

Classification and research progress of CAD/CAM ceramic materials

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ABSTRACT: Currently, the most commonly used dental CAD/CAM restorative systems are ceramic materials, which can be divided into resin-ceramic composites, polycrystalline ceramics and glass ceramics according to the differences in composition. Different types of ceramics have major differences in mechanics and aesthetics and need to be selected according to clinical needs and patient demands. Each material has its own advantages and disadvantages, for example, glass ceramics are highly transparent but brittle, polycrystalline ceramics are strong but less transparent, and resin-ceramic composites combine the advantages of glass ceramics and resin materials but are less strong. In this paper, we systematically review the compositional classification, the characteristics of each type of ceramic, and recent research advances to help guide clinical selection of CAD/CAM materials.

KEYWORDS: CAD/CAM; Glass ceramics; Polycrystalline ceramics; Resin-ceramic composites

With the development of technology in recent years, computer aided design and computer aided manufacture (CAD/CAM) restoration systems have become popular. Compared to traditional restoration methods, this system is more time efficient, especially for high-strength ceramics, and can save up to 90% of the time^[1]. In addition, CAD/CAM systems cut the whole piece, resulting in a more homogeneous material and fewer fractures. Current CAD/CAM systems can produce inlays, high inlays, veneers, full crowns, three-unit bridges, and implant abutments for a wide range of applications^[2]. At the same time, the development of CAD/CAM machinable ceramic materials is changing rapidly, each with its own advantages and disadvantages, taking into account both mechanical and aesthetic needs. At this stage, CAD/CAM ceramic materials on the market are complicated, the classification is not

yet uniform, and ceramics of different materials show different characteristics. Depending on the presence or absence of glass phase and resin matrix, CAD/CAM ceramic materials can be classified into resin-ceramic composites (resinmatrix ceramics), polycrystalline ceramics, and glass-matrix ceramics^[3]. In this paper, we introduce the classification of CAD/CAM ceramic materials according to their composition and their respective properties, and review the research progress in this field.

1 Resin-ceramic composite

Although glass-ceramics have been dominant in CAD/CAM machinable materials, its brittleness and large difference in elastic modulus with dental tissue may lead to fracture of abutment teeth; composite resin has good ductility but insufficient strength, so in recent years, some scholars have combined these two materials to complement each other's strengths and form the resin-ceramic composite materials which are now widely used,

also known as hybrid ceramic^[4]. hybrid ceramic^[4]. According to the microstructural composition of ceramics and resins, they are usually classified into resin-based nanoceramic and resin infiltrated ceramic network (PICN). Compared to glass ceramics, resin-ceramic composites are less costly, more fatigue resistant, have higher flexural strength, less fracture generation during cyclic loading, and they are softer than glass ceramics, reducing drill pin wear during processing^[5]. In addition, resin-ceramic composites are easier to repair in the mouth if breakage occurs, and the repair visually differs little from the original^[6].

1.1 Resin permeable ceramics

PICN is a type of two-phase permeable composite (IPC). IPC is a composite formed by infiltration of one liquid-phase material into another porous solid matrix, and usually IPC is more resistant to damage than its original material^[7]. Similarly, PICN has a ceramic mesh framework and the resin polymer infiltrates into the porous structure of the ceramic when in the liquid phase^[8]. However, the shrinkage of the resin polymer exerts pressure on the ceramic mesh framework and cracks tend to develop between the two, thus affecting the transparency of the material^[9]. To address this problem, Sadoun^[10] used high temperature and high pressure conditions to influence the polymerization of the resin with good results, and he found that high temperature accelerates the molecular movement of the resin and reduces the pressure on the ceramic support, while high pressure compensates for the volume of resin shrinkage so that the gap between the resin and the ceramic support can be minimized.

PICN is represented by Vita Enamic from Vita Zahnfabrik, which contains 86wt% of feldspathic inorganic phase and 14wt% of di-methacrylate organic phase. While conventional composites have a more homogeneous resin matrix, Enamic's resin matrix and ceramic framework form a double mesh structure that is cross-linked to each other, compensating for the shortcomings of the brittle and bendable ceramic and the soft and weak resin, combining elastic ductility and

strength^[11]. The hardness of this material is lower than that of glass-ceramics, which is closer to the dental tissue and therefore causes relatively less wear on the opposing jaw teeth during long-term human chewing^[12]. Moreover, its elastic modulus is close to that of dentin, so that load loading at the dentin-porcelain interface is less likely to produce fissures^[13]. It also has a modulus of elasticity close to that of bonding resin, which facilitates the dispersion of masticatory pressure.

