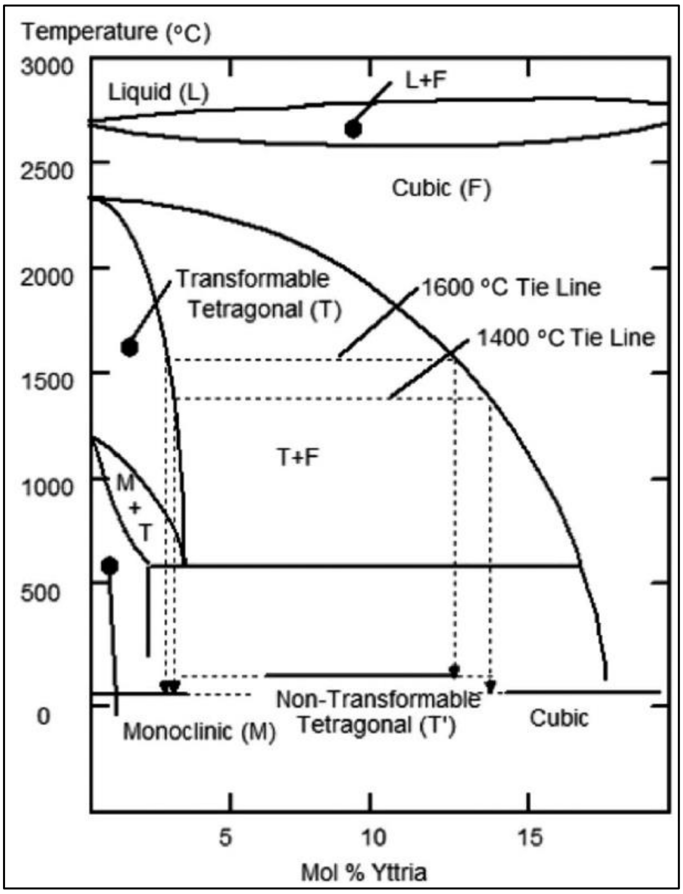

Figure 2.2 Phase equilibrium diagram for the zirconia yttria system and showing the phase transformation with variation temperature vs. mol% of Y_2O_3 (Gautam *et al.*, 2016)

2.7 Stabilizing oxides of pure zirconia

Pure zirconia can be alloyed with stabilizing oxides such as calcium oxide (CaO), magnesium oxide (MgO), alumina oxide (Al_2O_3) and yttria oxide (Y_2O_3) and others (Lughi *et al*., 2010). This process is known as transformation toughening (Garvie and Nicholson, 1972). It was discovered that such strong ceramic could result from alloying of pure zirconia with lower valance oxides, such as MgO, Al_2O_3, CaO and Y_2O_3, and this decreased the amount of strained m phase at room temperature and favoured more symmetric c and t lattice structures. These c and t phases are analogous to those in pure zirconia but have dopant ions substituted on Zr^{4+} sites and have a fraction of oxygen sites vacant to retain charge neutrality (Chevalier *et al.*, 2004).

Hence, fracture toughness can also be enhanced with the addition of the stabilizing oxides. Various studies have used CaO, MgO, Al_2O_3, CeO_2 and Y_2O_3 as a stabilizer for biomaterial applications, however $ZrO_2 – Y_2O_3$ bioceramic has reached the ISO standard for medical application and are now well established.In early stages of the development, several oxides material such as calcium oxide (CaO), magnesium oxide (MgO), alumina oxide (Al_2O_3) and yttria oxide (Y_2O_3) were investigated for biomedical application, however in recent stages of research appeared to be more focused on zirconia-yttria ceramics (Piconi *et al.*, 1999). By adding stabilizing oxides, the volume expansion can be controlled and zirconia can be partially stabilized in the tetragonal phase at room temperature (Kohal *et al.*, 2004).

