

Ceramic materials in dentistry: historical evolution and current practice

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ABSTRACT

Dental ceramics are presented within a simplifying framework allowing for facile understanding of their development, composition and indications. Engineering assessments of clinical function are dealt with and literature is reviewed on the clinical behaviour of all-ceramic systems. Practical aspects are presented regarding the choice and use of dental ceramics to maximize aesthetics and durability, emphasizing what we know and how we know it.

Keywords: Ceramics, particle-filled glasses, polycrystalline ceramics, CAD/CAM, all-ceramic restorations.

Abbreviation: LTD = low temperature degradation.

CERAMICS IN DENTISTRY – WHERE DID THIS STUFF COME FROM?

It is quite useful reviewing how and why ceramics came to be used in dentistry. This account serves three purposes: (1) to alert practitioners to the fact that the use of ceramics, since the very beginning, always represented the adoption of ‘high technology’ versus ‘craft art’; (2) to reinforce the concept that ceramics and improved ceramics were introduced in order to solve specific problems or to increase restorative versatility; and (3) to provide a gentle background into the nature and science of ceramics. Astute readers are also provided with clues as to where to watch for the emergence of new ceramic technologies.

Since a distinction was drawn between ‘high technology’ and ‘craft art’ it is useful to provide some basic defining characteristics of each. Many would agree that ‘high technology’ should include: (1) dentistry borrowing materials/processes shortly after their being developed by an unrelated industry; (2) incorporation of new learning from recent scientific literature outside of dental medicine; and (3) the spread of outright new inventions within dentistry. ‘Craft art’, on the other hand, brings to mind materials and techniques borrowed from those involved in jewellery making, the arts and the manufacture of everyday goods. All audiences the senior author has spoken to before have chosen

‘craft art’ as the likely source of ceramics introduced into dentistry at any stage of development.

In the early 1700s many European rulers were spending enormous sums importing porcelain from China and Japan. Figure 1, from Schloss Charlottenburg in Berlin, is representative of just small portions of one of these collections. The collection of Augustus III of Saxony was perhaps the largest and is now on display at the Zwinger Museum in Dresden, his former palace. Such activity led China to be characterized as being ‘the bleeding bowl of Europe’. Between 1604 and 1657 alone, over three million pieces of Chinese porcelain reached Europe.¹ In 1700, ‘East Indiamen’ ships unloaded 146 748 pieces in a European port in just one day as the market for porcelain grew insatiable.¹

One response to this situation involved state sponsored research into ‘porcelain discovery’. Notable European leaders including Augustus (III) the Strong, King of Poland and Elector of Saxony along with the Medici family of Florence, Italy were independently sponsoring research into the development of a European porcelain to match the hard, translucent and sonorous material developed in eastern Asia nearly 1100 years earlier. Europeans strived at ‘porcelain discovery’ without much success for about 200 years and this activity is credited with being largely responsible for the growth of modern analytical chemistry



Fig 1. Schloss Charlottenburg in Berlin is representative of just small portions of one of the extensive porcelain collections popular with European royalty.

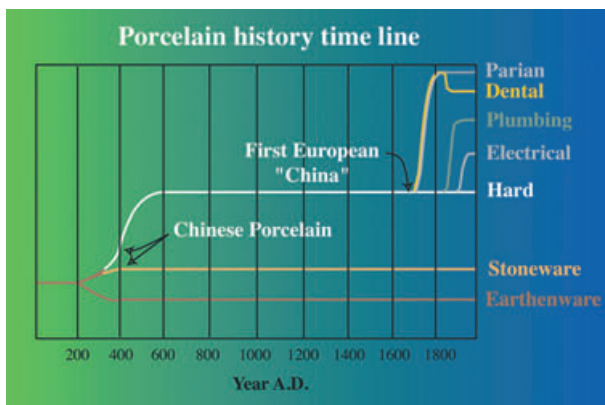


Fig 2. Timeline of porcelain development from ancient China to modern formulations.

from its roots in alchemy. An historical timeline of porcelain discovery appears as Fig 2.

During the late 1600s and early 1700s the first examples of state sponsored research were being initiated in France and the Germanic state of Saxony. One example that becomes important for dentistry involves the efforts of Count Walther Von Tschirnhaus in developing the mineral resources of Saxony on behalf of Augustus III. One method Von Tschirnhaus used involved subjecting minerals to extensively high temperatures (easily in excess of $1436\text{ }^{\circ}\text{C}$)² produced in the focal spot of a series of large 'burning lenses' (magnifying glasses up to one metre in diameter), creating a solar furnace. About this time in Berlin (Germanic state of Prussia), Johann Friedrich Böttger was reaching the level of journeyman apothecary. Böttger had a cute parlour trick involving melting base metals such as silver coins to which he added a dose of the Arcanum of the philosopher's stone.³ When poured into moulds and

cooled, the resulting product was analysed to be pure gold! Böttger inadvisably performed this 'transmutation' demonstration at his employer's house to impress some important guests that resulted in a summons by King Frederick I (Prussian king) for a command performance. Placing discretion ahead of valour led Böttger to flee south to Saxony where he attempted to study medicine at Wittenberg. Wanted posters had appeared in Berlin and a price was on the head of Böttger. The arrival of a contingent of a dozen troops from King Frederick seemed out of proportion, to the local Wittenberg representative of Augustus III, for the capture and return of a supposedly common criminal. Böttger was placed under house arrest for months while Augustus was alerted and the situation explored. With the presence of foreign troops confounding the situation, Böttger was finally spirited away by coach in the dead of night using back roads to avoid Prussian troops and delivered to Augustus in Dresden. The Prussians were additionally deceived as the Saxons continued to bring food to the room of Böttger. This 'base-metals-to-gold thing' was simply far too important to any state needing to support armies, and Böttger was put as a prisoner under the wing of Von Tschirnhaus to perfect gold production.

Serendipity and a clever intuition prevailed to save Böttger from certain execution following over three years of unsuccessful gold making, a project costing Augustus a small fortune. Experimenting with his burning lenses, Von Tschirnhaus discovered that while neither sand nor lime (calcium oxide) would fuse individually, they would do so when combined, and presented this at a meeting of the Academy of Sciences of Paris in 1799.² In fact, the resulting white product

looked suspiciously like porcelain. What had been discovered was the use of a ‘flux’ to create lower melting intermediate compounds, allowing the fusion of the high-silica sand. Since it was known that high quality clay was a major ingredient in Chinese porcelain, Saxony was secretly scoured for sources of purest clay. Böttger, whose expertise in chemistry was by then extensive, realized that porcelain had to have a glassy component resulting from very high temperature reactions. Building on the discovery of Von Tschirnhaus, he reasoned that lime added to clay was worth exploring.