A new direction in the research of PICN materials is the functionally graded polymer infiltrated ceramic network (FG-PICN). The mechanical properties such as modulus of elasticity and hardness of each point of human enamel and dentin are actually different and vary continuously, while most restorative materials on the market are cut in one piece and the modulus of elasticity of each point is uniform, which will cause stress concentration at the junction of porcelain and tooth and lead to fracture. In contrast, FG-PICN has a different elastic modulus per layer with a gradual change, which can adapt to the change in the elastic modulus of the dental tissue^[14]. This material is expected to be put into practical production in the future.

1.2 Resin-based nano

Ceramics differ from PICN in that the resin matrix of resin-based nanoceramics is homogeneously distributed and nanoceramic fillers are dispersed in it, with different types and diameters of fillers exhibiting different mechanical properties^[8]. A common brand is Lava ultimate produced by 3M, which consists of a resin matrix and 80% of nanoceramic particles. The nanoceramic fillers include silica with a diameter of 20 nm, zirconia with a diameter of 4 ~ 11 nm and zirconia-silica nanoclusters^[15]. The resin matrix is urethane dimethacrylate (UDMA), which replaces Bisphenol A Dyligidil Metacrilate (Bis-GMA) commonly used in conventional resin composites, the former contains more double bonds, is more prone to cross-linking reactions, and has a higher degree of light-curing polymerization, but shrinkage after polymerization will be stronger than the latter^[4].

The hardness of Lava ultimate is lower than that of Vita Enamic, which may be related to the microstructure of resin-based nanoceramics, so some scholars have tried to add a new material sea urchin-like hydroxyapatite (urchin-like hydroxyapatite) to composite resins containing silica particles, which can significantly improve the microhardness and strength of the material^[16].

Another resin-based nanoceramic is Cerasmart composite ceramics produced by GC, Japan, whose resin matrix contains 71% inorganic fillers of 20 nm diameter silica and 300 nm diameter barium glass, respectively. The flexural strength and elastic modulus of Cerasmart are comparable to those of Lava ultimate, but the microhardness is lower than the latter^[15]. The smaller the diameter of the nanofiller, the more the mechanical strength and flexural resistance of the porcelain block will be improved^[17]. The diameter of the filler of Cerasmart is significantly larger than that of Lava ultimate, and Cerasmart contains a glass component in the amorphous phase, resulting in a lower hardness than Lava ultimate^[18].

The adhesion of Cerasmart to dentin is stronger than that of Lava ultimate, probably because Cerasmart containing glass filler is more prone to roughness during mechanical polishing and more likely to form resin protrusions with resin bonding agents^[19].

1.3 Biocompatibility of resin-ceramic composites

Compared to glass-ceramics, resin-based porcelain blocks have smoother edges after cutting and lower flexural modulus and higher resilience modulus, which compensate for the brittle nature of ceramic materials^[20]. However, the biocompatibility of resin-ceramic composites has been questioned because the monomers released may be harmful to humans^[21]. The more common monomers are low molecular weight bisphenol-A (bisphenol A), hydroxyethyl methacrylate (HEMA), and triethylene glycol dimethacrylate (TEGDMA), which can cause pulp cell damage, dentin-forming cell dysfunction, and other undesirable problems^[4]. Currently, it has been found that the re-

lease of resin monomer becomes lower with high temperature and high pressure curing instead of conventional light and heat curing^[22]. Also in recent years the resin matrix of resin-ceramic composites has gradually evolved from Bis-GMA to UDMA, which is less irritating to the tissue and has less monomer release^[4]. Resin-based ceramics are commonly used for less stressed restorations such as partial crowns, inlays, high inlays and single crowns for anterior and posterior teeth.

2 Polycrystalline ceramics

Polycrystalline ceramics is a non-metallic inorganic ceramic material that differs from glass ceramics in that it does not contain any glass phase matrix and all crystals are regularly and closely arranged, this structure reduces the possibility of crack expansion and determines its strength and hardness to be higher than glass ceramics and less susceptible to destruction^[3]. However, the absence of the glass phase causes polycrystalline ceramics to be less susceptible to acid etching by hydrofluoric acid, which requires longer time and higher temperature, and their transparency is somewhat weaker than that of glass ceramics^[23]. The main polycrystalline ceramics available on the market are mostly zirconium dioxide matrix.