2.8 Yttrium-oxide tetragonal zirconia poly-crystals (Y-TZP)

The use of the toughened oxide ceramics such as yttrium-oxide tetragonal zirconia poly-crystals (Y-TZP) has widened the indication of ceramic materials, enable the uses for fixed prosthodontic treatment which high stress rate are expected whose minimal requirements as implants for surgery are now described by the Ceramic Specification Standard, ISO 13356. Besides, Y-TZP appeared to be give more advantages as it has higher fracture toughness and flexural strength for dental implants and has also been successfully used in orthopaedic surgery to manufacture ball heads for total hip replacements (Özkurt et al., 2011). Additionally, the development of computer-aided design/computer aided manufacturing (CAD/CAM) systems has been introduced into restorative dentistry for crown and bridges frames. This technique has gained importance in fabricating crowns and fixed partial dentures (FDPs) using the Y-TZP through milling technique by CAD/CAM systems (Luthardt *et al.,* 2004). The mechanical properties of Y-TZP bioceramic shows as Table 2.3.

Table 2.3 The mechanical properties of Y-TZP bioceramic (Vitti *et al.,* 2019).

Properties	**Mean values**
Compressive strength	4900 Mpa
Flexural strength	900-1600 Mpa
Vickers hardness	1200 kgf/mm^2
Tensile strength	413 Mpa
Density	6.05 g/cm^3
Porosity	<0.05%
Shear strength	70 Gpa

Y-TZP bioceramics gives a stable zirconia stabilized ceramic oxides to form at yttria-rich triple junctions and grain boundaries at temperatures between 1300 °C and 1500° C, with smooth surface under morphological study observation to be used in medical and clinical applications (Kelly *et al*., 2008). This is due to the fact that in areas of crack propagation in yttrium-stabilized tetragonal zirconia or partially stabilized Y-TZP, there is a local transformation from the tetragonal to monoclinic phases because of the internal stresses. However, addition of minor amount % mol of ceramic oxides lessen the crack propagation. Transformation occurs because there is movement of atoms that can cause a change in crystal structure, which can lead to crack propagation. Hence, to prevent catastrophic failure, the method of alloying zirconia with stabilizing oxides were used by producing multiphase ceramic material known as partially stabilized zirconia (PSZ). This mechanism can give the stabilized materials such as Y-TZP to be used in world of technologies and in medical applications due to the ionic charge of Y_2O_3 in the ZrO_2 lattice provide balance charge caused by the stabilization effect of oxygen vacancies mechanism (Lughi *et al*., 2010) (Vonk *et al.*, 2013) as shown in Figure 2.3.

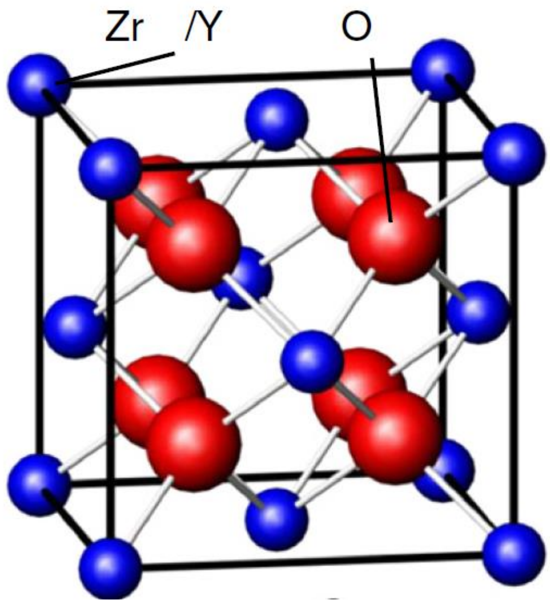

Figure 2.3 Atomic crystal structure of yttrium-oxide stabilized zirconia (Vonk *et al.*, 2013)