Research was conducted under extreme secrecy beginning in the Albrechtsburg Castle in Meissen (modern photograph in Fig 3) and then in the dungeon basement of the feared *Jungfernbastei* (Maiden’s Bas-

tion) in Dresden between 1704 and 1708, utilizing an approach known today as ‘Edisonian research’, where a wide variety of formulations were systematically tried. Pages from his lab notebook memorializing the successful mixture of clay and lime (calcined alabaster; pulverized and heated to drive-off water and sulfur leaving fine calcium oxide powder) appear in Fig 4. Manufacturing operations were established back in the Albrechtsburg Castle in Meissen and by 1708 the first pieces were being demonstrated at the Leipzig Easter Fair with production for sale beginning in 1710. In about 1710 Böttger substituted feldspar for lime as the flux, a move that cleanly put the Meissen formulation within that of the Chinese ‘triaxial’ porcelains (Fig 5) and introduced feldspathic glass which will later

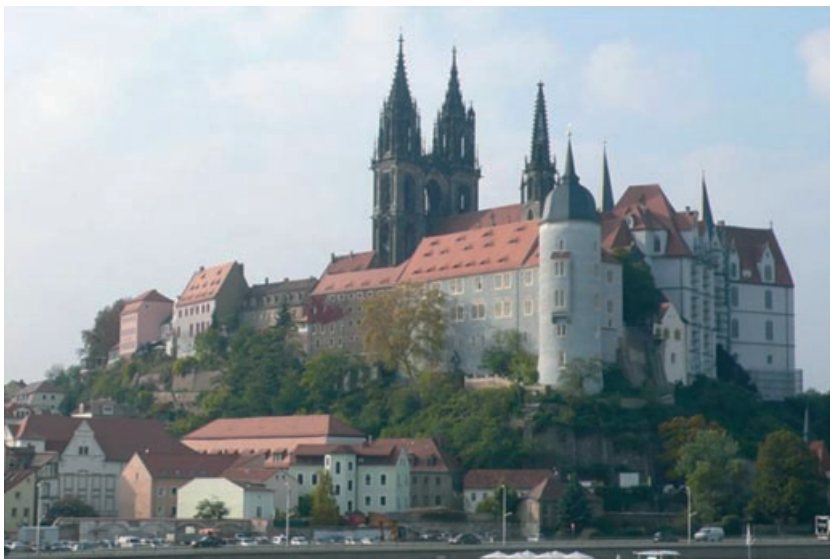


Fig 3. Albrechtsburg Castle in Meissen, Germany, site of an early porcelain discovery laboratory and the first manufacturing site of European porcelain rivalling that from China.

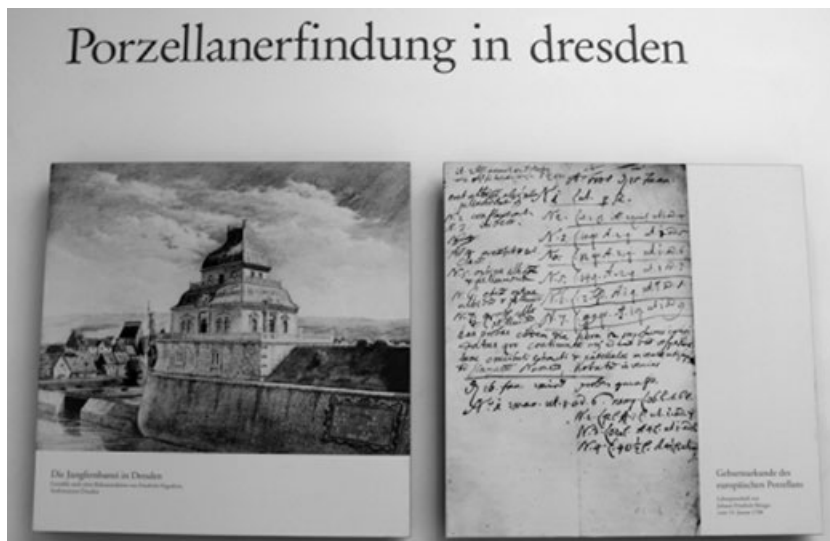


Fig 4. Page from laboratory notebook of Böttger memorializing the successful mixture of clay and calcined alabaster in January 1708. Early depiction of the feared *Jungfernbastei* (Maiden’s Bastion) in Dresden, site of secret porcelain discovery research.

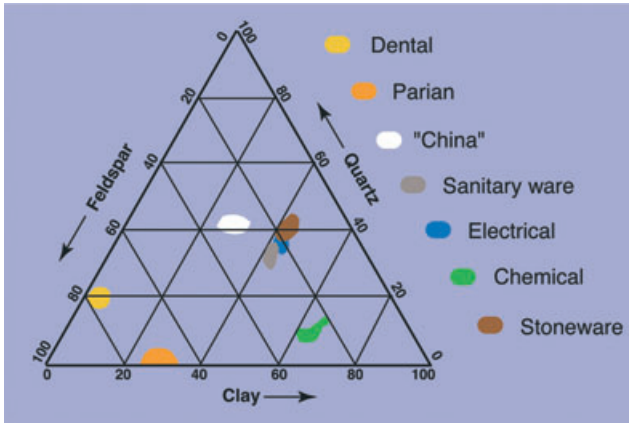


Fig 5. Tertiary phase diagram of quartz (sand), clay and feldspar. Dental formulations began in middle of diagram and evolved towards feldspar-rich compositions to improve aesthetics. In Chinese formulations feldspar was the flux.

become the main ingredient in aesthetic porcelain formulations for dentistry. This high temperature reaction of the kaolin-type clay (essentially heavily weathered granite or feldspathic rock) and feldspar yielded a high silica glass containing needle-like crystals of mullite.²

Although Saxony tried to maintain a monopoly on porcelain making, the secret escaped via a combination of its role in state prestige, industrial espionage and greed within the Meissen porcelain works. By 1776, porcelain making was the topic of a review paper given at the Academy of Sciences in Paris. In 1770 another apothecary, Alexis Duchateau, tired of his stained and malodorous dentures, sought assistance from Parisian dentist Nicholas Dubois de Chémant. Working with porcelain formulations and (then) high technology kilns of the Guehard Porcelain Factory, they succeeded by 1774 in fabricating a complete denture for Duchateau. Porcelain dentures represented a huge step forward in personal hygiene, leading public honours for de Chémant from the likes of Edward Jenner (smallpox vaccine), the Academy of Sciences and the Academy of Medicine of Paris University. Since porcelain was a new invention in Europe and only available in collaboration with a high technology company – from the very beginning its use in dentistry was certainly not craft art.

de Chémant fled to England ahead of the French Revolution where he refined formulations in collaboration with Josiah Wedgwood at the beginning of his famous manufacturing company. de Chémant presumably worked to improve translucency moving from the centre of the ternary (three-part) phase diagram towards a feldspar-rich formulation, characteristic of today's feldspathic materials (Fig 5).

