

Chapter 3.4

DENTAL CERAMICS

INTRODUCTION

It could be said that the ceramic material known as porcelain holds a special place in dentistry because, notwithstanding the many advances made in composites and glass-ionomers, it is still considered to produce aesthetically the most pleasing result. Its colour, translucency and vitality cannot as yet be matched by any material except other ceramics.

CLINICAL SIGNIFICANCE

Ceramic restorations are indicated where aesthetics is needed and when the size of the preparation exceeds the limit for the use of direct composite resins.

Traditionally, its use is in the construction of artificial teeth for dentures, crowns and bridges. From the 1980s onwards the use of ceramics has been extended to include veneers, inlays/onlays, crowns and short-span anterior bridges. The construction of such restorations is usually undertaken in dental laboratories by technicians skilled in the art of fusing ceramics.

As people retain their teeth for much longer than in the past, the need for aesthetically acceptable restorations is continuing to increase. This is reflected in the growing use by dentists of restorative procedures using ceramics.

CLINICAL SIGNIFICANCE

The demand for ceramic crowns has been increasing at the rate of 50% every 4 years; therefore, ceramics will continue to be important restorative materials for many years to come.

HISTORICAL PERSPECTIVE

Pottery in Europe up to AD 1700

The achievement of making usable pottery was a considerable feat, and involved many trials and tribulations for the early potters. The raw material used for pottery is clay, and this presented the potter with two major problems.

The first problem encountered by the primitive potter was how to get the clay into a form that provided the best consistency for manipulation and firing. Clay is usually too sticky to handle when simply mixed with water, and this problem was overcome by the addition of sand and ground seashells. In addition, clay shrinks as it dries out and hardens. If this shrinkage is non-uniform, either in rate or in overall amount, the pots will crack even before they have been fired. Again, the addition of a coarse-grained filler went some way towards overcoming this problem.

It was during the firing of the pots that the prob-

lems really began to be serious. Gases present in the mixture, whether air bubbles or gases formed during heating (such as water vapour and CO_2), create voids in the clay and may even cause the clay to fracture during firing. Early potters overcame this problem by beating the clay prior to moulding to get rid of the air. (*Wedging* is the term often used by the craftsmen to describe this process.) Another development was the technique of raising the temperature very gradually during the firing process so that the steam and gases could diffuse out of the clay slowly, rather than bursting out and causing the pot to crack.

The most serious obstacle during this phase in the development of ceramic technology was the temperature at which the pottery could be fired. The conversion of clay from a mass of individual particles loosely held together by a water binder to a coherent solid relies on a process known as *sintering*. In this process, the points at which the individual particles are in contact fuse at sufficiently high temperatures (**Figure 3.4.1**).

The process relies on diffusion, which is greatly accelerated by elevated temperatures. The demand for high, uniform temperatures could not be met by the traditional open fires, and this led to the invention of the *kiln*. The earliest of these was the *up-draught kiln*, in which higher temperatures and greater uniformity of temperature were obtained by drawing air through the fire and putting the pots in the rising hot gases.

Early kilns were able to reach temperatures of up to 900°C , and pottery fired at this temperature is called *earthenware*. The resultant pottery is porous, as the sintering process has only just managed to fuse the particles of clay where they touch. Such pots were suitable for the storage of solid foods but could not hold any liquids. This problem was overcome eventually by fusing a thin layer of a glassy material, i.e. a glaze, over the surface of the pot. This technology was used as far back as 5500 BC in various places, including Turkey.

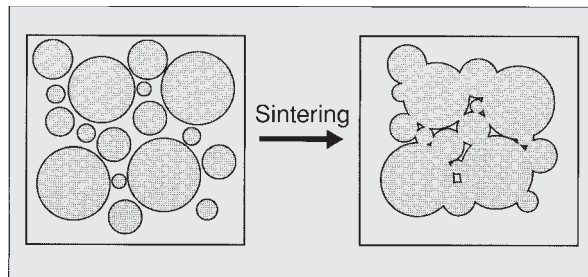


FIGURE 3.4.1 Sintering of ceramic particles

Gradual progress was made towards higher kiln temperatures, so that many more clays could be partially melted. The liquid phase would invariably solidify as a glass, resulting in impervious pottery that is generally known as *stoneware*. Stoneware appeared in Europe in the 15th and 16th centuries AD.

Chinese Porcelain

In contrast to what was happening in Europe, stoneware had been produced in China by 100 BC, and, by the 10th century AD, ceramic technology in China had advanced to such a stage that they were able to produce:

A ceramic so white that it was comparable only to snow, so strong that vessels needed walls only 2–3 mm thick and consequently light could shine through it. So continuous was the internal structure that a dish, if lightly struck would ring like a bell.

This is porcelain!

As trade with the Far East grew, this infinitely superior material came to Europe from China during the 17th century. Until then, there had been a distinct lack of interest in tableware. The majority of the population ate from wooden plates, and the nobility were satisfied with eating from metal plates. For special occasions, gold and silver tableware would be used.

This all changed with the introduction of Chinese porcelain, which stimulated demand for high quality ceramic tableware. There was no way in which the trade with the Far East could possibly satisfy this demand, so strenuous efforts were made by the European pottery industry to imitate the Chinese porcelain.

Passable imitations were made by using tin oxide as a glaze (producing the white appearance of porcelain), but it was found impossible to reproduce the translucency of Chinese porcelain. For example, Meissen in Germany in 1708 managed to produce what they called 'white porcelain', but their product more closely resembled northern Chinese stoneware. Many other manufacturers, now well established names, were unable to produce genuine porcelain but still made a name for themselves with high quality stoneware, such as Majolica from Italy, Wedgwood from England and Delft's Blue from Holland.

In the up-draught kiln they had the technology to produce high temperatures, although the Chinese down-draught kiln was somewhat superior at controlling the temperature. The problem of reproducing Chinese porcelain was essentially one of selecting the

material and the method of processing. Many, such as John Dwight of Fulham, who was granted a patent by Charles II in 1671, claimed to have discovered the secret of Chinese porcelain, but really only managed to make white stoneware.

In order to produce porcelain, the material has to remain or to become white on firing, and must be so strong that vessels with walls less than 3 mm thick can be produced. If the product needs to be made with walls thicker than 3 mm, even porcelain appears opaque. So, the major differences between stoneware and porcelain are that porcelain is white and can be made in such thin sections that it appears translucent. Stoneware could be made to look white, but had to be used in such a thickness that it was invariably opaque.

This situation prevailed for some time, until, in 1717, the secret was leaked from China by a Jesuit missionary, Father d'Entercolles. He performed his missionary work in a place called King-te-Tching, which, at that time, was the porcelain centre of China. Going amongst the people in their place of work he managed to acquire samples of the materials used. He sent the samples to a French friend of his, together with a detailed account of how the porcelain was manufactured. The samples and the description were passed on to M. de Reamur, a scientist, who was able to identify the components used by the Chinese as kaolin, silica and feldspar.

Kaolin, known as china clay, is a hydrated aluminosilicate. The silica is in the form of quartz, and remains as a fine dispersion after firing, and the feldspar is a mixture of sodium and potassium–aluminium silicates. These were mixed in proportions of 25–30% feldspar, 20–25% quartz and 50% kaolin. It should be said that by the early 1700s the Meissen factory in Dresden was already producing a very passable porcelain based on kaolin, silica and alabaster.

