

Chapter 2

Selection Criteria of Ceramics for Medical Applications

2.1 Biocompatibility

Biocompatibility relates to the actions of the biomaterials when brought in contact with the living tissues and how these materials are able to integrate and react with the surrounding tissue. Biocompatibility is defined as:

“The ability of a material to function in a specific application in the presence of an appropriate host response”

The biocompatibility is the most important issue for the application of medical ceramics whether biopassive, bioactive, or resorbable ceramics. Medical ceramic materials often include glasses, glass ceramics, and ceramic–polymer bioactive composites. The ceramics may be manufactured either in porous or in dense form, in bulk or in granules or in the form of coating layers. The biocompatibility is considered to be one of the most beneficial factors in using synthetic ceramics innovations in medicine. Any new glasses and glass–ceramics developed for medical purposes should possess this extremely important property of biological compatibility with living tissue.

During the past three decades, there have been major advances in the development of medical ceramics for skeletal repair and reconstruction and the biological side effects of dental ceramics compared with other restorative materials is considered to be low. For example, restorative dental ceramics are generally considered to be the most biocompatible of all dental materials. They are not generally known to cause biological reactions, except for wear on the opposing dentition and/or restorations. All implanted dental devices must fulfill the requirement of being biocompatible and the bioactivity of dental ceramics will differ according to the proposed application.

A range of tests can be conducted to establish the biocompatibility of a biomaterial. These include in vitro test for cytotoxicity, microbial test to determine whether or not the material inhibits or stimulate the growth of microorganisms and genotoxicity/mutagenicity and carcinogenicity tests to assess possible systemic

reactions. There is also a range of *in vivo* test that can be conducted, which include animal implantation tests to assess the local tissue response based on histological assessments, systemic toxicity tests such as LD_{50} (lethal dose for 50% of the test animals after oral uptake), sensitization, and/or irritation tests or pulp tests to determine the specific local reactions when considered relevant.

The preclinical evaluation of the cytotoxicity of biomaterials is conducted according the methods described in ISO 7405:1997. These tests generally involve producing a monolayer of cells on the surface of the material and monitoring the cellular response. The relative toxicity of materials can be determined by measuring cell death using an Alamar Blue staining technique from which it is possible to calculate the LD_{50} level of exposure. Further research is in process to develop more sophisticated models such as 3D skin and oral mucosal models that can examine the histology and measure local inflammatory markers.

Another aspect of the biocompatibility of ceramics is the potential for a radioactive component to be incorporated as one uses a wide range of natural minerals. For example, some of the products used in the early 1990s raised concerns about radioactivity because of impurities such as uranium and thorium in the zirconium oxide powder. Uranium, thorium, and some of their decay products can be present as impurities in zirconia powders even if powder manufacturing processes provide for an efficient separation of such elements with a different concentration according to the level of purification of the material and of the powder manufacturing process.

2.2 Radioactivity

All glasses and ceramics to be used for medical and dental applications should be tested for the presence of radioactivity. This can be done by taking a 500-g sample of the as received of the product powder, milling it in a suitable ball mill and sieving to yield powder with particle size of less than 75 μm . A sample volume of 60 ml of the ceramic powder is placed in a scintillation counter to determine the activity concentration of uranium-238 by neutron activation. The activity concentration should be no more than 1.0 Bq/g of uranium-238 (ISO 13356).

2.3 Esthetics

Esthetics is a primary consideration in the use of ceramics to replace missing tooth structure. Today esthetics are of such paramount concern that the only medical materials that in any way provide a durable and satisfactory solution to the esthetic repair of teeth are ceramics. For example, dental porcelains attempt to meet the challenges to achieve an appropriate visual appearance, whilst providing sufficient

strength to accept the loads placed upon teeth during function. The esthetics of dental ceramics are characterized by three optical properties, namely: color, translucency, and texture.

- *Color* – The color of an object our eye detects is a function of the light source, providing the spectrum of light (380–700 nm) hitting surface, how the object transforms this spectrum and the ability of our eyes to detect the colors.
- *Translucency* – The amount of light reflected and the spectrum of light reflected from the object and detected by the eye, will depend on the ability of the light to travel through the material, where it will change due to absorption and scattering properties of the material and the background against which it is held.
- *Surface texture* – Light can be reflected from a surface, as from a mirror, or scattered in all directions. In the first case the surface is an ideal reflecting polished surface, while in the second case is a matte scattering surface.

The translucency is one of the primary factors in controlling esthetics and a critical consideration in the selection of materials for dental ceramic applications. However, an increase in crystalline content, while achieving greater strength, generally results in greater opacity. If the majority of light passing through a ceramic is intensely scattered and diffusely reflected, the material will appear opaque. If only part of the light is scattered and most is diffusely transmitted, the material will appear translucent. The amount of light absorbed, reflected, and transmitted depends on the amount of crystals within the core matrix, their chemical nature, and the size of the particles compared to the incident light wavelength. The scattering of light in a glass–ceramic is a function of the relative refractive index of the phases.