In 1808 another Parisian dentist, Giuseppangelo Fonzi, significantly improved the versatility of ceramics by firing individual denture teeth, each containing a

platinum pin. This invention allowed teeth to be fixed to metal frameworks enabling: (1) partial denture fabrication; (2) repairability; and (3) increased aesthetics. Platinum had only been known to Europeans since around 1741 and given its extremely high melting point (1769 °C) was generally only worked into small wires and crucibles by hammering individual red-hot nuggets. Platinum was not used in jewellery until 1915.⁴ In 1808 platinum was used by alchemists in early chemistry experimentation, so it is likely that Fonzi obtained platinum wire from a local university or an early 'scientific supply house'. It was also the only metal that would not crack the denture tooth on cooling given its closely matched coefficient of thermal contraction. Again, this next major improvement in our ability to use ceramics in dentistry clearly stands as 'high technology'.

Leucite filler crystals in porcelain – metal-ceramic systems and strengthened 'pressable' ceramics

Many other advances contributed to both the use of ceramics and the discipline of fixed prosthodontics, including: (1) the electric porcelain furnace; (2) elastomeric impression materials; and (3) the high-speed handpiece. One major advance in porcelain itself came in 1962 with the development of a formulation that could be fired on common dental casting alloys. This invention built on a paper published in the *Journal of the American Ceramic Society* (JACS) demonstrating an oddity in the thermal expansion of a certain feldspar rock (with a potassium content over 11%) when melted and cooled quickly, forming a glass.⁵ When reheated, this glass had an extremely high thermal expansion due to the formation of a new crystalline component not in the original rock, called leucite (formed as the rock melted by a process known as 'incongruent melting'). Weinstein *et al.*, again using the 'Edisonian research technique' (and hiring co-author Koenig of the JACS paper as a consultant), finally arrived at what they called 'component number 1' – a porcelain frit that had a thermal expansion coefficient of nearly $20 \times 10^{-6}/^{\circ}\text{C}$, allowing it to be mixed in any ratio with the normal expansion porcelain frit (thermal expansion of $8 \times 10^{-6}/^{\circ}\text{C}$) to 'dial in' an expansion/contraction to match any dental alloy.⁶ So this represents an invention built on a paper published in a scientific journal outside of dentistry, and therefore again, high technology.

Most dental alloys having expansions in the range of 12 to 14 ($\times 10^{-6}/^{\circ}\text{C}$); their matching porcelains have leucite contents around 17 to 25 mass%. Manufacturers have found that having the porcelain with a slightly higher expansion/contraction than the metal makes for more durable restorations, presumably by leaving the porcelain in a state of slight tangential compression.

Leucite was later used for dispersion strengthening at 35 to 50 mass% in both powdered ceramics and later in the first pressed ceramics. Leucite was a good choice as a strengthening filler since its index of refraction is close to that of the feldspathic glass, so moderate strengthening could be achieved without severely increasing opacity. These compositions are also easily etched to create micromechanical features for resin bonding. All-ceramic systems based on leucite-filled feldspathic glasses remain some of the most aesthetic and popular dental ceramics, and have been extensively studied clinically and found to be highly reliable.⁷ The use of a feldspathic glass dates back to Böttger in 1710. It became the major component of dental formulations with the work of de Chémant in England in the early 1800s and a special property of high potassium feldspars was taken advantage of in 1962, leading to the vast majority of aesthetic dental ceramics in use today, either metal-ceramic or all-ceramic.

Non-shrinking ceramics

Except for pressing ingots, by the mid 1980s all dental ceramic 'parts' started as powders or mixtures of clay and power particles. Shrinkage is inherent to the making of 'parts' from such starting materials since the volume fraction of porosity is over 30% in the starting greenware and nearly 0% in the finished product. Seven different approaches were developed beginning in the mid 1980s through to the late 1990s to deal with or avoid shrinkage to provide prostheses that were, what an engineer would call, being made to a 'net shape': (1) a pressed ceramic powder/polymeric binder that expanded and crystallized during firing to fill a lost-wax mould (Cerestore; Johnson & Johnson, New Brunswick, NJ, USA);^{8,9} (2) casting of a special glass into a lost-wax mould, embedding the clear-glass casting in an investment and heat-treating to form crystals within the glass (termed a 'glass ceramic', trade named DICOR; Dentsply International, York, PA, USA); (3) lightly sintering aluminum oxide (and later magnesium aluminate spinel and zirconia/alumina) to form necks between touching particles and then infiltrating this porous ceramic with glass (In-Ceram; Vita Zahnfabrik, Bad Säckingen, Germany);¹⁰ (4) pressing solid ingots of filled-glass (leucite or lithium disilicate) into a lost-wax mould (Empress; Ivoclar Vivadent, Schaan, Liechtenstein);¹¹ (5) computer-aided machining of 'net-shape' parts from solid, full-dense blocks (CEREC; Sirona, Bensheim, Germany);¹² (6) computer-aided fabrication of an oversized die, pressing of alumina powder onto the die creating an oversized part and sintering to final size (Procera; Nobel Biocare, Zürich, Switzerland);¹³ and (7) computer-aided machining of oversized parts from lightly sintered blocks of zirconia and alumina which are then sintered

to final size (Cercon, Lava, Vita YZ, Ivoclar e.max zirCAD).¹⁴

Approach number (1) provided the first introduction of advanced ceramics processing equipment into the dental laboratory and approach (2) introduced 'glass ceramics' into dentistry; where strengthening filler particles are grown inside of the glass from the chemistry of the glass (during a special heat treatment called 'ceramming') as opposed to being added as separate powder particles. Both of these involved collaborations with specialty ceramics firms, Coors Ceramics for (1) and Corning Glass Works for (2).

Chairside CAD/CAM

While all seven approaches stand clearly as being high technology, numbers (5) and (7) can be viewed as being revolutionary. In 1987, Mörmann and Brandestini¹² introduced a prototype machine that would capture a 3-D image of a prepared tooth. They used 3-D design software to iteratively develop a proposed restoration and then directed the computer-aided milling of inlays and onlays from solid blocks of aesthetic, filled-glass (see next section) ceramics (CEREC I, then Siemens Dental now Sirona, Bensheim, Germany). Machining of aesthetic glass-based ceramics is relatively straightforward and special formulations were quickly developed that were much higher quality than what was available from dental laboratory processing based on either strengthened and fine grained feldspathic ceramics (Mark II, Vita) or the first glass-ceramic introduced for dental use (containing interlocking tetrasilicic fluoromica flakes, DICOR-MGC, Dentsply International).