2.9 Computer-aided design/computer aided manufacturing (CAD/CAM) system

New development of computer-aided design/computer aided manufacturing (CAD/CAM) system has gained interest in fabrication for all-ceramic restorations especially in dental crowns. Their popularity is due to its benefits in terms of time saving, materials saving, standardisation of the material process and predictability of the restorations. Moreover, the data and information for the material restorations can be saved and represents non-destructive methods (Brenes, 2017). There are few types of CAD/CAM methods CAM that contribute for dental restorations such as glass ceramics, alumina based ceramics, lithium disilicate and zirconia-based ceramics, which also widely used as an elements in fabricating CEREC Sirona Dental blocks (Y-TZP) (Luthardt *et al.*, 2004).

All ceramics is designed by CAD/CAM system using scanner, design computer and a milling machine or 3-D printer. In one of the systems, restorations designing is done by dentists using CEREC InLab CAD software (Sirona Dental). With this software, the dental technician is able to scan their own models using Sirona in Eos X5 (Sirona Dental) scanner and design the restoration, once this process is completed, the file can be sent to a remote milling machine or a milling centre for fabrication in a wide range of materials as shows in Figure 2.4. There is also chairside CAD/CAM system system, whereby the dentist design the restoration and it is then milled using chairside milling machine. This system helps reduce the appointment time.

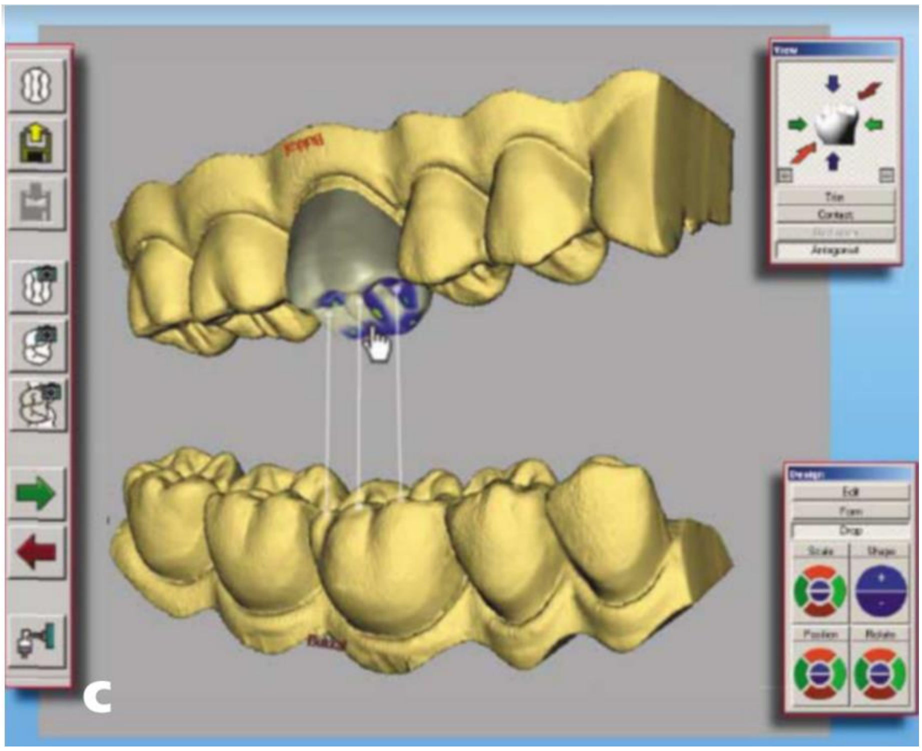

Figure 2.4 CEREC 3 software (Sirona Dental Systems GmbH, Bensheim, Germany) (Mörmann, 2006).