2.4 Refractive Index

The use of glasses or glass ceramics in dental restorations requires knowledge of the refractive index and how this will affect the translucency of the ceramic. For example in the construction of glass ceramic veneers for metal substructures, the color of the metal needs to be masked by an opaque layer before the more translucent and more esthetic layers are laid down. The higher the opacity, the greater the hiding power and the thinner the layer of opaque glass ceramic that can be used effectively, leaving more room for the more translucent esthetic ceramic layers.

The refraction of light by mineral phases suspended in the clear glassy matrix is the main reason for opacity. The opacity can thus be controlled by a difference in refractive index between two phases in the glass ceramic, which can be as small as 0.05 from the glass. Since all opacifiers (see Table 2.1) have high indices of refraction, it might be concluded that a glass with a low index of refraction would be the most desirable for developing the opacity.

The index of refraction tends to increase with the specific gravity and the degree of opacity depends not only on the relative refractive index of the phases, but also

Table 2.1 Examples of indices of refraction of ceramics

Material	Refractive index
Leucite	1.5058
K-Feldspar	1.52–1.53
Albite	1.535
Quartz	1.55
Lithium disilicate	1.55
Apatite	1.63–1.64
Spinel	1.712–1.736
Aluminum oxide	1.766–1.774
Zirconium oxide	2.15–2.18
Zinc oxide	2.4
Titanium oxide	2.7

on other factors including the particle size of the mineral phases dispersed in the glass and the degree of particle size distribution. So, the smaller the particle size and uniform the dispersion, the more effective the opacity. The opacity is found to increase as the number of reflecting particles per unit volume increases. Also the degree of opacity is affected by the nature of grain boundaries between the opacifying particles and the hosting matrix.

However, the translucency of dental glass ceramic depends on several factors namely the refractive index of the developed mineral phases, their content in the glass ceramics, the refractive index of the residual glassy phase and its content in the glass ceramics.

There are several mineral phases such as leucite and lithium disilicate that have more or less the same refractive index as the glassy phase and thus can be produced with high degrees of translucency. Thus, the crystallization of these mineral phases in the glassy matrix will never have as great an influence on the translucency of the developed glass ceramics as would be the incorporation of some of the metal oxides such as titania.

The leucite crystals have a refractive index that is very close to that of the feldspathic glass. It is this fact that helps to make leucite based dental ceramics esthetically the best ceramics for dental applications.

2.5 Chemical Solubility

In order to be able to elucidate the chemical solubility in dental ceramics, it is important to understand the conditions that directly affect the ceramics. First one has to consider the type of response one seeks to achieve. If the material is to survive for a long time then a low chemical solubility is desirable, whereas if the material is meant to resorb then a high, but controlled solubility is desirable.

Thus for dental ceramics to survive not only do they need to be strong and tough to resist the biting forces, they also have to be able to resist the acidic/alkaline

corrosive environment of the oral environment. The ISO standard for dental ceramics states that for ceramics in direct contact with the fluids in the oral environment the ceramic must have a chemical solubility of $<100 \mu\text{g}/\text{cm}^2$ after soaking 16 h in 4% boiling acetic acid. So, the only reliable solution is to search for mineral phases to be developed in glass ceramics that provide it with the appropriate characteristics.

The method for measuring the chemical solubility involves the production of ten disk specimens; 12 mm in diameter and 2 mm thick. The samples need to be polished to a smooth surface finish using different grades of abrasives. The samples are washed and dried at $150 \pm 5^\circ\text{C}$ for 2 h and weighed and the total surface area is calculated. The specimens are then placed in 4% acetic acid solution (analytical grade) while refluxing for 16 h at 80°C . The samples are rinsed and dried at $150 \pm 5^\circ\text{C}/2 \text{ h}$ and reweighed to calculate the chemical solubility, which is presented in terms of micrograms per square centimeter.

In order to show the importance of chemical solubility as a factor controlling the use of a ceramic in the oral cavity, an interesting example is the fluorocanase glass ceramic. Although the canasite monophase glass ceramic has a high strength and toughness and good microhardness, its Achilles heel is that it has a low chemical solubility. This problem makes canasite unsuitable as a glass ceramic candidate for the construction of dental restorations that come in direct contact with the oral fluids. According to the British standard of dental ceramics, the glass ceramic to be used in the construction of a ceramic core must have chemical solubility of $<2,000 \mu\text{g}/\text{cm}^2$.

Unfortunately, the chemical solubility of canasite glass ceramics is found to be anything up to $4,000 \mu\text{g}/\text{cm}^2$. Additionally, the tested samples show an extensive decrease in strength of the samples after soaking in acetic acid and looks like a chalk. The excellent mechanical properties makes it worthwhile to extensive research canasite to improve its chemical solubility to $<2,000 \mu\text{g}/\text{cm}^2$ for it to be used as a core material and better still $<100 \mu\text{g}/\text{cm}^2$ to be able to use it as a single unit restoration without the need to veneer it.