Green machining of oversized parts

Machining of tougher structural ceramics such as alumina and especially transformation toughened zirconia (see following section) was much more difficult, requiring heavier machinery, longer milling times and quite often involved limited tool life. Further advances in the manipulation of 3-D data sets along with the fruits of a decade of research into ceramics processing provided the underpinning for an innovative solution proposed by Filser and Gauckler at the University of Zürich. This involved machining of an oversized part from a ceramic block only lightly sintered to what is termed the 'initial sintering' stage.¹⁵⁻¹⁷ With very careful control over both the ceramic powder particle size distribution and particle packing density, it became possible to predict the oversized shape needed that would then shrink to the desired 'net shape'. This technique has been variously termed 'green machining' or 'soft machining' in dental literature. This technique allowed the individually customized and high tolerance parts dentistry requires to be

manufactured from polycrystalline ceramics such as alumina and zirconia.

As of today, the last major advance in dental ceramics comes with the introduction of transformation toughened zirconia.^{17–19} This ceramic is arguably the most complex material ever introduced for dental use and, as will be discussed later, its introduction has not been without a ‘learning curve’ that we are still climbing. Two other major changes currently underway involve: (1) the establishment of dedicated industrial-quality manufacturing centres for fabrication of prostheses; and (2) the application of engineering design research into clinical and laboratory practices to optimize durability and aesthetics. Fruits of this second activity will be discussed in the last section of this paper.

BACKGROUND CONCEPTS IN CERAMICS SCIENCE

There are two quite useful concepts that help demystify dental ceramics by providing a structure within which to organize thinking. First, there are only three main classes of dental ceramics: (1) predominantly glassy materials; (2) particle-filled glasses; and (3) polycrystalline ceramics.^{6,20,21} Defining characteristics will be provided for each of these ceramic types as they are represented in Fig 6. Second, virtually any ceramic within this spectrum can be considered as being a ‘composite’, meaning a composition of two or more distinct entities. Quite a number of seemingly different dental ceramics can be shown to be quite similar or closely related to each other when reviewed within the framework these two simplifying concepts provide. Additionally, the rationale behind the development of ceramics of both historic and recent interest can be more easily understood. Two examples of the utility of these concepts include these basic statements: (1) highly aesthetic dental ceramics are predominantly glassy and higher strength substructure ceramics are generally crystalline; and (2) the history of development of

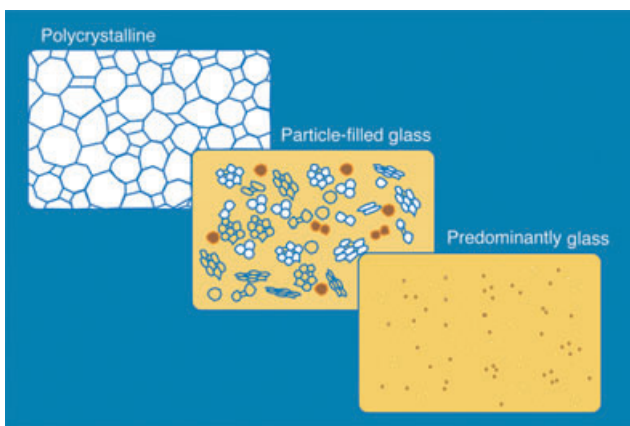


Fig 6. Based on their microstructure, dental ceramics fall within three basic classes: (1) predominantly glass; (2) particle-filled glass; and (3) fully polycrystalline. Each of these is discussed in detail in the text.

substructure ceramics simply involves an increase in crystalline content to fully polycrystalline. Figures 7a and 7b provide basic composition details and commercial examples of many aesthetic and substructure dental ceramics organized by these three main divisions using the ‘composite’ concept (based on matrix and filler).

Predominantly glassy ceramics

Dental ceramics that best mimic the optical properties of enamel and dentine are predominantly glassy materials. Glasses are 3-D networks of atoms having no regular pattern to the spacing (distance and angle) between nearest or next nearest neighbours, thus their structure is ‘amorphous’ or without form. Glasses in dental ceramics derive principally from a group of mined minerals called feldspar and are based on silica (silicon oxide) and alumina (aluminum oxide), hence feldspathic porcelains belong to a family called aluminosilicate glasses.²¹ Glasses based on feldspar are resistant to crystallization (devitrification) during firing, have long firing ranges (resist slumping if temperatures rise above optimal) and are extremely biocompatible. In feldspathic glasses, the 3-D network of bridges formed by silicon-oxygen-silicon bonds is broken up occasionally by modifying cations such as sodium and potassium that provide charge balance to non-bridging oxygen atoms (Fig 8). Modifying cations alter important properties of the glass, e.g. by lowering firing temperatures or increasing thermal expansion/contraction behaviour.

Particle-filled glasses

Filler particles are added to the base glass composition in order to improve mechanical properties and to control optical effects such as opalescence, colour and opacity. These fillers are usually crystalline but can also be particles of a higher melting glass. Such compositions based on two or more distinct entities (phases) are formally known as ‘composites’, a term often reserved in dentistry to mean resin-based composites. Thinking about dental ceramics as being composites is a helpful and valid simplifying concept. Much confusion is cleared up in organizing ceramics by the filler particles they contain (and how much), why the particles were added, and how they got into the glass.