In a way, it is a little surprising that it took so long before the composition of the Chinese porcelain was unravelled. The art of making porcelain involves no complex chemistry, as the process is one of taking three rather common minerals (kaolin, feldspar and flint) and firing them at high temperatures. Once the mystery had been unravelled however, it did not take long for new porcelains to be developed in Europe. Soon it was possible to make it in any shade or tint, and its translucency gave such a depth of colour that it was not long before the dental potential of this material was recognised.

The dental application of porcelain dates from 1774, when a French apothecary named Alexis

Duchateau considered the possibility of replacing his ivory dentures with porcelain. Ivory, being porous, soaks up oral fluids and eventually becomes badly stained, as well as being highly unhygienic. Duchateau, with the assistance of porcelain manufacturers at the Guerhard factory in Saint Germain-en-Laye, succeeded in making himself the first porcelain denture. This was quite a feat, as the porcelain shrinks considerably on firing. This shrinkage had to be taken into account if the denture was going to fit at all well in the mouth. Since then, other materials such as vulcanite, and more recently polymethyl methacrylate, have helped to replace porcelain for denture applications.

Porcelain teeth, in conjunction with an acrylic denture base, are still extensively used. However, the most important application of dental porcelain is in the construction of veneers, inlays, crowns and bridges, where the aesthetic qualities of the porcelain are still superior to that of any other substitute for enamel and dentine.

Porcelains were the first materials used in the construction of the porcelain jacket crown. Many new materials that are described as porcelains have appeared on the market over recent years; these are, in fact, very different forms of ceramic when compared with the early porcelains.

CLINICAL SIGNIFICANCE

It is now more appropriate to use the general description of *dental ceramics*, within which the *dental porcelains* are but one group of materials.

COMPOSITION OF DENTAL PORCELAIN

The earliest dental porcelains were mixtures of kaolin, feldspar and quartz, and were quite different for earthenware, stoneware and domestic porcelain, as indicated in **Figure 3.4.2**. It was not until 1838 that Elias Wildman produced dental porcelain with the translucency and shades that reasonably matched those of the natural teeth. The compositions for domestic and dental porcelain are shown in **Table 3.4.1**.

Kaolin is a hydrated aluminium silicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and acts as a binder, increasing the ability to mould the unfired porcelain. It is opaque, however, and when present, even in very small quantities, it meant that the earliest dental porcelains lacked

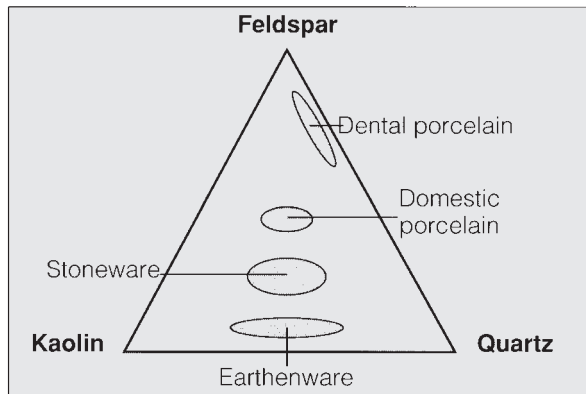


FIGURE 3.4.2 Relative composition of ceramic products based on feldspar, kaolin and quartz

Porcelain	% Kaolin	% Quartz	% Feldspar
Household	50	20–25	25–30
Dental	0	25	65

adequate translucency. Thus, for dental porcelains the kaolin was omitted and could therefore be considered to be a feldspathic glass with crystalline inclusions of silica.

The quartz remains unchanged during the firing process and acts as a strengthening agent. It is present as a fine crystalline dispersion throughout the glassy phase that is produced by the melting of the feldspar. The feldspar fuses when it melts, forming a glass matrix.

The feldspars are mixtures of potassium aluminosilicate ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) and sodium aluminosilicate, also known as albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). Feldspars are naturally occurring substances, so the ratio between the potash (K_2O) and the soda (Na_2O) will vary somewhat. This affects the properties of the feldspar, in that the soda tends to lower the fusion temperature and the potash increases the viscosity of the molten glass.

During the firing of porcelain there is always the danger of excessive pyroplastic flow, which may result in rounding of the edges and loss of tooth form. It is important that the correct amount of potash is present to prevent this. These alkalis are present either as a part of the feldspars, or they may be added as carbonates to

TABLE 3.4.2 Typical oxide composition of a dental porcelain

Material	wt %
Silica	63
Alumina	17
Boric oxide	7
Potash (K_2O)	7
Soda (Na_2O)	4
Other oxides	2

ensure the correct ratio. The typical oxide composition of a dental porcelain is presented in **Table 3.4.2**.

The porcelain powder used by the dental technician is not a simple mixture of the ingredients in **Table 3.4.2**. These powders have already been fired once. The manufacturer mixes the components, adds additional metal oxides, fuses them and then quenches the molten mass in water. The resultant product is known as a *frit*, and the process is known as *fritting*. A consequence of the rapid cooling is that large internal stresses build up in the glass, resulting in extensive cracking. This material can be ground very easily to produce a fine powder for use by the dental technician.

During the firing of a porcelain jacket crown for example, there is no chemical reaction taking place; the glass is simply melted above its glass transition temperature, when the particles fuse together by liquid phase sintering, and cooled down again. Thus, all that has happened is that the individual particles have fused together by sintering to produce a coherent solid.

The particle size distribution is critical in ensuring that the particles pack together as tightly as possible, in order that the shrinkage on firing is minimised. The average particle size is generally in the region of $25 \mu m$, with a wide distribution of other particle sizes such that the smaller particles fill the spaces in between the larger particles. Some porcelain powders have a multimodal particle size distribution to increase the packing density.

A number of other ingredients will be present in dental porcelain powders. These include metal oxides, which provide the wide variety of colours of the porcelain; for example, oxides of iron act as a brown pigment, copper as a green pigment, titanium as a yellowish-brown pigment, and cobalt imparts a blue colour. A binder, consisting of starch and sugar, may also be present to help in the manipulation of the powders.

PROCESSING

The production of a porcelain jacket crown involves three technical stages:

- compaction
- firing
- glazing.

Compaction

In the construction of a porcelain jacket crown, the porcelain powder is mixed with water and made into a paste. This paste is applied to the die, which has been coated beforehand with a very thin platinum foil to allow the porcelain crown to be separated from the die and transported to the furnace.

A porcelain jacket crown is made from a number of porcelain powders because it is impossible to recreate all of the aesthetic features of a tooth by the use of a single porcelain. Conventionally, three basic types of porcelain powder are used. These are: an opaque shade to mask the colour of the underlying structure, which may be an amalgam or a metal post and core construction; then a dentine shade is applied; and finally an enamel shade. The exact enamel shade is selected from a guide that is used for comparison with the shade of the natural tooth. The final construction is as shown in **Figure 3.4.3**.