Zirconia is known for its high hardness and strength, and can withstand the highest fracture loads^[24]. It has better bending strength and fracture toughness than other ceramics, low modulus of elasticity and thermal conductivity, less susceptibility to bacterial plaque adhesion, and high biocompatibility^[25]. One reason for the higher toughness stems from its phase change toughening phenomenon. Due to mechanical stimulation, zirconium dioxide can transform from a sub-stable tetragonal phase to a monoclinic phase, which is accompanied by a volume expansion of 3% ~ 5%, with compressive stresses at the crack tip and an increase in fracture work, preventing further crack propagation^[26]. However, if the mechanical stimulus is too large, the phase transition scale is also too large and the phase toughening is unable to stop the crack expansion, this principle is applied

to the surface treatment of zirconium dioxide. yttria-stabilized tetragonal polycrystalline zirconia (3Y-TZP) is used in CAD/CAM, because the surface is not easily acid etched due to the lack of glass phase and the silane coupling agent treatment is also less effective^[27]. The surface was modified by sandblasting to produce a surface compression layer by mechanical stimulation from the tetragonal phase to the monoclinic phase^[28]. However, if the intensity of sandblasting is too high to reach the strength limit of the repaired material, it will cause surface defects in 3Y-TZP, so the size of sandblasting particles and the pressure of sandblasting need to be controlled.

The excellent properties of zirconia ceramics are gradually being recognized, but they are less transparent and take too long to crystallize compared to glass ceramics^[29]. In order to meet the demands of time, cost, and ceramic transparency for chair-side CAD/CAM, a rapid sintering approach has been proposed^[30]. This method with fast heating, fast cooling, and short sintering time produces dense, very fine Y-TZP particles that can reach below 100 nm, allowing direct light passage with little scattering. However, the surface of the ceramic sintered in this way is not as flat as that of the ceramic sintered by conventional methods. The representative brand is CEREC Zirconia from Germany. Another method is to dope the optically homogeneous cubic phase zirconium dioxide into the tetragonal phase zirconium dioxide, which requires an increase in the yttrium content, i.e., a change from the commonly used 3 mol% 3Y-TZP to 4 mol% 4Y-PSZ or 5 mol% 5Y-PSZ^[31]. However, the presence of the cubic phase reduces the phase change toughening phenomenon, which leads to the reduction of the strength and toughness of the material. To address this problem, the latest research direction is to infiltrate the surface of 5Y-PSZ with feldspathic glass-ceramics, which not only improves the transparency of the ceramics, but also increases the flexural strength, facilitates acid etching thus facilitating the bonding of resin adhesives^[32]. Clinically zirconia-based ceramics are mostly used in multi-unit bridges and single crowns of posterior teeth because of the

high forces exerted by the restorative material and zirconia is recognized as a high-strength ceramic. Although the main drawback of polycrystalline ceramics is poor transparency, at this stage more and more manufacturers are developing highly translucent and ultra-translucent zirconia materials that gradually meet the aesthetic requirements of patients.

3 Glass-ceramics

Glass-ceramics, also known as microcrystalline glass, is structurally a mixture of glass and crystalline phases and was the first and most used material in CAD/CAM chairside restorative systems. The greatest advantage of the presence of the glass phase is that it can be acid etched by hydrofluoric acid, which facilitates the bonding to the dental tissue; and the glass matrix defines the aesthetic properties of the ceramic, the higher the vitrification rate, the higher the translucency^[8]. However, the more glassy the phase, the less mechanical strength of the material and the more susceptible to fatigue^[33]. Therefore, the use of materials such as white garnet, lithium silicate, and zirconium dioxide to strengthen glass-ceramics can achieve more desirable results. According to the materials, CAD/CAM glass-ceramics can be divided into feldspathic ceramics, leucogranite-reinforced glass-ceramics, lithium silicate reinforced glass-ceramics, and zirconium dioxide reinforced lithium silicate glass-ceramics.

3.1 Feldspathic ceramics

Feldspar is mainly based on silica and alumina and is highly biocompatible^[8]. The first generation of feldspathic ceramics was Vita Mark I, produced by Vita Zahnfabrik and the first CAD/CAM dental ceramic restorative material in the world^[1]. A follow-up showed that the 17-year restorative success rate of Vita Mark I was 88.7% with more satisfactory results^[34]. The second generation of feldspathic ceramics, Vita Mark II, has improved production techniques and improved the mechanical properties of the product, with flexural strengths up to 100 MPa and, when glazed,

up to 160 MPa, but still far below IPS Emax, Vita Suprinity, and other reinforced glass ceramics. Vita Mark II has the lowest fracture strength when the restoration thickness is also 1 mm^[35]. In recent years, it is common to add other reinforcing materials to feldspathic ceramics to improve the mechanical properties. The follow-up showed that Vita Mark II had a 97% retention rate at 5 years and 90% at 10 years, which is an ideal level^[36]. Sirona's Cerec Blocs are also feldspathic ceramics, similar in structure and performance to the Vita Mark II, but with a completely different shade system.