Whereas in the case of a load bearing dental ceramic the chemical solubility wants to be as low as possible, this is not so for bioresorbable ceramics that are used for such biomedical applications as drug delivery, temporary fracture fixation, or for the fabrication of temporary tissue engineering (TE) scaffolds. Depending on the desired function these may remain in the body for weeks, months, or even years. Accurately predicting and evaluating the degradation rate of these materials is critical to their performance, especially if it involves the controlled release of bioactive agents.

One example is the need to use antimicrobial agents that are effective against biofilm-complex aggregations of microorganisms, which are believed to be involved in a wide variety of microbial infections in the body. Phosphate based glasses in the ternary $\text{P}_2\text{O}_5\text{--CaO--Na}_2\text{O}$ system are resorbable and this can be controlled by the CaO content. Those incorporating silver ions have potential as temporary antibacterial devices. By controlling the degradation of these glasses, silver ions can be released slowly and continuously over time when in contact with an aqueous medium.

2.6 Mechanical Properties

Glasses and ceramics are very brittle, so it is very important to show the effect of different parameters on the mechanical strength. There are three types of mechanical strengths, which are distinguished according to the way the force is applied. The three types of mechanical strengths include the tensile strength, bending (flexural) strength, and the compressive strength.

On taking tensile strength as unity, the bending strength is approximately twice as high as the tensile strength and the compressive strength is approximately ten times as high as the tensile strength. As the tensile strength is the weakest type of strength, the fracture generally occurs at the point in which the glass ceramic is subjected to a concentrated tensile stress.

In brittle materials, failure takes place at much lower tensile stresses compared with compressive stresses. The strength of a glass and glass ceramic depends to a large degree upon its surface conditions. Tiny cracks in the surface lead to weakening and failure by brittle fracture. Glass and glass ceramics also become weaker with time when subjected to the application of a cyclic stress (Fatigue).

The mechanical properties of glass ceramics are evaluated using a tensile tester and the associated software such as the one shown in Fig. 2.1. Three point bending strength, biaxial flexural strength, and fracture toughness can be measured. The machine deforms a specimen until it breaks, measuring the force required and the deformation at which the break occurred and record stress and strain too if the specimen dimension are measured.

Most applications of bioceramics require them to be used as load bearing structures, especially when used as a bone substitute material or a dental restorative material (see Table 2.1). Thus, the mechanical properties that may be considered of immediate relevance to the clinical use of bioceramics include strength, toughness, and hardness.

When measuring the strength of a ceramic, what can be obtained is not just one value for strength but a range of values, that is, a distribution of strengths, as shown

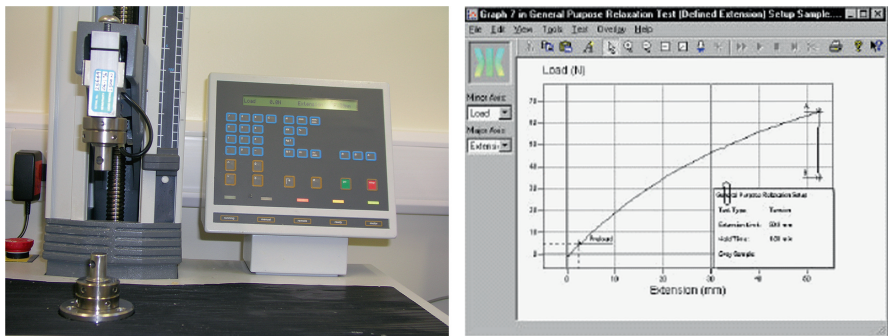


Fig. 2.1 Example of a tensile tester and associated software



Fig. 2.2 Normal strength distribution curve for a ceramic

in Fig. 2.2, although what is often only reported is the average strength. The reason for this is that the strength is determined by the size, number, and orientation of structural defects. These defects can consist of cracks or holes within the ceramic structure or anything else that can create a local stress concentration. Since each specimen that is tested will have a different arrangement of defects, this will give rise to a different value for the strength.

The other factor that plays an important role is the fracture toughness of the ceramic. Fracture toughness represents the resistance of a material to the propagation of cracks. Thus, when a ceramic contains a crack, the fracture toughness determines how easy it is for this crack to grow. Various mechanisms can be employed to make it more difficult for cracks to grow such as hard or rubbery inclusions or transformation toughening.

Thus it is important to appreciate is that the strength of bioceramics is driven by two factors, namely (1) the inherent flaw size and the (2) the fracture toughness. These three parameters are related by the following equation:

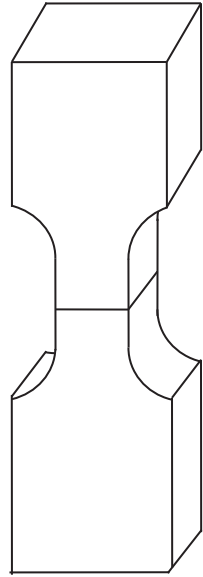
$$\sigma_f = K_{Ic} / \sqrt{\pi a},$$

where σ_f is the tensile strength, K_{Ic} is the fracture toughness and a is the inherent flaw size. Hence whenever one seeks to characterize the fracture resistance of a ceramic ideally one should determine both the tensile strength and the fracture toughness.