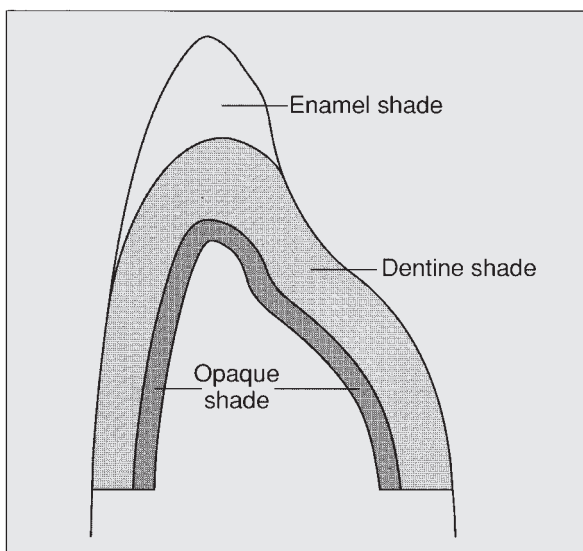


FIGURE 3.4.3 Porcelain build-up for a jacket crown

The powder is mixed with water and a binder to form a slurry, which can be applied to the die in a number of ways, such as spatulation, brush application, whipping or vibrating, all of which are aimed at compacting the powder. The objective of these condensation techniques is to remove as much water as possible, resulting in a more compact arrangement with a high density of particles that minimises the firing shrinkage. The particle size and shape are extremely important, as they affect the handling characteristics of the powder and have an effect on the amount of shrinkage on firing. The binder helps to hold the particles together, as the material is extremely fragile in this so-called *green state*.

Firing

Initially, the crown is heated slowly in the open entrance to the furnace. This is carried out in order to drive off excess water before it has a chance to form steam. If the water in the mix was allowed to turn into steam, it would cause the fragile powder-compact to crack as the steam tried to escape to the surface. Once the compact has been dried, it is placed in the furnace and the binders are burnt out. Some contraction occurs during this stage.

When the porcelain begins to fuse, continuity is only achieved at points of contact between the powder particles. The material is still porous, and is usually referred to as being at the *low bisque stage*. As the exposure to the elevated temperature continues, more fusion takes place as the molten glass flows between the particles, drawing them closer together and filling the voids. A large contraction takes place during this phase (~20%), and the resultant material is virtually non-porous. The cause of the high shrinkage of porcelain on firing is therefore due to the fusion of the particles during sintering, as the powder particles are brought into close contact.

The firing of the porcelain must be carried out exactly according to the manufacturer's instructions. If the crown should remain in the furnace for too long it will lose form, due to *pyroplastic flow* (flow of the molten glass), and will become highly glazed.

A very slow cooling rate is essential in order to avoid the possibility of cracking or crazing. The furnaces available usually offer a considerable degree of automation, and can be used for air- or vacuum-firing. Vacuum-firing produces a denser porcelain than air-firing, as air is withdrawn during the firing process. Fewer voids are formed, resulting in a stronger crown

with a more predictable shade. Areas of porosity in air-fired porcelain alter the translucency of the crown, as they cause light to scatter. An additional problem is that air voids will become exposed if grinding of the superficial layer should be necessary, giving rise to an unsightly appearance and a rough surface finish.

Glazing

There will always be some porosity in the porcelain, with small air voids being exposed at the surface. These will allow the ingress of bacteria and oral fluids and act as potential sites for the build-up of plaque. To avoid this, the surface is glazed to produce a smooth, shiny and impervious outer layer. There are two ways in which this can be achieved:

1. Glasses that fuse at low temperatures are applied to the crown after construction, and a short period at a relatively low temperature is sufficient to fuse the glaze.
2. Final firing of the crown under carefully controlled conditions fuses the superficial layer to an impervious surface glaze.

PROPERTIES OF DENTAL PORCELAIN

Dental porcelain is chemically very stable, and provides excellent aesthetics that do not deteriorate with time. The thermal conductivity and the coefficient of thermal expansion are similar to those of enamel and dentine, so, in the presence of a good marginal seal, marginal percolation is less likely to be a problem.

Although the compressive strength of dental porcelain is high (350–550 MPa), its tensile strength is very low (20–60 MPa), which is typical of a brittle solid. The material, being primarily a glass, lacks any fracture toughness. The maximum strain that a glass can withstand is less than 0.1%. Glasses are extremely sensitive to the presence of *surface microcracks*, and this represents one of the major drawbacks in the use of dental porcelain. On cooling from the furnace temperature, the outside of the porcelain will cool more rapidly than the interior, particularly as the porcelain has a low thermal conductivity. The outside surface contracts more than the inside initially, resulting in a compressive load on the outside and a residual tensile stress on the inside, as the interior is being prevented from shrinking by the outside skin.

CLINICAL SIGNIFICANCE

If the differential dimensional change is sufficiently high, the internal surface layer that is under tension will rupture to relieve the stresses. This will result in the fitting surface of the crown containing a large number of minute cracks, and it is these that will ultimately cause the crown to fracture catastrophically (Figure 3.4.4).

The application of a glaze with a slightly lower coefficient of expansion would potentially fill in the cracks and also place the surface under compression. Unfortunately, this is not possible on the fitting surface of the crown, as it may result in the crown not seating properly. The porcelains were thus not strong enough to be used for the manufacture of multiunit bridges, and problems even arose for anterior porcelain jacket crowns, especially when they were used in situations of heavy occlusion. The tiny surface flaws in the interior of the crown act as initiating sites for catastrophic failure. The inherently low tensile strength of feldspathic porcelains (<60 MPa) restricted their use to very low stress bearing anterior applications. The answer is to provide a high strength support for the

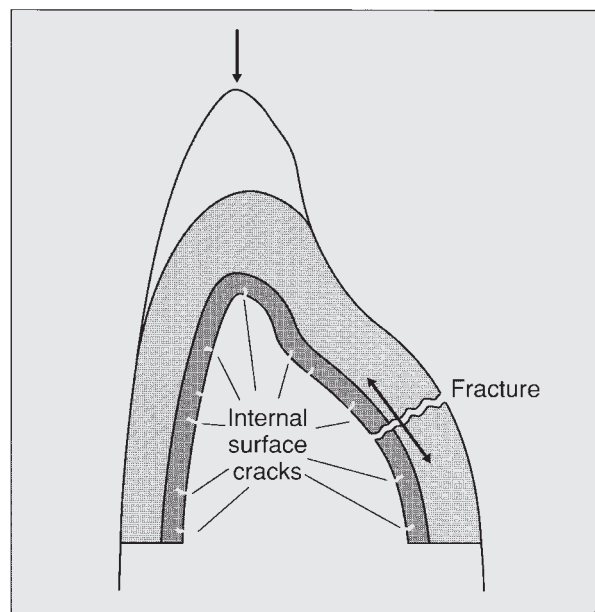


FIGURE 3.4.4 Palatal fracture of a porcelain jacket crown initiated from an internal surface flaw

porcelain and nowadays a number of different systems are available.