The first fillers to be used in dental ceramics contained particles of a crystalline mineral called leucite.^{20,21} As mentioned in the history section above, this filler was added to create porcelains that could be successfully fired onto metal substructures.^{22,23} Leucite has a very high thermal expansion/contraction coefficient (around $20 \times 10^{-6}/^{\circ}\text{C}$) compared to feldspathic glasses (around $8 \times 10^{-6}/^{\circ}\text{C}$). Dental alloys have expansion/contraction coefficients around 12 to 14 ($\times 10^{-6}/^{\circ}\text{C}$). Adding about 17 to 25 mass% leucite filler

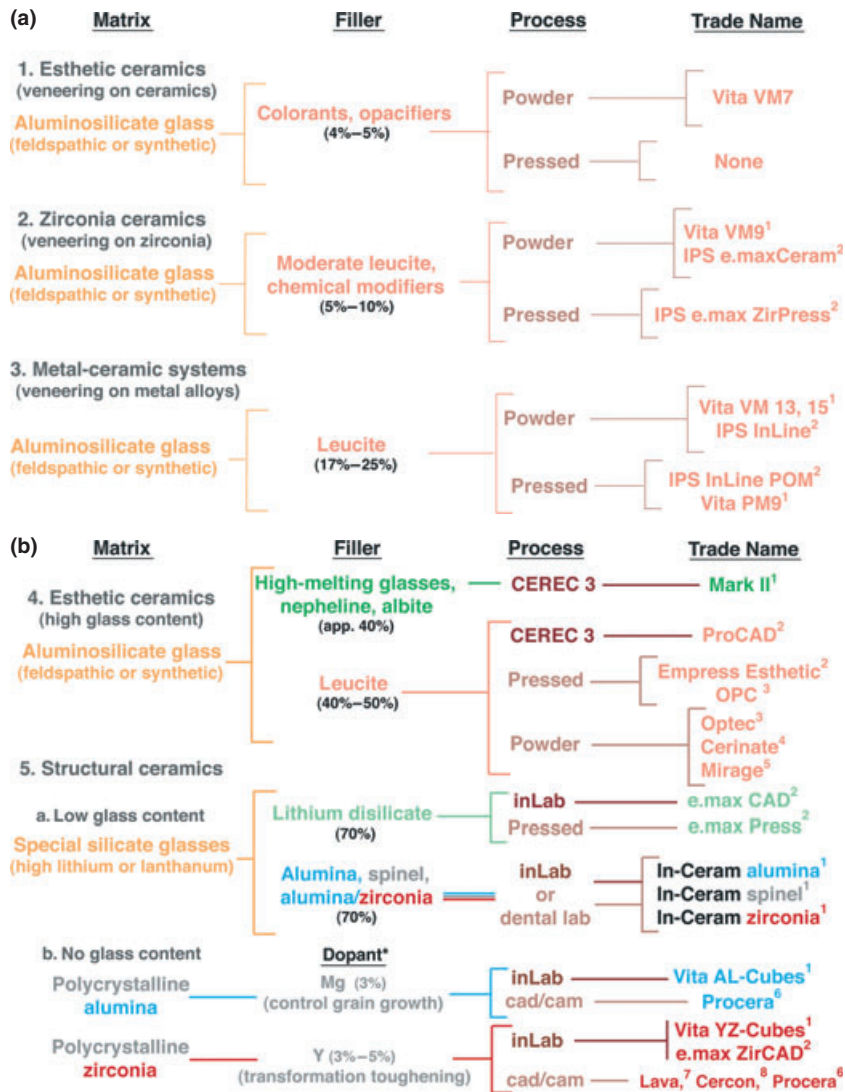


Fig 7. Composition of dental ceramics based on their being composites consisting of a 'matrix' and 'fillers'; (a) veneering ceramics; (b) structural and CAD/CAM ceramics.

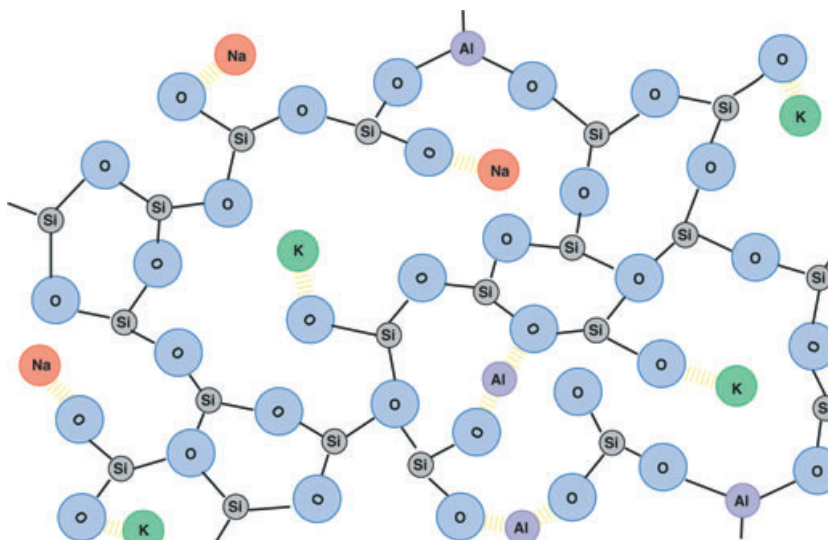


Fig 8. In feldspathic glasses, the 3-D network of bridges formed by silicon-oxygen-silicon bonds is broken up occasionally by modifying cations such as sodium and potassium that provide charge balance to non-bridging oxygen atoms.

to the base dental glass create porcelains that are thermally compatible during firing with dental alloys. Metal-ceramic systems, first developed in 1962, are used to fabricate 70 to 80% of fixed prostheses.

Moderate strength increases can also be achieved with appropriate fillers added and uniformly dispersed throughout the glass, a phenomenon termed 'dispersion strengthening'. The first successful strengthened substructure ceramic was made of feldspathic glass filled with particles of aluminum oxide (app. 55 mass%).²³ Leucite is also used for dispersion strengthening at concentrations of around 40 to 55 mass%, much higher than needed for metal-ceramics. Commercial ceramics incorporating leucite fillers for strengthening include a group that are pressed into moulds at high temperature (OPC, Pentron; Empress Esthetic, Ivoclar Vivadent and Finesse All-Ceramic, Dentsply Prosthetics) and a group provided as a powder for traditional porcelain build-up (OPC Plus, Pentron; Fortress, Mirage Dental Systems).

Beyond thermal expansion/contraction behaviour, there are two major benefits to leucite as a filler choice for dental ceramics; the first intended and the second probably serendipitous. First, leucite was chosen because its index of refraction is very close to that of feldspathic glasses; an important match for maintaining some translucency. Second, leucite etches at a much faster rate than the base glass and it is this 'selective etching' that creates a myriad of tiny features for resin cements to enter, creating a good micromechanical bond.

Glass-ceramics (special subset of particle-filled glasses)

Crystalline filler particles can be added mechanically to the glass, e.g. by simply mixing together crystalline and glass powders prior to firing. In a more recent approach, the filler particles are grown inside the glass object (prosthesis or pellet for pressing into a mould) after the object has been formed. After forming, the glass object is given a special heat treatment, causing the precipitation and growth of crystallites within the glass. Since these fillers are derived chemically from atoms of the glass itself, it stands to reason that the composition of the remaining glass is altered as well during this process (termed 'ceraming'). Such particle-filled composites are called glass-ceramics. The material Dicor (Dentsply), the first commercial glass-ceramic available for fixed prostheses, contained filler particles of a type of crystalline mica (at app. 55 vol%).²⁴ More recently, a glass-ceramic containing 70 vol% crystalline lithium disilicate filler has been commercialized for dental use (Empress 2, now e.maxPress and e.maxCAD, Ivoclar-Vivadent).