2.6.1 Tensile Strength

There are a variety of methods to determine the tensile strength of a material. These include tensile strength, flexural strength, and biaxial flexural strength. The tensile strength is in many ways the simplest to understand as it is based on the idea that we apply a tensile force to the material until such time that it fails. However, when conducting such an experiment it is important that the experimental design is such that the stress and strain at failure can readily be calculated and for that to be

Fig. 2.3 Simple dumbbell design used in tensile strength tests



possible the stress generated within the specimen as a consequence of the applied force needs to be distributed uniformly across the full cross-sectional area of the specimen.

The simplest specimen design that will ensure that is the case is a rod or wire of uniform cross-section. One potential problem with a simple rod or wire is that there is a danger that the specimen could fail at the point at which it is clamped, which would invalidate the result. In order to avoid this problem the specimen design has been modified to provide a thicker cross-section in the clamping part of the testing machine. The design that is most favored is the dumbbell as depicted in Fig. 2.3.

The dumbbell design ensures that the failure is most likely to take place in the central region of the specimen where the cross-sectional area is reduced, such that it is possible to calculate the stress at failure as the force/cross-sectional area (F/A). If the failure were to take place outside this region then the result would have to be discarded. One of the limitations of this design is that for brittle materials, localized high stresses in the clamping zone can cause failure in those areas and consequently many specimens have to be rejected. Thus an alternative and more effective method of assessing the tensile strength of brittle materials needs to be used.

2.6.2 Flexural Strength

The flexural strength test for measuring the tensile strength of brittle materials is based on a simple beam that is subjected to a bending force until such time that it

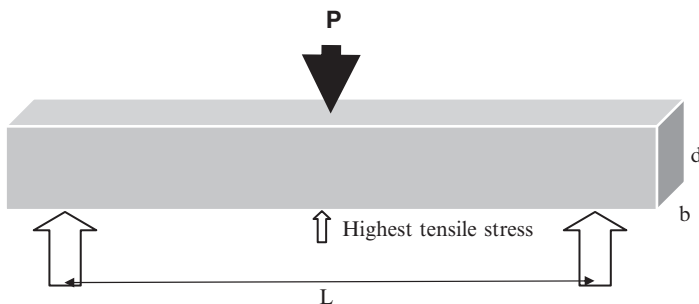


Fig. 2.4 Experimental design for a flexural strength test of a brittle material

fractures (Fig. 2.4). When the beam fails the highest stress will be central to the bottom surface of the beam and is given by:

$$\sigma = 3PL/2bd^2$$

where σ is the stress, P is the applied load, L is the span of the beam between the supports, b is the breadth and d is the depth of the beam. The stress at failure is the flexural strength, also referred to as the modulus of rupture.

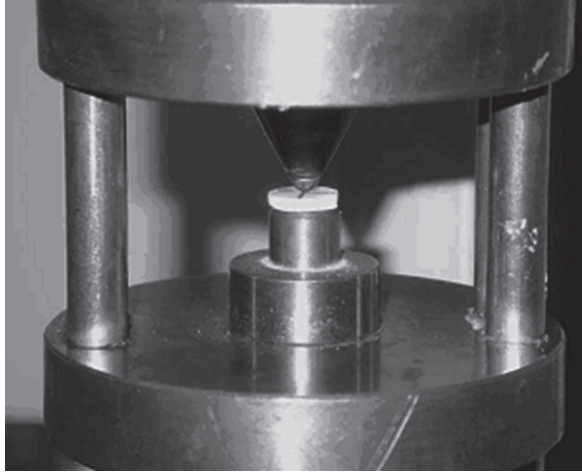
Typically, ten standardized bar specimens; 30 mm long and 4 mm width and 4 mm depth are prepared. The specimens are dried and polished to a good surface finish, typically 1 μm , using different grades of abrasives. The specimen is loaded in the central point of the test span at a cross-head speed of 1 mm/min. The load is applied at the midpoint between the two supports by using a knife-edge with a rounded radius of 0.5 mm.

2.6.3 Biaxial Flexural Strength

There are some instances when it is simply easier to make a circular disk of a material with a uniform thickness than it is to make beams, especially as in the case of the beams it is not easy to avoid edge chipping, etc. Many studies of the fracture strength of dental ceramics now prefer to use this method. Essentially the specimen consists of a disk of uniform thickness, typically 12 mm in diameter and approximately 2 mm thick, which is placed on a circular support and loaded centrally with a ball ended loading device (Fig. 2.5).

Typically ten standardized disk specimens, 12 mm long and 2 mm thick, are prepared. The surfaces of the specimens need to be polished very well using different grades of abrasives to produce a consistent surface finish. They can then be centered and loaded on the test machine and tested with a cross-head speed of 1 mm/min. The load is usually applied at the midpoint by a ball shape edge rounded

Fig. 2.5 Test arrangement for a biaxial flexural strength test



to a radius of 0.5 mm. When testing is carried out to meet an ISO standard, for the batch to pass the test at least eight of each sample of ten specimens need meet the requirements for strength.