The interest in fabricating restorations using milling systems continuous to grow worldwide. The evolution of CEREC system which was implemented since 1983 which started with CEREC 1 unit (Sirona Dental Systems GmbH, Bensheim, Germany). A CEREC team at Seimens (Munich, Germany), equipped the CEREC 2 with an additional cylinder diamond enabling the form-grinding of partial and full crowns. CEREC 3 skipped the wheel and introduced the two-bur-system The “step bur,” which was introduced in 2006, reduced the diameter of the top one-third of the cylindrical bur to a small diameter tip enabling high precision form-grinding with reasonable bur life. The evolution of CEREC Sirona grinding systems shows as Figure 2.5 (Mörmann, 2006).

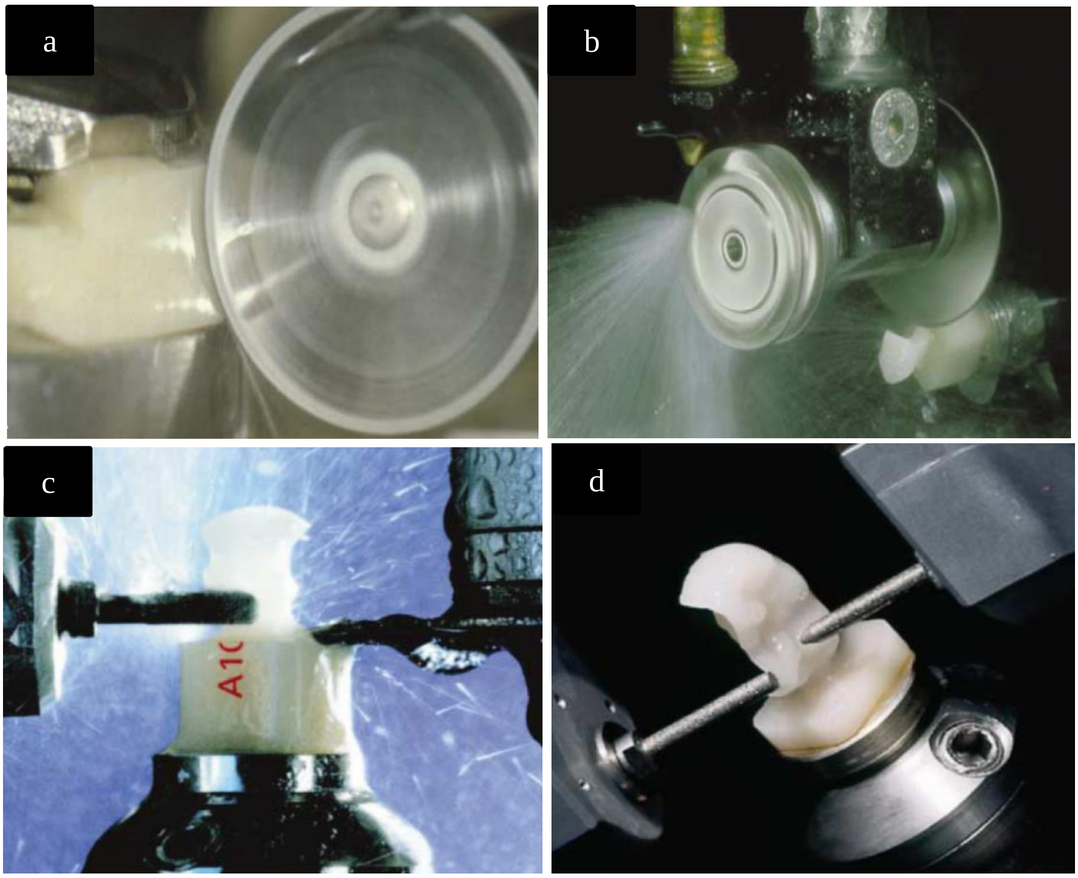

Figure 2.5 CEREC (Sirona Dental Systems GmbH, Bensheim, Germany) form-grinding evolution: feldspathic block ceramic. a) Basic grinding trial with diamond coated wheel. b) CEREC 1: water turbine drive. c) CEREC 2: cylindrical diamond bur and wheel. d) CEREC 3: cylindrical diamond and tapered burs.