CLASSIFICATION OF MODERN DENTAL CERAMICS

One of the most serious drawbacks with the early dental porcelains described above was their lack of strength and toughness, which seriously limited their use. As early as 1903, Land described, in an issue of *Dental Cosmos*, how to make porcelain crowns, but came up against the problem that the crowns would break too easily. Similarly, Pincus described the concept of the ceramic veneer in an article in the *Californian Dental Association Journal* of 1938, but was also frustrated by the lack of strength of the porcelains available at the time. By that time, for reasons of aesthetics, the porcelain used contained little or no kaolin.

In order to overcome the problem of lack of strength and toughness of dental porcelains, there are two possible solutions to the problem. One solution is to provide the dental porcelain with support from a stronger substructure. The other option is to produce ceramics, which are stronger and tougher. In this context, it is possible to consider dental ceramics to fall into three categories, based on the nature of the supporting structure:

- reinforced ceramic core systems
- resin-bonded ceramics
- metal–ceramics.

In each case the philosophy is to provide a high strength supporting structure for the ceramic providing the aesthetic finish. Obviously, the ideal ceramic would have both the strength and the aesthetics to perform both functions.

In the case of the reinforced ceramic core systems, the support for the aesthetic ceramic is provided by another ceramic material, which has the necessary high strength and toughness but may lack the desired aesthetics.

In contrast, in the case of the resin-bonded ceramic, the support of the ceramic is provided by the tooth structure itself, by bonding the aesthetic ceramic directly to the enamel and dentine. In this instance the ceramic provides the necessary aesthetics and the strength is provided by the ability to bond to the tooth tissues.

CLINICAL SIGNIFICANCE

For resin-bonded ceramic restorations, success depends on the quality of the bond, as bond failure will lead to a loss of support of the ceramic restoration and eventually result in its fracture.

This approach only became possible with the advent of enamel and dentine bonding procedures discussed in Chapter 2.5 and resin–ceramic bonding discussed in Chapter 3.6. A combination of aesthetics and high strength would be ideal, as this removes the high reliance on the bond and also provides the opportunity to develop resin-bonded ceramic bridges.

In the case of the metal–ceramic restoration, the aesthetic ceramic is supported by a strong and tough metal. This system is considered in detail in Chapter 3.5.

A detailed account of the procedures and materials for the cementation of the ceramic and metal–ceramic restorations can be found in Chapter 3.6.

REINFORCED CERAMIC CORE SYSTEMS

The early work by Land and others had shown that one of the problems with the all-ceramic anterior crown was that the porcelain would fracture from the fit surface outwards. Some improvements in the strength of porcelain was achieved by the introduction of vacuum firing furnaces, which helped to minimise porosity and raised the flexural strength of the porcelain from 20–30 MPa to approximately 50–60 MPa. However, this did not prove to be adequate and thus the search was on for a core material that would provide the necessary strength and toughness to prevent fractures arising from cracks propagating from the fit surface of the crown.

Since ceramics tend to fail at the same critical strain of ~0.1%, one means of achieving an increased fracture strength is to increase the elastic modulus of the material. If, at the same time, the propagation of cracks is made more difficult, such that a greater strain can be supported, a higher strength ceramic will result (**Figure 3.4.5**). The flexural strengths of a number of ceramics are shown in **Table 3.4.3**. As the tensile strength is a difficult property to measure (giving rise

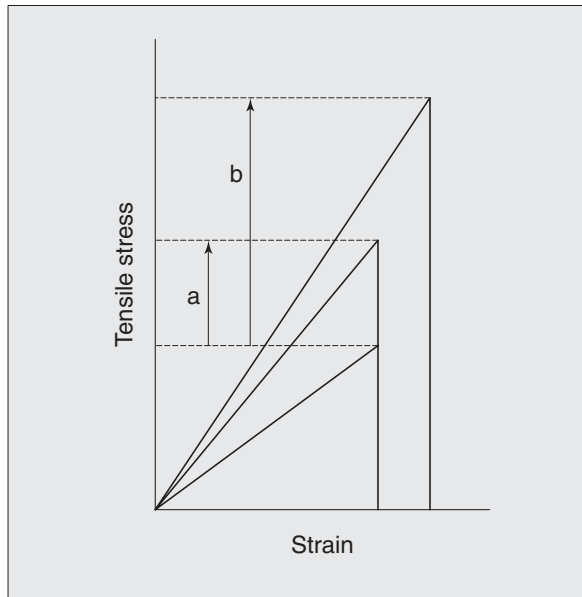


FIGURE 3.4.5 Improvements in the strength of ceramics by (a) raising the elastic modulus and (b) increasing the resistance to crack propagation

TABLE 3.4.3 Typical strength values for high strength ceramics

Type of ceramic	Flexural strength (MPa)
Hot-pressed silicon nitride	800–900
Hot-pressed silicon carbide	400–750
Partially stabilised zirconia	640
Alumina 98% pure	420–520

to a wide degree of scatter in the data), it is common practice to determine the flexural strength. Although the silicon nitrides and carbides are attractive from the viewpoint of strength, they are not suitable because of the difficulties associated with the manufacture of individual crowns, the colour differences and the mismatch in the coefficient of thermal expansion.

CLINICAL SIGNIFICANCE

Alumina and zirconia are white and strong and therefore these ceramics are now used in a number of dental ceramic systems.

In the mid-1960s, McLean and Hughes developed a core material based on the reinforcement of a feldspathic glass with alumina, commonly referred to as

the alumina-reinforced porcelain jacket crown. Since then, other systems have been developed. In the 1980s the glass-infiltrated high strength ceramic cores were developed (In-Ceram, Vita Zahnfabrik, Bad Säckingen, Germany) and in the 1990s the all-alumina core made its first appearance (Techceram, Techceram Ltd; Procera AllCeram, Nobel Biocare).

Alumina-Reinforced Porcelain Jacket Crown (PJC)

The alumina-reinforced feldspathic core was introduced in the early 1960s by Hughes and McLean. The material consists of a feldspathic glass containing 40–50% alumina (**Figure 3.4.6**). The alumina particles are far stronger than the glass, are more effective at preventing crack propagation than quartz and act as crack stoppers (**Figure 3.4.7**). Whereas the flexural strength of feldspathic porcelain is at best some 60 MPa, this is raised to 120–150 MPa for the aluminous core porcelains.

In the construction of a crown, the opaque shade shown in Figure 3.4.3 is made with an aluminous core porcelain. It is still necessary to use the weaker dentine and enamel shades of the feldspathic porcelains because it is not possible to produce aluminous porcelains with the required translucency; the alumina causes the porcelain to appear dull and opaque.

The main application of the alumina-reinforced porcelain jacket crown is for the restoration of anterior teeth. Although the improvement in strength is considerable, it is still insufficient to allow its use posteriorly and the construction of even a three-unit bridge is out of the question.

CLINICAL SIGNIFICANCE

Yet stronger core materials are needed if the use of ceramics is to be extended to the posterior teeth.

Glass-infiltrated High Strength Ceramic Core Systems

The addition of alumina to the feldspathic glass during the prefitting process limits the amount of alumina that can be incorporated to about 40–50 vol. %. An alternative approach has been adopted in a new system called In-Ceram (Vita). This core material has an alumina content of ~85%.