The biaxial flexural strength is determined using the equation:

$$\sigma_{\max} = \frac{P^2}{h} \left\{ 0.606 + \log_e \left(\frac{a}{h} \right) + 1.13 \right\}$$

where $\sigma_{\max}$ is the biaxial flexural strength, P is the load to fracture, a is the radius of the knife-edge support and h is the sample thickness.

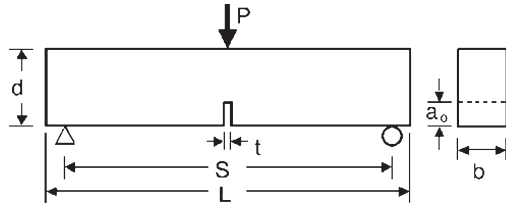
2.6.4 Fracture Toughness

As with strength measurements there are a number of ways in which the fracture toughness of a ceramic can be measured. The methods most commonly used with ceramics are the single-edge notch test and the indentation test.

2.6.4.1 Single-Edge Notch

The fracture toughness can be determined by a single-edge notch three point bend test. This is a variant on the flexural strength test described above in that the distinction is that the surface under tension has been precracked to form a notched bar. The beam will have dimensions that are typically 4 mm wide [b], 3 mm high [d] and 30 mm long. Using a fine diamond saw, possibly 0.5 mm thick, and with copious

Fig. 2.6 Schematic of Single-Edge Notched beam



water coolant, the specimen is notched in the middle of the 4 mm wide surface to a depth of 1 mm (a_o) (see Fig. 2.6). The notched bars are placed in a three point bend testing arrangement, which will typically have a span length of some 20 mm and are tested at a cross-head speed of 0.5 mm/min. The load at fracture (P) is recorded and the fracture toughness is calculated from the fracture load using the standard equation:

$$K_{Ic} = YP/bd^{0.5}$$

where Y is a geometric correction factor.

2.6.4.2 Indentation Method

The fracture toughness can be determined by the indentation technique using a Vickers Hardness tester. The specimens need to have a 1- μm surface finish in order to be able to clearly see the indentation. The specimen is indented under a load that depends on the material and that will ensure that an acceptable crack pattern is obtained. The technique requires that all cracks originate at the corners of the indent and the presence of only four radial cracks with no chipping or crack branching. The radial cracks are measured immediately after each indentation. The fracture toughness is measured using the formula:

$$K_{Ic} = \chi P/c^{3/2}$$

where $\chi=0.0824$, P the indentation load in Newtons, and c the radial crack length in meters.

2.6.5 Microhardness

The hardness is not a precisely defined property. There are a number of methods for hardness determination including the Moh's method (scratch resistance) and the Vickers and Knoop method, which are based on an indentation method and are the ones most commonly used in engineering for precise results.

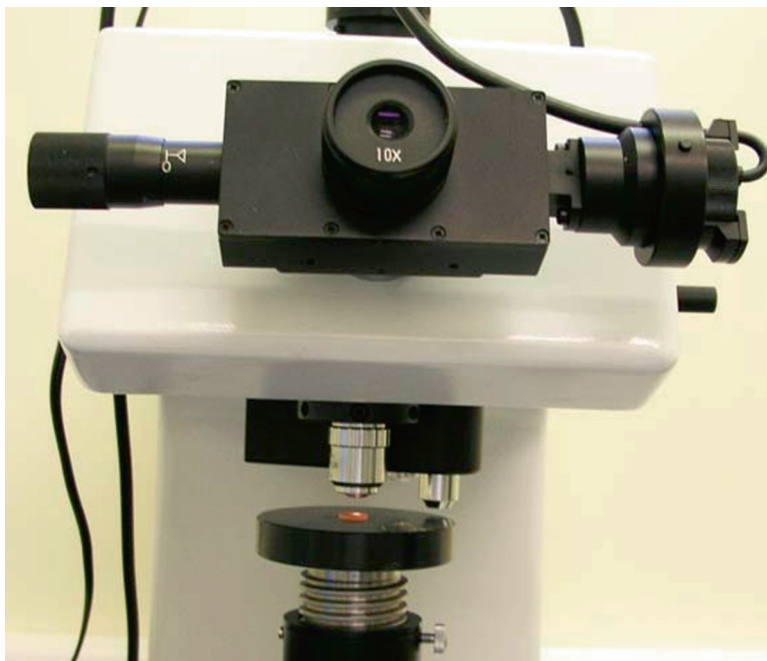


Fig. 2.7 Microhardness indenter

The ability of a harder material to scratch a softer one is the basis for the Moh's scale of hardness, starting from 1 (soft) to 10 (hard). Moh's method assesses the hardness of a material according to which in a series of minerals of successively increasing hardness can scratch the glass and which cannot. The test does not determine the accurate hardness and can only be used for comparison of different glasses.

The most convenient widely used measurement of the hardness of glasses and ceramics is the indentation method. These include the Vickers and Knoop hardness and both use a diamond pyramid indenter (Fig. 2.7).