Polycrystalline ceramics

Polycrystalline ceramics have no glassy components; all of the atoms are densely packed into regular arrays that

are much more difficult to drive a crack through than atoms in the less dense and irregular network found in glasses. Hence, polycrystalline ceramics are generally much tougher and stronger than glassy ceramics. Polycrystalline ceramics are more difficult to process into complex shapes (e.g. a prosthesis) than are glassy ceramics. Well-fitting prostheses made from polycrystalline ceramics were not practical prior to the availability of computer-aided manufacturing. In general, these computer-aided systems use a 3-D data set representing either the prepared tooth or a wax model of the desired substructure. This 3-D data set is used to create either an enlarged die upon which ceramic powder is packed (Procera, NobelBiocare, Zurich, Switzerland) or to machine an oversized part for firing by machining blocks of partially fired ceramic powder (Cercon, Dentsply Prosthetics; Lava, 3M-ESPE; Y-Z, Vita Zahnfabrik). Both of these approaches rely upon well-characterized ceramic powders for which firing shrinkages can be predicted accurately.^{13,14}

Polycrystalline ceramics tend to be relatively opaque compared to glassy ceramics, thus these stronger materials cannot be used for the whole wall thickness in aesthetic areas of prostheses. These higher strength ceramics serve as substructure materials upon which glassy ceramics are veneered to achieve pleasing aesthetics. Laboratory measures of the relative translucency of commercial substructure ceramics are available, both for a single-layer of materials and for those that are veneered.^{25,26} It should be noted, however, that while laboratory measures of opacity have equated some polycrystalline ceramics to cast alloys, all ceramic substructures transmit some light and metals simply do not.

Substructure ceramics

The development of higher strength ceramics for veneered all-ceramic prostheses can be represented as a transition towards increases in the volume percentage of crystalline material with decreasingly less glass and finally, no glass. In 1965, John McLean reported on the strengthening of a feldspathic glass via addition of aluminum oxide particles,²³ the same year that General Electric first applied that new technology (dispersion strengthening of glasses) to high-tension power line insulators. In the late 1980s, a method was realized to significantly increase the aluminum oxide content (from app. 55 mass% to 70 vol%) by first lightly firing packed alumina powder and then infiltrating the still porous alumina compact with glass.¹¹ During the first light firing, adjacent alumina particles become bonded where they touch, forming a 3-D network of linked particles. Infiltration involves a low viscosity glass drawn into the porous alumina network by capillary pressure, thus forming an interpenetrating 3-D composite (both the alumina and glass being continuous throughout the

ceramic, neither representing an isolated 'filler'). Although with only 70 vol% aluminum oxide, this ceramic (In-Ceram Alumina, Vita) has a strength and fracture toughness identical to many 100% polycrystalline alumina ceramics.

Two key developments allowed fully polycrystalline ceramics to become practical for fixed prostheses: (1) the availability of highly controlled starting powders; and (2) the application of computers to ceramics processing. Unlike glassy ceramics, polycrystalline ceramics cannot be simply pressed as a fully dense material into slightly oversized moulds (moulds that have expanded just enough to compensate for cooling shrinkage – as is done in the casting of metals). Polycrystalline ceramics are formed from powders that can only be packed to around 70% of their theoretical density. Hence polycrystalline ceramics shrink around 30% by volume (10% linear) when made fully dense during firing. In order for the final prostheses to fit well, the amount of shrinkage needs to be accurately predicted and compensated for. Well-characterized starting powders that can be uniformly packed are a prerequisite for achieving predictable and reproducible shrinkage. Research in ceramics processing science from the late 1980s through to the 1990s led to the commercial availability of powders suitable for dental use. Almost simultaneously with high technology powder refinement came the development of computer-aided machining and the ability to capture and manipulate 3-D data sets.

Two different approaches are now being offered commercially for fabrication of prostheses from polycrystalline ceramics, both of which create oversized greenware (unfired part) using 3-D data sets and the specific shrinkage characteristics of well-behaved starting powders. In the first approach, an oversized die is manufactured based on app. 20 000 measurements taken during the mechanical scanning of a laboratory die. Either aluminum oxide or zirconium oxide is pressed onto the oversized die and predictably shrunk during firing to become well-fitting single-crown substructures (Procera, Nobel Biocare).¹³ In the second approach, blocks of partially fired (app. 10% complete) zirconium oxide are machined into oversized greenware for firing as single- and multiple-unit prosthesis substructures (Cercon, Dentsply Prosthetics; Lava, 3M-ESPE; Y-Z, Vita; e.max ZirCAD, Ivoclar). In these systems, individual blocks are bar coded with the actual density of each block (for the fine-tuning of shrinkage calculations) and the milling machines can keep track of the number of blocks milled and automatically change milling tools to further assure accuracy of fit.¹⁴

Transformation toughened zirconium oxide

Potentially the most interesting polycrystalline ceramic now available for dentistry, transformation toughened

zirconia, needs further explanation since its fracture toughness (and hence strength) involves an additional mechanism not found in other polycrystalline ceramics. While fracture toughness and strength are outside the scope of this paper, it is sufficient here to understand toughness simply as meaning the difficulty in driving a crack through a material.

Unlike alumina, zirconium oxide is transformed from one crystalline state to another during firing. At firing temperature, zirconia is tetragonal and at room temperature monoclinic, with a unit cell of monoclinic occupying about 4.4% more volume than when tetragonal. Unchecked, this transformation was a bit unfortunate since it would lead to crumbling of the material on cooling. In the late 1980s, ceramic engineers learned to stabilize the tetragonal form at room temperature by adding small amounts (app. 3–8 mass%) of calcium and later yttrium or cerium.¹⁸ Although stabilized at room temperature, the tetragonal form is really only 'metastable', meaning that trapped energy still exists within the material to drive it back to the monoclinic state. It turned out that the highly localized stress ahead of a propagating crack is sufficient to trigger grains of ceramic to transform in the vicinity of that crack tip. In this case, the 4.4% volume increase becomes beneficial, essentially altering material conditions around the crack tip, shielding it from the outside world (more formally stated, transformation decreases the local stress intensity).

Although most dental zirconia is a bit opaque and copings need to be veneered for high aesthetics, these prostheses can be quite lifelike. Zirconia is not as opaque as In-Ceram alumina and can be internally coloured as can lithium disilicate. Figure 9 is a clinical case involving both central incisors where zirconia was chosen over crowns done in three other systems by the same technician (In-Ceram alumina, Vita; e.maxCAD, Ivoclar; Captek, Precious Chemicals Company, Altamonte Springs, FL, USA).