A ceramic core is formed onto a refractory die from a fine slurry of alumina powder by a process

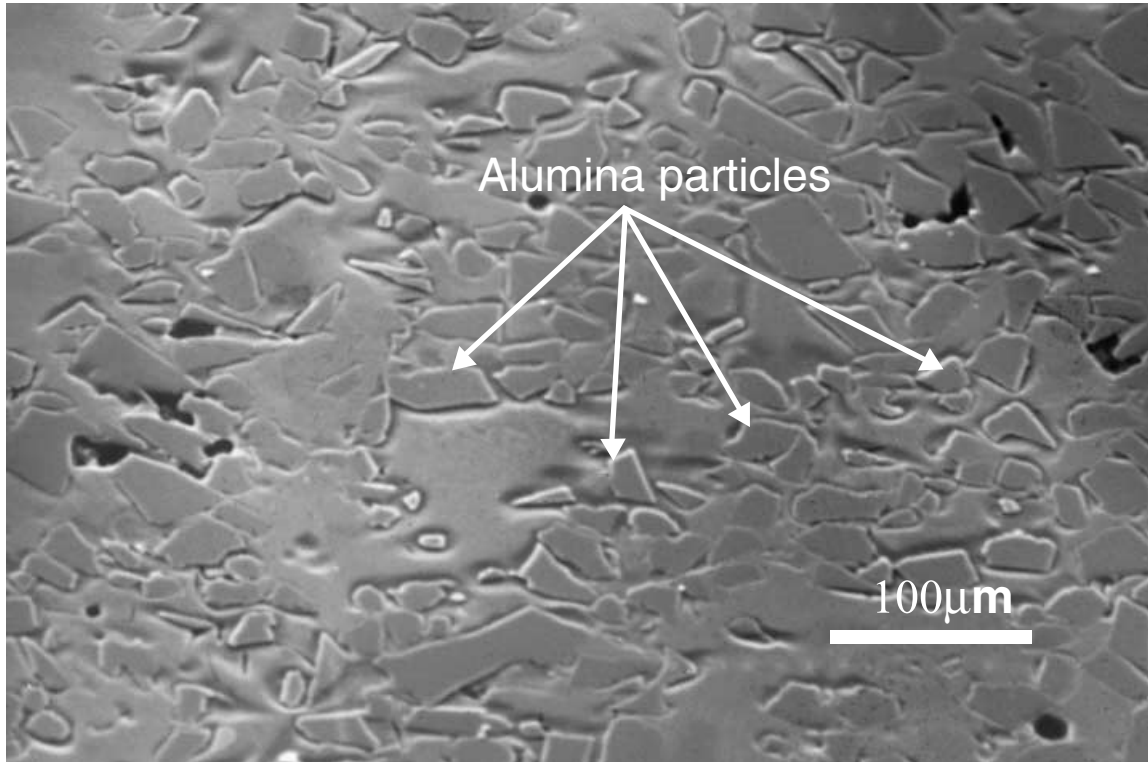


FIGURE 3.4.6 SEM of an alumina-reinforced core material showing the alumina particles embedded in a glassy matrix composed of feldspar

known as slip casting. After the die has dried, it is sintered for 10 hours at 1120°C. The melting temperature of alumina is too high to produce full densification of the powder by liquid phase sintering, and solid phase sintering alone occurs. Consequently, the coping thus created is only just held together at the contact points between the alumina particles, and a porous structure is the result. The strength of this porous core is only about 6–10 MPa. The porous structure is then infiltrated with a lanthanum glass, which has a low viscosity when fired at 1100°C for 4–6 hours. The molten glass is able to penetrate into the pores, producing a dense ceramic. The aesthetics and functional form are then achieved by the use of conventional feldspathic dental ceramics.

CLINICAL SIGNIFICANCE

Very high flexural strength values (400–500 MPa) have been claimed for this core ceramic, which makes this system suitable for anterior and posterior crowns, with excellent results.

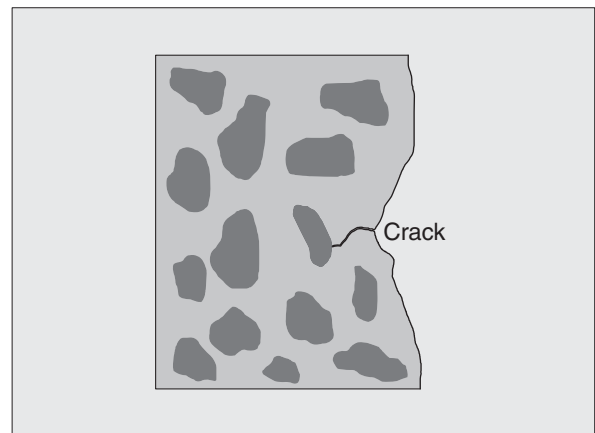


FIGURE 3.4.7 Alumina particles acting as crack stoppers

Several attempts have also been made at producing anterior cantilever and posterior three-unit bridges; this is a highly ambitious use of ceramics but shows considerable promise.

A similar approach has been adopted with spinel

(MgAl_2O_4) or zirconia replacing the alumina. The In-Ceram-Spinel offers superior aesthetics over the In-Ceram-Alumina at a slightly reduced flexural strength (~ 350 MPa) and is recommended for inlays. The In-Ceram-Zirconia is based on the In-Ceram-Alumina, but with the addition of 33 wt % zirconia, and produces a ceramic core with a strength of some 700 MPa.

An alternative approach to the slip casting route described above is now also available for the CAD-CAM production route using either the CEREC system from Siemens or the Celay system from Vident. The In-Ceram-Spinel/Alumina/Zirconia blocks from which the restorations are machined are produced by dry-pressing the powder such that the open pore structure is denser and more homogeneous, leading to a yet higher flexural strength after glass infiltration.

Pure Alumina Cores

It would seem a natural extension from the alumina-reinforced core systems described above to consider the possibility of a pure alumina core. There are at least two systems on the market that offer pure alumina cores, the Procera AllCeram (Nobel Biocare AB, Gotenburg, Sweden) and the Techceram system (Techceram Ltd, Shipley, UK). The potential advantages are increased strength and superior translucency compared with the glass-infiltrated core materials.

Production of the Procera AllCeram core involves producing a die from the impression, digitising the geometry of the desired coping using specially designed computer software, and transferring this information down a modem to a laboratory in Stockholm. This is all done by a designated dental laboratory that is a member of the Procera Network. The coping is produced by a special process, which involves sintering 99.5% pure alumina at $1600\text{--}1700^\circ\text{C}$ such that it is fully densified. The coping is then returned to the dental laboratory for building in the crown's aesthetics using compatible feldspathic glasses. Turnaround time is approximately 24 hours. The flexural strength of the Al_2O_3 core materials is in the region of 700 MPa, and thus similar to that achieved with the In-Ceram-Zirconia.

The Techceram system uses quite a different approach. In this system the impression can be sent to Techceram Ltd, who will produce a special die onto which the alumina core is deposited using a thermal gun-spray technique. This process produces an alumina core with a density of 80–90%, which is subsequently

sintered at 1170°C to achieve optimum strength and translucency. The alumina coping is then returned to the dental laboratory, where the ceramist will develop the final contour and aesthetics using conventional feldspathic glasses.

CLINICAL SIGNIFICANCE

One of the potential benefits of producing a pure alumina core is that the translucency is claimed to be better than that of the glass–alumina composite structures.