The Vickers method is advantageous in that the ratio of the hardness numbers corresponds approximately to the actual ratios of hardness of substances. The shape of the indentation is created with a square diamond pyramid. The hardness is determined by measuring the diagonals of the indentation in the glass surface.

For example a substance with a hardness of 400 is four times as hard as a substance with a hardness of 100 HV. The microhardness is calculated from the following equation

$$HV = 1.854P/d^2 = \text{Nm}^{-2}$$

where P is the force acting on the Indenter in Newtons and d is the diagonal of the rhomb impression in micrometers.

The Knoop hardness is a modification of the Vickers method and differs only in the shape of the indenter in that the shape of the indentation is rhomboid. The Knoop hardness is calculated using the following equation:

$$H_k = 1.4513P/d^2$$

where P is the force acting on the Indenter in Newtons and d is the length of the longer diagonal. The smaller the area of indentation of a fixed load, the harder is the material.

The microhardness depends on the surface finish of the specimen to be measured and until now there is no accurate method for calculating the microhardness of the materials. For this reason, the most useful hardness measurements are made by comparing surfaces treated in the same manner with the same measuring method and load. The indentation method is also used in calculating the fracture toughness.

2.6.6 *Machinability*

The advent of advanced manufacturing technologies such as CAD-CAM means that there is a growing interest in the machinability of medical ceramics. Particularly in dentistry this has become a major means of producing dental restorations such as veneers, inlays, crowns, and bridges. Some ceramics can be machined directly in its final state such as the feldspathic glasses, whereas other ceramics need a two stage process because the final product is too difficult to machine. For example, partially stabilized zirconia would be very difficult to machine in its final state and therefore a process known as “soft machining” has evolved. This involves producing a porous block of the ceramic, which is easy to machine but can shrink up to 20% on densification.

Once the component has been machined, which takes account of the amount of shrinkage, it is then put through a densification firing cycle. Another example is the machining of components from a glass ceramic such as lithium disilicate. Again in its final state it is difficult to machine and in order to overcome this problem the glass–ceramic is partially crystallized, the component is machined from the partially crystallized block and the final product is then given a further crystallization firing cycle. The advantage is that the second firing cycle does not involve any shrinkage and thus the size of the component is not compromised.

The machinability of glass ceramics is found to be affected mainly by the type of mineral phases in the glass. For example, simultaneous crystallization of fluorophlogopite and beta-spodumene solid solutions results in a machinable ceramic. However, the beta-spodumene phase tends to harden the body by increasing the microhardness and thereby impair the machinability character. The ceramic will be no longer machinable when the beta-spodumene proportion approaches more than 50% (Table 2.2). On the other hand, the beta-spodumene phase will improve the

Table 2.2 Microhardness of beta-spodumene–fluorophlogopite

Temp. (°C)	Microhardness values (kg/mm ²)		
	F_1 (10% spodumene)	F_3 (30% spodumene)	F_6 (60% spodumene)
850	50.70	53.90	101.00
900	62.00	96.60	110.20
950	113.50	118.10	117.50
1,000	75.60	168.80	217.00
1,050	80.40	132.90	689.70
1,100	95.60	105.50	911.00

microhardness without impairing the machinability if it occurs in an amount <30%. The two mixes F_1 and F_3 have been shown to be readily machinable glass ceramics. In addition, the presence of beta-spodumene solid solution enables lower expansion coefficient to demonstrate excellent resistance to thermal shock.

The best machinability can be secured at the highest concentrations of fluormica and wherein the fluorophlogopite has plate-like grains with a grain size of less than 5 μm . Mica grains with a uniform size and randomly distributed in the glassy matrix are known to produce glass ceramics with a very good machinability.

The machinability of a ceramic is not easy to quantify. Various parameters have been suggested as a “measurement” of the machinability, such as tool wear, surface roughness, cutting force, cutting energy, drilling rates. A more practical suggestion is that it can be assessed from a calculation of the brittleness index. The brittleness index, as suggested by Lawn and Marshall in 1979, is a ratio of the Vickers hardness to the fracture toughness and is calculated using the following formula:

$$B = H_V / K_{Ic}.$$

Boccaccini (1996) has shown that the brittleness of glasses and glass–ceramics can be calculated using the following equation:

$$B = 1.599 P^{-1/4} (c/a)^{3/2}.$$

In this equation, B is the brittleness index in $\mu\text{m}^{1/2}$, P the indentation load (N), which should be set at 49 N for median cracking, c is the median crack length and a is the contact diagonal of the indent in mm. A brittleness index lower than 4.3 $\mu\text{m}^{1/2}$ is considered to be within the range for good machinability.

2.7 Thermal Behavior

The thermal behavior of glasses and glass ceramics is very important for various applications. Many features result from heating the glass or glass ceramics which are either desirable or undesirable according to the application of the material.

Measuring the thermal behavior of the ceramic is very important during the annealing of glass, coating substrates with glass, or glass ceramics, the crystallization and nucleation of the glass, the thermal shock resistance of the materials, etc. The thermal behavior can be evaluated using both a dilatometer and differential thermal analysis (DTA).