3.2 White garnet reinforced glass-ceramics

White garnet-reinforced ceramics are represented by IPS Empress CAD from Ivoclar Vivadent and Paradigm C from 3M ESPE, containing 45% and 30% fine-grained white garnet, respectively, which can better resist mechanical damage^[1]. The advantages of adding white garnet are its similar refractive index to the feldspar matrix, which ensures the translucency of the ceramic, and the fact that white garnet etches faster than the glass matrix, creating more "micro-pits" during the etching process, which facilitates the entry of the resin bonding agent and results in better adhesion^[37]. The flexural strength and fracture toughness of Empress CAD are strong enough to resist strong occlusal forces in the oral cavity and are less abrasive than zirconia ceramics on the contralateral teeth.

3.3 Lithium silicate reinforced and zirconium dioxide strengthened lithium silicate glass-ceramics

Compared to leucogranite-reinforced ceramics, lithium silicate reinforced ceramics have more crystalline phases, a reduction up to 30% on the volume of the glass matrix, and a reduction in crystal size and increased interlocking, resulting in higher strength^[38]. This material is represented by IPS e. max CAD, also known as blue porcelain, because it is blue before crystallization and requires further sintering and crystallization after mechanical cutting, followed by changes in the

microstructure of the product, with an increase in hardness and a color change to the corresponding glaze shade. This type of processing is called soft processing and is more economical in terms of cutting turning needles. e.max CAD has significantly higher flexural strength and fracture toughness than Empress CAD, and has a longer service life and higher performance in all aspects. It was found that the use of Empress gradually decreased after 2010 while e.max increased year by year^[33]. e.max CAD restorations have a 4-year success rate of 96.3%, which is comparable to that of conventional lithium silicate ceramic hot die cast full crowns^[39].

In recent years, polycrystalline ceramic zirconium dioxide has been added to lithium silicate glass-ceramics, and the resulting material has been found to have stronger aesthetic and mechanical properties than conventional lithium silicate ceramics. In this material, zirconium dioxide may affect the crystallization process of lithium silicate, resulting in a crystal size of 0.5~1 μm , which is six times smaller than the normal lithium silicate glass-ceramic grains (2~3 μm)^[40]. The presence of zirconium dioxide and the finer grain size of lithium silicate directly determine the high flexural strength and the superior transparency of this material^[34]. In addition, the glass matrix of zirconia-reinforced lithium silicate glass-ceramics still retains a certain percentage and remains favorable for machine cutting^[40]. The zirconia-reinforced lithium silicate glass-ceramics currently available on the market are Suprinity and Celtra Duo from Germany. Suprinity, also known as amber porcelain, is in a pre-sintered state with a transparent amber color and needs to be sintered in a furnace after grinding, while Celtra Duo is a fully sintered product without secondary sintering. Zirconium dioxide. One of the disadvantages of lithium silicate based glass-ceramics is that the surface is more likely to be rough after mechanical processing, and simple polishing can not reduce the roughness, but after glazing the surface is obviously smooth. Therefore it is a soft processed porcelain block and glazing is a necessary step after machine cutting^[41].

4 Summary and Outlook

The greatest advantage of classifying CAD/CAM machinable ceramics according to the composition of the material is that the composition of the material determines its properties, and usually ceramics of the same type have similar properties, allowing a more convenient selection according to clinical needs^[3]. Each material has its own advantages and disadvantages, and at this stage there is no material that can fully achieve the ideal level of mechanics and aesthetics, so the choice of porcelain block needs to be combined with the actual situation. For the high aesthetic requirements of the anterior teeth, you can choose glass ceramic or resin-ceramic composite, for the chewing force of the posterior teeth, you can choose polycrystalline ceramic or glass ceramic in the strength and hardness of the material. At the same time, traditional materials should not be completely discarded, and the advantages of the original materials should be combined while developing new materials to make up for the shortcomings.

The development of CAD/CAM ceramic materials is changing rapidly, and in the future it is expected to combine the advantages of various materials to develop more durable composite materials. The resin-ceramic composites that have been widely used have improved the weakness of traditional ceramics that are brittle, but the hardness and strength are still not high enough. At this stage, scholars are trying to bury reinforcing particles such as hydroxyapatite and polycrystalline ceramics into the resin matrix, and have made relatively good progress, which is expected to be put into practical production in the future. Another direction is to permeate glass-ceramics on the surface of polycrystalline ceramics^[32] to improve their transparency, which may also become the leading CAD/CAM ceramic material in the future.

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