One drawback with all the high strength core systems described above is that none of them is amenable to acid etching to produce a micromechanically retentive surface, although some bonding with the cementing medium will arise owing to the roughness of the surface from processing. Since the fit surface is made of alumina rather than silica, no coupling agents are available that can effectively bond the core to resins. Without an effective coupling agent or an ideal micromechanically retentive surface, these systems cannot be resin-bonded to the tooth tissues and will not derive the added benefit associated with resin-bonded ceramic restorations.

CLINICAL SIGNIFICANCE

The reinforced core ceramic restoration must rely primarily on the strength and toughness of the core material and appropriate design to resist the forces of occlusion.

RESIN-BONDED CERAMICS

One way in which the traditional approach of cemented restorations is being challenged is the development of new adhesive techniques. These have extended the use of ceramics to areas not previously thought possible. The combination of adhesion to enamel, dentine and ceramic and improved strength characteristics of the ceramics has produced restorations with excellent mechanical integrity. In fact, the adhesive bond has the effect of eliminating the internal surface flaws and thus reduces the potential for fracture. This has led to a growth in the use of ceramics for crowns, veneers and inlays.

The concept of using ceramics as veneers is not new, and can be traced back to Dr Charles Pincus of

Beverly Hills, who constructed porcelain veneers for actors in Hollywood. The porcelain veneers were baked on platinum foil and retained on the teeth by denture powder. However, the veneers often broke because the thin porcelain was brittle and they were frequently removed from the teeth. When acrylic resin was introduced in 1937, he switched to this material for the production of veneers for the acting profession. This eventually developed into the use of composite veneers, and ceramics were not used for a long time.

The re-emergence of all-ceramic veneers can be traced back to the early 1980s. At that time Dr Horn, in America, fabricated veneers on a foil backing and discovered that the fitting surface could be etched with hydrofluoric acid, thus improving the micromechanical retention (see Chapter 3.6). Using the phosphoric acid-etch technique on enamel he was able to bond the ceramic veneers permanently to the teeth with a resin-based composite. Bonding to ceramic has since been improved by the additional use of a silane coupling agent.

CLINICAL SIGNIFICANCE

Before the advent of resin-bonded ceramic veneers, the only options available were the composite veneer, the porcelain jacket crown and the metal-ceramic crown.

Ceramic veneers are considered superior to composites because of their superior aesthetics, colour stability, surface finish, abrasion resistance and tissue compatibility. They are also chemically very stable and have a coefficient of expansion similar to that of enamel. The finishing of porcelain veneers is more difficult than that of composites due to their high hardness. The thin feathered margins are more easily damaged than the margins of crowns, both in the laboratory and in the surgery. The ceramic veneers have the distinct advantages over crowns that improved aesthetics can be achieved with minimal tooth reduction, and the palatal surface of the tooth is unchanged so that incisal guidance is maintained.

Since then, there has been a major development of new ceramics suitable for use as resin-bonded all-ceramic restorations. These new materials have allowed the extension of the use of all-ceramic restorations from veneers to anterior and posterior crowns and inlays. The materials available for resin-bonded ceramic restorations are in essence varieties of a special

group of ceramics known as glass ceramics. The nature of glass ceramics will be considered next. The various dental glass-ceramics that have been developed for resin-bonded ceramic restorations will then be described, together with some of the new processing techniques that have evolved at the same time.

Glass Ceramics

Glass ceramics were first developed by Corning Glass Works in the late 1950s. In principle, an article is formed while liquid, and a metastable glass results on cooling. During a subsequent heat treatment, controlled crystallisation occurs, with the nucleation and growth of internal crystals. This conversion process from a glass to a partially crystalline glass is called *ceraming*. Thus, a glass ceramic is a multiphase solid containing a residual glass phase with a finely dispersed crystalline phase. The controlled crystallisation of the glass results in the formation of tiny crystals that are evenly distributed throughout the glass. The number of crystals, their growth rate and thus their size are regulated by the time and temperature of the ceraming heat treatment.

There are two important aspects to the formation of the crystalline phase: crystal nucleation and crystal growth. The schematic in **Figure 3.4.8** shows that the rate of crystal nucleation and the rate of crystal growth are at a maximum at different temperatures. The ceraming process consequently involves a two-stage heat treatment. The first heat treatment is carried out at the temperature for maximum nucleation of crystals, to maximise the number of crystals formed. The material temperature is then raised, after a suitable period of time, to the higher temperature to allow crystal growth. It is held at the higher temperature until the optimum crystal size is formed.

To ensure a high strength for the glass ceramic it is important that the crystals are numerous and are uniformly distributed throughout the glassy phase. The crystalline phase will grow during ceraming, and can eventually occupy from 50% to nearly 100% of the material.

Mechanical Properties of Glass Ceramics

The mechanical properties are believed to be greatly influenced by:

- particle size of the crystalline phase
- volume fraction of the crystalline phase
- interfacial bond strength between phases

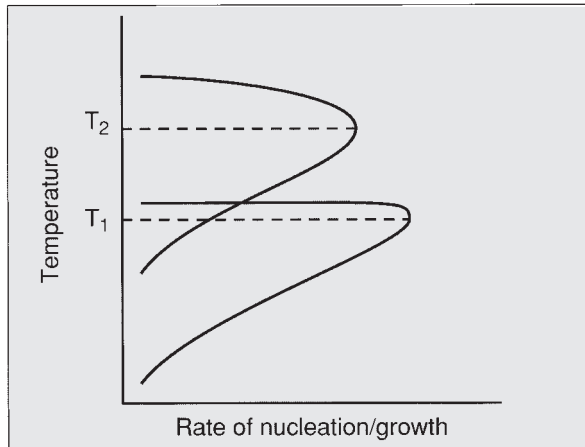


FIGURE 3.4.8 Rate of nucleation (T_1) and growth (T_2) of crystals in a glass ceramic

- differences in elastic moduli
- differences in thermal expansion.

Fracture in brittle solids is nearly always initiated at a small internal or surface defect, such as a microcrack, that acts as a stress raiser. If the crystalline phase is relatively strong, then the cracks will form in the glassy phase. The dimension of these microcracks can thus be limited to the distance between the crystalline particles. Therefore, the critical parameter is the mean free path, in the glassy phase, L_s , which is given by:

$$L_s = d(1 - V_f)/V_f$$

where d is the crystal diameter and V_f is the volume fraction of the crystalline phase. Thus, the smaller the crystals and the larger the volume fraction of the crystals, the shorter the mean free path will be, and, consequently the greater the strength of the material.

CLINICAL SIGNIFICANCE

A feature of glass ceramics is that the size and the amount of the crystalline phase can be carefully controlled during the ceraming process.

Most glass ceramics are opaque or cloudy and would not be suitable for dental use. The first glass ceramic employed in dentistry was introduced by MacCulloch in 1968 for the construction of denture teeth, and was based on the $\text{Li}_2\text{O} \cdot \text{ZnO} \cdot \text{SiO}_2$ system. At the time, the use of acrylic denture teeth was becoming popular, and the idea of glass ceramics was not

exploited further. Now we have a wide range of glass ceramics and processing routes for the construction of resin-bonded ceramic restorations.