2.7.1 Thermal Expansion

When a glass ceramic material is heated, the extra energy absorbed causes the atoms to vibrate with increased amplitude and the ceramic expands. This change in length, when determined per unit length for a 1°C change in temperature, is called the thermal expansion coefficient (TEC) and is expressed in terms of parts per million per degree centigrade ($\text{ppm}/^{\circ}\text{C}$).

Internal stresses generally generate due to strains resulting from irregular thermal expansion of the ceramic. For example, if a glass ceramic is heated on one face and cooled on the other face, compressive stresses are set up on the hotter face and tensile stresses are generated on the cooler face. Whether or not a uniform temperature gradient is established across the thickness of the glass ceramic depends on the thickness of the sample.

With sudden heating and cooling, very high stresses can be generated resulting in the development of compressive stresses at the surface. Rapid cooling results in a greater initial contraction of the surface layer than the interior of the glass which places the surface under tension. Glass and glass ceramic objects are much more likely to fail if the object is already in a state of tension due to differential thermal contraction.

There are a number of instances where the thermal expansion of the ceramic is a matter of concern. For example, when using a glass ceramic such as a feldspathic glass ceramic containing leucite as a veneering material for a metal substrate, as in dental crowns and bridges, it is vital that the mismatch in the TEC is not too great, otherwise on cooling the ceramic layer may crack or peel and separate from the metallic substrate.

The thermal expansion of a glass ceramic is very important for the thermal compatibility in different applications. If a glass ceramic is needed with a good thermal shock resistance then a low thermal expansion glass ceramic is desirable. On the other hand, a glass ceramic with a high TEC, probably between 13 and $15 \times 10^{-6}/^{\circ}\text{C}$, would be needed if it is to be used to conceal a Ni–Cr alloy by acting a surface coating. Thus, by adjusting the TEC this can help to fix various industrial problems.

Another area of increasing interest is the coating of metallic implants with bioactive glasses in order to improve the ability of the inactive implant to bond to living tissue, particularly bone. The TECs of bioactive glasses are typically much larger than those of Ti alloys. Typically the TEC of a bioactive glass is in the region of $15 \times 10^{-6}/^{\circ}\text{C}$ whereas that for a $\text{Ti}_6\text{Al}_4\text{V}$ alloy it is around $10 \times 10^{-6}/^{\circ}\text{C}$. Whilst the

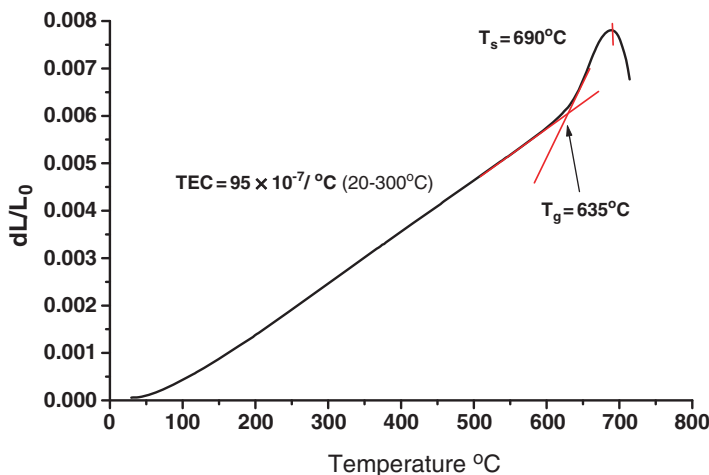


Fig. 2.8 Thermal expansion curve for a leucite glass ceramic

simplest way to reduce the thermal expansion of a bioactive glass is to increase the SiO_2 content and decrease the alkali oxides contents of the glass, this is unfortunately at the expense of the bioactivity, which is significantly reduced.

The thermal shock resistance is a practical example of the importance of expansion measurement which depends mainly on the value of the TEC. The extent to which the material can withstand sudden temperature changes without fracture is referred to as the thermal shock resistance. The thermal shock resistance is defined in terms of the maximum temperature interval through which the material can be rapidly heated and cooled without fracturing. So the thermal shock resistance is important for ceramics exposed to sudden cooling and heating applications.

The expansion curve of a glass is a very important factor in the construction of a crystallization heating schedule for a glass into glass ceramics. Several significant points in the expansion curve of glass can be predicted from the thermal expansion curve of glass, including the lower annealing point, transformation temperature, the upper annealing point, and the softening point in addition to the nature of the melting. The information on T_g and T_s are very important in determining the best crystallization schedule (Fig. 2.8). Also the annealing temperature of the glass during preparation of glass blocks for production of dental glass ceramics for a CAD–CAM machine can be predicted.

The measurement of this expansion is carried out by taking a length of material, heating it to a certain temperature and then measuring the resultant change in length using a dilatometer; Specimens are prepared as rods having a length of 25 mm and cross-sectional diameter not greater than 5 mm. The ends of the specimens are ground to yield flat surfaces to the perpendicular the long axis of the specimen. The samples must be well annealed to avoid the false results.