2.10 Types of dental ceramic materials used with CAD/CAM system

The used of advanced dental ceramics and ceramic prosthesis in restorative dentistry has become popular and many of these restorations can be fabricated by both traditional laboratory methods and CAD/CAM machination system *(Li et al., 2014; Miyazaki et al.,* 2013; Takaba *et al.,* 2013). The traditional methods of ceramic fabrication have been described to be time-consuming, technique sensitive and unpredictable due to the many variables and CAD/CAM may be a good alternative for both the dentists and laboratories, since CAD/CAM system has advantages in produce a restoration in a short time, led to minimizes human mistake or laboratory fabrication process to produce restoration (Miyazaki *et al.,* 2013).

Table 2.4 shows the summary of several types of dental ceramic materials used in the market for CAD/CAM machination system. The first CAD/CAM produced inlay was fabricated in 1985 using a ceramic block comprising fine grain feldspathic ceramic VitaTM Mark I (Li *et al.,* 2014). The block was fully sintered for hard machining and was used for the clinical performance of these CAD/CAM for inlays and onlays with success rate of 90.4% was achieved. Therefore, the successful fabrication of Vita Mark I, VitaTM Mark II was introduced specifically for CEREC (CerecTM 1-Siemens GmbH, Bensheim, Germany) in 1991, exhibited better mechanical properties with a reported flexural strength from about 100 MPa to 160 MPa when glazed and are made of materials similar to the conventional feldspathic ceramic (Li *et al.,* 2014). CerecTM Blocs (Sirona Dental Systems, Bensheim, Germany) are similar in structure to VitaTM Mark II but use a different shading system. They are also available in aesthetically pleasing multi-shade blocks (Giordano *et al.,* 2006).

However, an ideal choice for higher aesthetic such as In-Cream Spinell was fabricated for the clinical performance of the anterior crowns with a flexural strength of 350 Mpa (Vichi *et al.,* 2013). Additionally, In-cream alumina has highest flexural strength of more than 1000 Mpa, thus it is suitable for anterior crowns and three units' anterior bridges (Pittayachawan *et al.,* 2009). Nevertheless, all materials mentioned are not strong enough to sustain an occlusal load Therefore, alumina and zirconia were chosen for posterior restoration due to their strengths of 750 MPa and 1000 MPa, respectively (Qu and Liu, 2021). In high-stress areas, especially for posterior crowns and multiple-unit posterior, In-Ceram zirconia or Yttrium-reinforced zirconia may be used (Pittayachawan *et al.,* 2009). Fully sintered alumina or zirconia were difficult to mill, and basically milling occurs at pre-sintered stage (Pittayachawan *et al.*, 2009; Qu and Liu, 2021).

Table 2.4 Summary of types of dental ceramic materials used for CAD/CAM system (Miyazaki *et al.,* 2013).

Dental ceramic materials	**Clinical performance**	**Flexural strength (Mpa)**
Vita Mark II (feldspathic)	Inlays, onlays, veneers, anterior crowns	100-160
In-Ceram Spinell	Crowns and anterior	350
In-Ceram Alumina (Aluminium oxide)	Crown and bridge	500
ProCAD	Inlays, onlays, veneers	150
In-Ceram zirconia (Zirconium oxide)	Crown and bridge	750
Partially sintered zirconia (Zirconium oxide)	Crown and bridge	800-1300
Fully sintered zirconia (Zirconium oxide)	Crown and bridge	> 1000

2.11 CEREC Sirona Dental Block

The emergence of CEREC milling system with a pre-sintered zirconium oxide block partially stabilized with yttrium oxide (Y-TZP) has used toughening mechanism. CEREC Zirconia dental block, which is also known as dental ceramic Y-TZP has been widely used in the market (Figure 2.6). The tetragonal crystalline particles of CEREC