Leucite-reinforced Feldspar Glass Ceramics

The ceramic used in the original experiments of Horn was a leucite (KAlSi_2O_6)-containing feldspathic glass, which he used in the construction of metal–ceramic restorations (see Chapter 3.5). This ceramic was optimised with regard to being able to bond to the metal surface. The ceramics used now for resin-bonded ceramic restorations are a modified version of the ceramic used by Horn. They differ from the ceramic used in metal–ceramics primarily in that the composition and microstructure have been changed in order to produce the best leucite crystalline phase distribution from the point of view of strength, as compatibility with a metal framework is no longer a consideration. This is achieved by careful control of the composition and the ceraming heat treatment.

Whereas the leucite-containing ceramics used in metal–ceramic restorations have a flexural strength of the order of 30–40 MPa, the leucite-reinforced glass ceramics have flexural strengths of up to 120 MPa. A typical example of the structure of leucite-reinforced ceramic is shown in **Figure 3.4.9**.

The construction of ceramic restorations using leucite-reinforced feldspars can be done either by sintering, using a modified version of the sintering process described earlier to construct the porcelain jacket crown, or by a process known as hot-pressing.

Sintering Process (e.g. Fortress and Optec-HSP)

In the sintering process, a slurry of the ceramic powder is applied to a refractory die (as opposed to a Pt foil coated die in the case of the porcelain jacket crown), dried and subsequently fired in a porcelain furnace. Multiple layers can be built up to develop characterisation. Great skill is required by the dental laboratory technician to get the best aesthetics and appropriate contour.

Hot-pressing (e.g. Empress, Ivoclar-Vivadent, Schaan, Liechtenstein)

In order to surmount the problems of the inherent inaccuracies of fit of the sintered ceramics, due to the high firing shrinkage, attention has recently been paid to the possibility of using glass ceramics, which employ a casting process for the manufacture of crowns, veneers and inlays. Hot-pressing is one such approach.

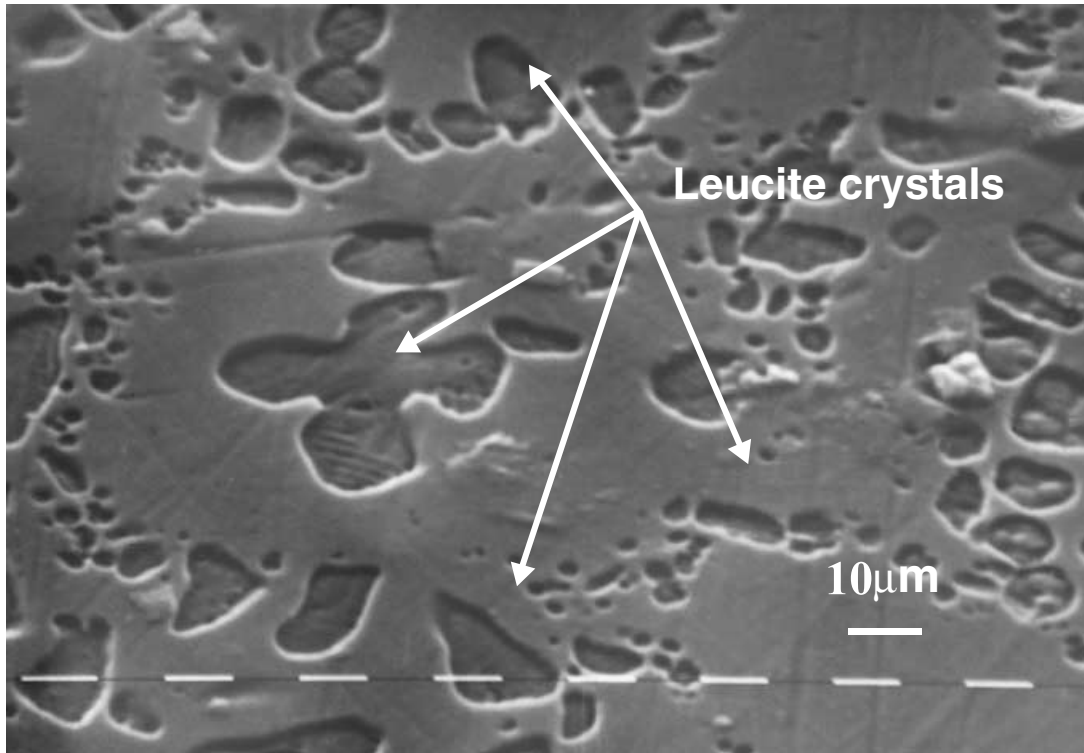


FIGURE 3.4.9 SEM of the structure of a leucite-reinforced ceramic

This method utilises parts of the lost-wax casting technique. As in lost-wax casting, a wax pattern is produced, which is then invested in a refractory die material. The wax is burnt out to create the space to be filled by the leucite-reinforced glass ceramic. A specially designed pressing furnace is then used to fill the mould space from a pellet of the glass ceramic using a viscous flow process at a temperature of 1180°C (Figure 3.4.10).

CLINICAL SIGNIFICANCE

The potential benefit of the hot-pressing route is that a higher degree of marginal fit can be achieved than with the sintering process.

For posterior restorations, the final shading may be done by applying surface stains. For anterior restorations, the crown or veneer is cut back and a powdered form of the leucite-reinforced glass ceramic is bonded using the conventional sintering technique. The aesthetic results are excellent due to the high translucency, fluorescence and opalescence of the

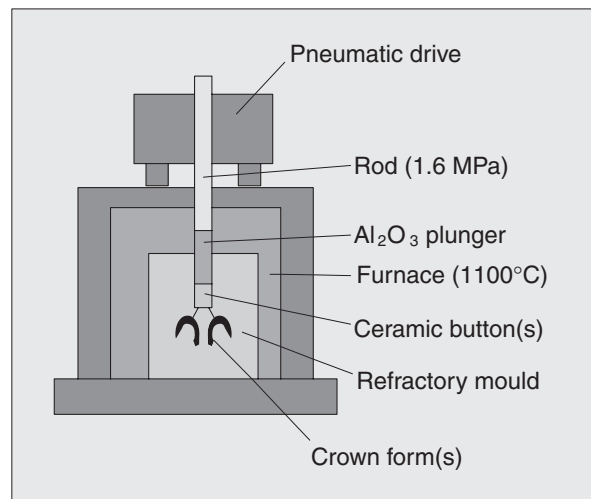


FIGURE 3.4.10 Schematic of the hot-pressing route for producing a leucite-reinforced glass ceramic restoration

leucite-reinforced glass ceramic; however, the mechanical strength is insufficient for this class of glass ceramic to be used in the construction of all-ceramic bridges.