With fracture toughness twice or more that of alumina ceramics, transformation toughened zirconia represents an exciting potential substructure material. Possible problems with these zirconia ceramics may involve long-term instability in the presence of water, porcelain compatibility issues, and some limitations in case selection due to their opacity. However, as of writing this, three-year clinical data involving many posterior single-unit and three-unit prostheses (plus 1 five-unit) have revealed no major problems (discussed more fully below).

Zirconia substructures issues

Two issues are of concern with zirconia, one quite real and one potential. Of real concern are reports of significant percentages of single-unit and multi-unit



Fig 9. Both central incisors were restored with veneered zirconia crowns (Y-Z, Vita). Mirror shot (top) demonstrates vital translucency.

prostheses having porcelain chipping and cracking (e.g. 25 to 50%).¹⁷ Of potential concern is the propensity for partially-stabilized zirconia to auto-catalytically transform at surface grain boundaries due to an interaction with water. This may create major structural issues in the future.

Many ‘authorities’ have offered numerous explanations for porcelain chipping that simply do not withstand critical thinking or analysis, including: (1) non-anatomic substructure design; (2) unsupported porcelain; (3) weaker porcelain; (4) thermal expansion/contraction mismatches; and (5) poor porcelain-zirconia bonding. More well-considered hypotheses have included: (1) residual stresses arising from thermo-mechanical parameters;²⁷ (2) auto-catalytic transformation during porcelain firing;²⁸ and (3) enhanced auto-catalytic transformation of green-machined structures at mouth temperature.²⁹ As yet unpublished research from three different sources strongly supports residual stresses within the porcelain developing as a result of too rapid cooling: (1) fractographic evidence for a crack originating 0.5 mm below the porcelain surface (Susanne Scherrer, University of Geneva); (2) optical interferometer measures of residual stress in fast-cooled versus slow-cooled zirconia crowns (Drs Norbert Thiel and Michael Tholey, Vita, with collaborators at the Fraunhofer Institute); and (3) measures of thermal gradients across fast-cooled crowns of up to 160 °C (Drs Norbert Thiel and Michael Tholey, Vita). In addition, many clinical authorities report that they stopped having porcelain problems when they enforced a slow-cooling protocol (including Drs Avi Sadan and Ed McLaren – personal

communications). One paper given at the 2010 meeting of the International Association for Dental Research (IADR) on clinical data from four private practices reported only 2% porcelain chipping in two to three years for 702 prostheses (authors D Nathanson, S Chu, H Yamamoto and C Stappert). These clinicians reported that their laboratories were aware of the need to cool slowly. Numerous dental material companies now include a caution to slow cool in written and web-based informational materials. This continues to be an active area of research.

All ceramics are susceptible to subcritical crack growth and corrosion effect caused by water, which breaks the bond between atoms at the crack tip, leading to slow growth of cracks, resulting in a decrease of materials’ strength. Partially-stabilized zirconia-based materials are uniquely susceptible to auto-catalytic transformation of the crystals from tetragonal to monoclinic at relatively low temperatures called low temperature degradation (LTD).³⁰ While generally studied at autoclave temperatures of a few hundred degrees centigrade, significant percentages of transformation can be extrapolated as being possible at oral temperatures using activation energy data from ceramics literature (Chevalier).²⁹ Another striking clinical study presented at the 2010 IADR examined partially-stabilized zirconia discs embedded in the flanges of mandibular partial dentures, demonstrating a much higher rate of transformation for a dental zirconia in two to three years than predicted for an engineering zirconia by Chevalier (author Tomaž Kosmač, Jožef Stefan Institute).

Water can ‘catalyze’ the process at surface grain boundaries and the transformation of crystal continues from layer to layer through the entire body, leading to microcrack formation, grain pullout and a decrease in strength.¹⁸ This phenomenon was particularly important in causing the failure of zirconia hip prostheses submitted to autoclave sterilization. Although the information presented above raises concern, both published clinical trials and those presented at international research meetings evidenced no bulk fracture in dental restorations under the observation time, indicating that LTD has no major influence on the clinical behaviour of dental restorations.³¹

Maximizing durability

Understanding how to maximize durability flows from understanding clinical failure and the factors influencing the stress state at failure that are within our clinical control. Efforts to understand clinical failure of single crowns has involved studying fracture surfaces (fractography), finite element modelling and developing a clinically-valid laboratory test.³² These all demonstrate that the main mechanism of failure does not involve damage from wear facets but

stresses on the cementation surface due to occlusal loading. Figure 10 is a cartoon representation of finite element modelling illustrating this stress state. These engineering analyses point to four clinical techniques for maximizing durability: (1) provide maximum occlusal thickness for the ceramic (strength increases with the square of the thickness); (2) use the highest elastic modulus (stiffness) substrate possible; i.e. metal or ceramic versus resin-based composite); (3) bond the restoration, ceramic-cement and cement-tooth (or substructure); and (4) develop broad, not pinpoint, occlusal contacts.

This thickness-squared relationship is illustrated in Fig 11 from calculations using the analytical solution of Hsueh.³³ For example, predicted failure loads for a lithium disilicate restoration increase from 1400 N to over 2000 N with a ceramic thickness increase from 1.6 mm to only 1.8 mm. Higher elastic modulus (stiffness) substructures decrease the stress for any given load. This effect has also been validated from clinical study of all-ceramic crowns.^{34,35} Failure loads of crowns have been found to be doubled with bonding in laboratory testing (L May, JR Kelly, University of Connecticut, unpublished research) and this effect has been verified in retrospective clinical studies of both inlays and crowns.^{36,37} Figure 10 also predicts that for any given total thickness there is little to no structural improvement from making the higher strength ceramic thicker. This counter-intuitive prediction is being verified in laboratory testing (R Yau, P Rungruangnunt, JR Kelly, University of Connecticut, unpublished data) and may allow crowns to be maximized for aesthetics without decreasing durability. Failure stresses also increase with decreased wear facet size, e.g. failure loads as a function of loading piston diameter were: 1 mm = 343 N; 2 mm = 382 N; and 3 mm = 522 N.³⁸

Etching and bonding

Ideal bonding involves having microstructural structures within the ceramic that can be selectively attacked by acids (etched) at a higher rate than surrounding

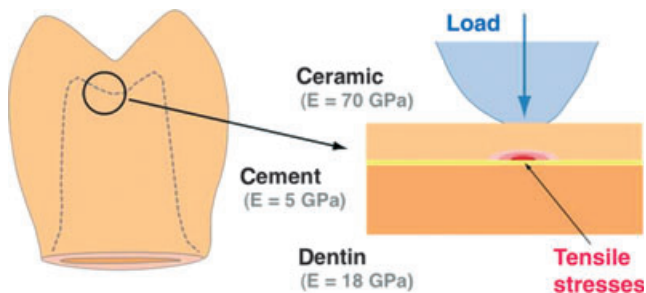


Fig 10. Failure stresses are linearly related to the elastic modulus different (ceramic-substrate) and to the square of the ceramic thickness.