The specimen is heated at a heating rate of $5^\circ\text{C}/\text{min}$ between room temperature and the softening point to determine the TEC, transition temperature, and the

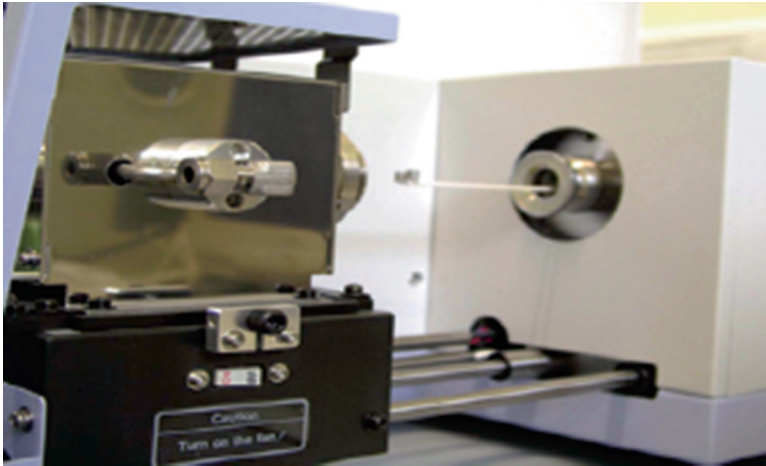


Fig. 2.9 DTA equipment

softening temperature. The glass transition temperature is estimated graphically for each ceramic specimen from the plotted curves of expansion versus temperature. The samples are prepared using the above mentioned preparation method and fired using the above firing schedule.

2.7.2 Differential Thermal Analysis

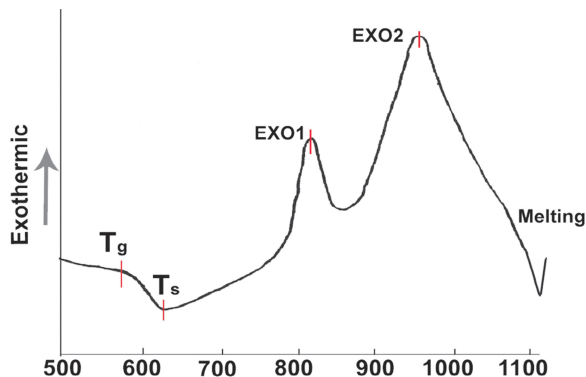
The chemical reactions or structural changes within the amorphous glass and the crystalline glass ceramics are accompanied by the evolution or absorption of energy in the form of heat. For example when a glass substance crystallizes, an exothermic effect occurs since the free energy of the developed regular crystal phase is less than that of the structurally disordered glass substance. The melting of crystalline glass ceramics is represented by an endothermic reaction as the liquid state needs a higher free energy than that of the glass.

Also it can be predicted if the glass ceramic contains a monocrystalline phase or multiphase crystalline materials from the shape of endothermic peak. Thus DTA is a technique that facilitates the study of phase development, decomposition, or phase transformations during the glass ceramic process (Fig. 2.9).

In this method the glass material under test is in the form of a finely divided powder placed in a small crucible of platinum or other suitable refractory crucible made of aluminum oxide. Adjacent to the test crucible is a second crucible containing an inert powder such as aluminum oxide, which does not exhibit endothermic or exothermic reactions.

The temperature difference between the tested sample and the reference sample powder (almost always inert alumina) is recorded during heating. The DTA curve

Fig. 2.10 DTA of apatite mica glass ceramic



is plotted. The exothermic reactions are represented as peaks and the endothermic reactions are represented by dips on the DTA curve.

The technique is considered a useful method for the characterization of the glasses and the determination of the optimum temperatures at which the different crystal phases are formed. The quality and the shape of the peaks are affected by the rate of heating and the fineness of the powder.

As the temperature is increased, a dip is observed on the DTA curve due to slight absorption of heat that occurs when the annealing point of the glass is reached. With further increase of the temperature, one or more quite sharp exothermic peaks are expected, corresponding to the development of various crystal phases. At a very high temperature the endothermic reaction peak relates to the early melting of the tested crystalline sample. The main features of a typical DTA curve of a glass are shown in Fig. 2.10. The curve shows the thermal behavior of a glass that can crystallize to yield two phase glass ceramics.

Therefore the DTA analysis yields a great deal of very useful information which is of great help in designing the heat treatment schedules for the crystallization of a glass into glass ceramics. The curve not only indicates the temperature range in which the nucleation and crystallization occurs, but also it indicates the maximum temperature to which the glass can be heated to prepare glass ceramics without exposing the glass ceramic to deformation due to melting of the crystal phases. Having determined the exothermic and endothermic peaks, the crystallization of the different crystalline phases can be perfectly assessed. In cooperation with the XRD data, one is able to assess the best schedule for a crystallization of a certain phase or phases.

Glasses and Glass Ceramics for Medical Applications

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2012, XXIV, 244 p., Hardcover

ISBN: 978-1-4614-1227-4