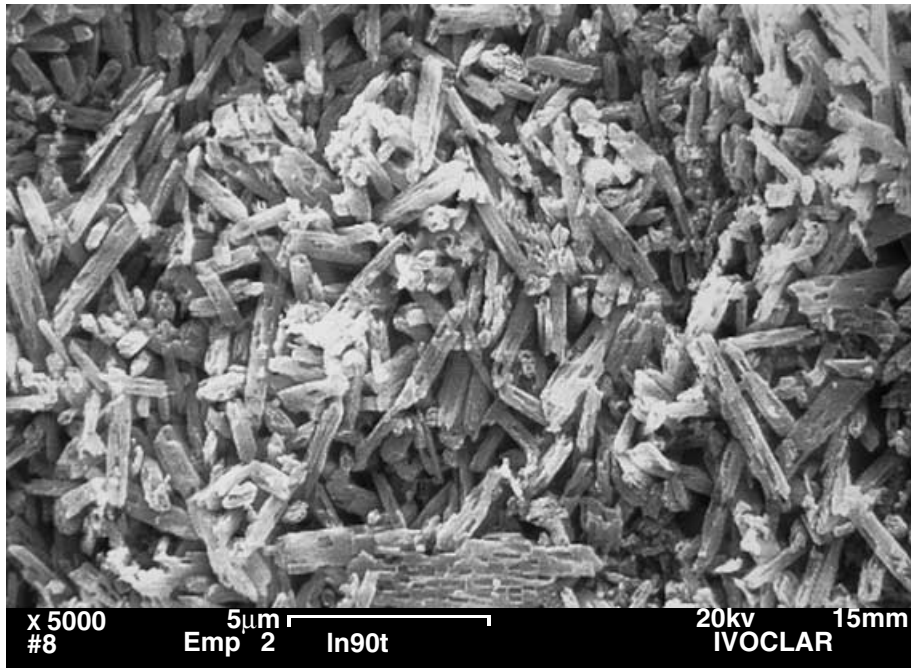


FIGURE 3.4.11 SEM of the microstructure of a lithium disilicate glass ceramic, showing the interlocking needle-like crystals. (Courtesy of Ivoclar-Vivadent UK Ltd, Leicester, UK)

Lithium Disilicate and Apatite Glass Ceramics

In order to be able to extend the use of resin-bonded ceramic restorations and possibly use them for bridge construction, a glass ceramic based on a $\text{SiO}_2\text{--Li}_2\text{O}$ system has been developed (Empress II, Ivoclar-Vivadent, Schaan, Liechtenstein).

The crystalline phase that forms is a lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) and makes up some 70% of the volume of the glass ceramic. Lithium disilicate has an unusual microstructure in that it consists of many small interlocking plate-like crystals that are randomly oriented (**Figure 3.4.11**). This is ideal from the point of view of strength because the needle-like crystals cause cracks to deflect, branch or blunt; thus, the propagation of cracks through this material is arrested by the lithium disilicate crystals, providing a substantial increase in the flexural strength.

A second crystalline phase, consisting of a lithium orthophosphate (Li_3PO_4) of a much lower volume, is also present.

The mechanical properties of this glass ceramic are far superior to that of the leucite glass ceramic, with a flexural strength is in the region of 350–450 MPa and a fracture toughness approximately three times that of the leucite glass ceramic.

CLINICAL SIGNIFICANCE

The high strength of lithium disilicate glass ceramics creates the possibility of not only producing anterior and posterior crowns, but also all-ceramic bridges.

The glass ceramic is claimed to be highly translucent due to the optical compatibility between the glassy matrix and the crystalline phase, which minimises internal scattering of the light as it passes through the material. The processing route is the same as the hot-pressing route described above, except that the processing temperature, at 920°C , is lower than for the leucite glass ceramic.

For the alumina-based core systems described earlier it is possible to use feldspathic glasses to provide the aesthetic surface layer, as their coefficients of expansion are closely matched at $\sim 7\text{--}8\text{ ppm}/^\circ\text{C}$. For the leucite glass ceramics the layering ceramic is identical to the core ceramic and so a mismatch in coefficient of expansion does not arise. However, for the lithium disilicate glass ceramic the coefficient of expansion is greater than $10\text{ ppm}/^\circ\text{C}$ and consequently a new compatible layering ceramic had to be developed. This new layering ceramic is an apatite glass ceramic. The

crystalline phase formed on ceraming is a hydroxy-apatite ($\text{Ca}_{10}(\text{PO}_4)_6\cdot 2\text{OH}$), which is the same basic constituent from which enamel is made. Thus, it represents a material that, at least in composition, is the closest match to enamel that has been achieved so far.

Fluoromica Glass Ceramics (e.g. Dicor)

Fluoromicas are products based on the composition $\text{SiO}_2\cdot\text{K}_2\text{O}\cdot\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$, with the addition of some fluorides to impart fluorescence in the prostheses, in a way similar to that encountered in the natural dentition. For this composition, the ceraming process results in the nucleation and the growth of tetrasilicate mica crystals within the glass. As with the lithium disilicate glass ceramic, the crystals are needle-like in shape and arrest the propagation of cracks through this material. Mechanical property measurements suggest the flexural strength is in the region of 120–150 MPa, which, when combined with the adhesion to tooth tissues, may just be adequate for posterior crowns but is insufficient for the construction of all-ceramic bridges.

The passage of light through the material is affected by the crystal size and the difference in the refractive indices of the glass phase and the crystalline phase. If the crystals are smaller than the wavelength of visible light (0.4–0.7 μm) the glass will appear transparent. The refractive index of the small mica crystals is closely matched to that of the surrounding glass phase, such that the tendency for light to scatter is lower than for the aluminous porcelains.

CLINICAL SIGNIFICANCE

This produces a translucency close to that of enamel.

The processing of this glass ceramic involves the same principles as for the lost-wax casting process of metallic restorations. The restoration is waxed up on a die, using conventional materials. The pattern is removed from the die and invested in a special phosphate-bonded investment. Then an ingot of the castable ceramic material is placed in a special crucible and centrifugally cast at a temperature of 1380°C. The casting then requires a further heat treatment to create the crystalline phase and develop the strength. The desired shade is achieved by firing self-glazing shading porcelains on the surface. The concept of producing ceramic restorations using a casting technique is by no means new, and was first attempted in the 1920s. It is only with the recent introduction of the castable glass ceramics that this has become possible.

SUMMARY

There has been a revolution in the provision of ceramics for dental restorations in the last 15 years, such that now all-ceramic restorations can be used both anteriorly and posteriorly. It is even possible to consider the limited use of all-ceramic bridges. There is no doubt that new materials and processing routes will continue

TABLE 3.4.4 The relative merits of a number of ceramic crown systems

System	Aesthetics			Relative cost			Popularity			Strength		
	High	Medium	Low	High	Medium	Low	High	Medium	Low	High	Medium	Low
<i>Porcelain jacket crown</i>												
Alumina-reinforced core			√			√			√			√
Glass-infiltrated alumina core	√			√					√	√		
Pure alumina core	√				√				√	√		
<i>Resin-bonded ceramic</i>												
Refractory die	√					√	√					√
Casting system		√			√				√			√
Hot-pressed leucite reinforced		√			√		√					√
Hot-pressed lithium disilicate reinforced	√				√			√				√

to be developed and that ceramics will play a growing role in the provision of aesthetic restorations. Deciding between different ceramic systems will be a difficult task: the relative merits that might be considered in the selection process are summarised in *Table 3.4.4*.

CLINICAL SIGNIFICANCE

There will be a growing need for dental practitioners to be aware of the rapidly changing field of dental ceramics to ensure that the correct choice is made for each patient.

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