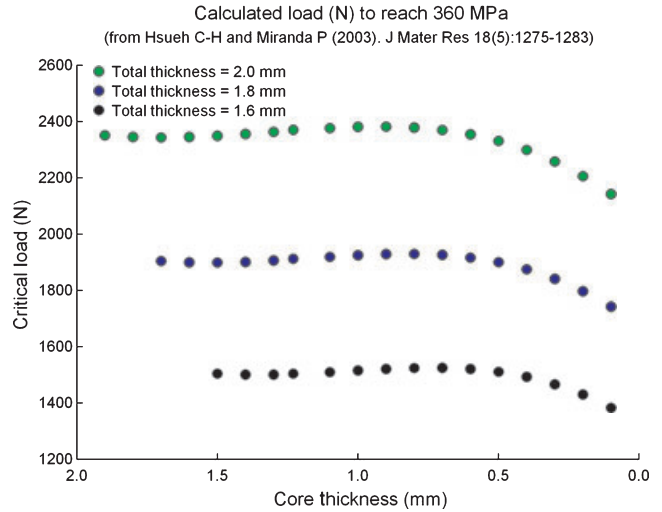


Fig 11. Calculated loads to reach 360 MPa (breaking strength of lithium disilicate) for three different thicknesses as a function of varying core thickness (remainder veneer).

ceramic leaving micromechanical features for cement infiltration. The selective etching of crystalline leucite, leaving behind microscopic glassy crypts, is the most common dental example. A second requirement for good bond formation relates to the size of the structure(s) formed by etching and how well they are still attached to the remaining bulk ceramic. For example, some selective etching of In-Ceram alumina is possible but the scale of roughness that develops is insufficient for good bond formation. Polycrystalline ceramics can be etched, revealing the boundary between crystalline grains, but these etched grain boundaries provide little micromechanical retention.

Chemical bonding is possible with virtually all dental ceramics, but only with the use of resin cements containing special adhesive molecules. The durability of chemical bonding between resin cements and substructure ceramics has not been definitively addressed. Laboratory data suggests that bonds can decrease significantly during water storage.³⁹

Aesthetic considerations

Achieving a lifelike match requires the clinician/technician to choose a base ceramic having an appropriate translucency (value in the Munsell system) for the patient. For a single anterior tooth, all ceramics have sufficient longevity based on clinical trial data, so the choice can be made on aesthetic capability alone. New research on comparative translucencies is in preparation that will update decades-old information.

Three things need to be measured and recorded for communication with the dental laboratory: (1) base shade (gingival one-half to one-third); (2) incisal enamel characterization; and (3) surface gloss. Base shade is best determined within a rational shade

Table 1. Recommendation for use of an all-ceramic restoration based on translucency (MO denotes moderate opacity and HO denotes high opacity)

High translucency	Moderate translucency	Low translucency
Empress Esthetic e.max Press Empress CAD In-Ceram Spinell	Vita Y-Z zirconia e.max Press MO Vita alumina In-Ceram alumina Lava zirconia	e.max Press HO In-Ceram zirconia

system such as 3-D Master (Vita). Numerous automated shade taking devices are also available, with the most highly regarded from laboratory research being the EasyShade (Vita).

Ceramic systems offer different levels of translucency and colour control. These are best learned by clinical practice. In general, an aesthetic match is best achieved by specifying a ceramic system offering the same translucency as the case being matched. Currently available ceramics are organized below by translucency measurements (L Spink, P Rungruangnunt, JR Kelly, University of Connecticut, unpublished research).

Many all-ceramic systems are clinically indicated for single-unit anterior teeth, including most in Table 1. Thus, clinicians are free to choose a system offering the best aesthetic match.⁷ Good choices (i.e. well-studied clinically) for posterior single-unit teeth include In-Ceram alumina (Vita), Empress Esthetic (Ivoclar), e.max Press or CAD (Ivoclar) and zirconia-based (various).⁷ Only the zirconia systems are indicated for multi-unit fixed prostheses.

Glazing versus polishing

Auto glazing (firing in air) and polishing are two options for finishing the surface of aesthetic porcelains. These two techniques received recent attention in a review of a number of studies comparing prepared surfaces using visual, microscopic and profilometry measures.⁴⁰ All studies agree that glazing can produce a smooth porcelain surface. However, polishing can produce as smooth a surface that can be more aesthetically similar to natural enamel. Many authorities favour polishing given that a higher level of control is possible over final surface finish and that an added firing can add problems and time to the delivery appointment.

Repair

Approaches to the repair of porcelains have been reviewed relatively recently.⁴¹ Repair often offers both dentist and patient a cost-effective alternative to replacement. Repair involves the bonding of resin-

based products to remaining porcelain. The porcelain-resin bond is formed by both etching the surface to create micromechanical attachment features and by the application of silane coupling agents to provide some chemical interaction between the silicon-based ceramic and carbon-based resins. It is reported that porcelain repair systems form durable bonds to fractured porcelain and exposed metal surfaces.⁴¹

SUMMARY

Ceramics are widely used in dentistry due to their ability to mimic the optical characteristics of enamel and dentine as well as for their biocompatibility and chemical durability. Most highly aesthetic ceramics are filled glass composites based on aluminosilicate glasses derived from mined feldspathic minerals. One common crystalline filler is the mineral leucite, used in relatively low concentrations in porcelains for metal-ceramic systems and in higher concentrations as a strengthening filler in numerous all-ceramic systems. In general, the higher the fraction of polycrystalline components, the higher the strength and toughness of a ceramic. The development of substructure ceramics for fixed prosthodontics represents a transition towards fully polycrystalline materials. While the strength rating of a dental ceramic can be a meaningful number, it is not really an 'inherent' property and varies due to testing parameters that are often not well controlled to optimize clinical relevance. Fracture toughness is a far more 'inherent' measure of the structural potential of a ceramic and represents a more easily compared value. Clinical data for all-ceramic systems is becoming increasingly available and results exist for many commercial materials, providing guidance regarding clinical indications.

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