Chapter 2

Literature Survey

Hydroxyapatite Structure

Hydroxyapatite belongs to a typical group of calcium phosphates which is regarded as bone substitute materials. The chemical formula of hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$ with the molar ratio of Ca/P equivalent to 1.67. In general various types of calcium phosphates having different Ca/P ratios from 0.5 to 2.0 can be synthesised. It has been shown that higenstockite having chemical formula, $Ca_4O(PO_4)_2$ possesses the highest Ca/P ratio as 2.0. However, the chemical composition of hydroxyapatite may be varied with a wide range of non-stoichiometric ratio depending upon the methods of preperation. Calcium deficient or partially dehydrated apatite is therefore formed.

It has been known that hydroxyapatite is formed as hexagonal crystal with cell dimension of a=9.423 Å and c=6.875Å. The structure is almost analogous to that of fluorapatite ($Ca_{10}(PO_4)_6F_2$) in which the fluorine atom is replaced by an hydroxyl group. In the study of hydroxyapatite crystal structure by X-ray diffractometry as shown in Fig. 2.1 , there are two crystallographically independent calcium atoms incorporated in the unit cell. Each calcium atom is surrounded by 6 oxygen atoms belonging to phosphate groups and by hydroxyl group respectively. The two calcium atoms are stacked together along the c-axis and rotate mutually 6 oxygen atoms from each other. The hydroxyl group is located along the a-axis whereas the phosphate group is almost tetrahedral with slight distortion.

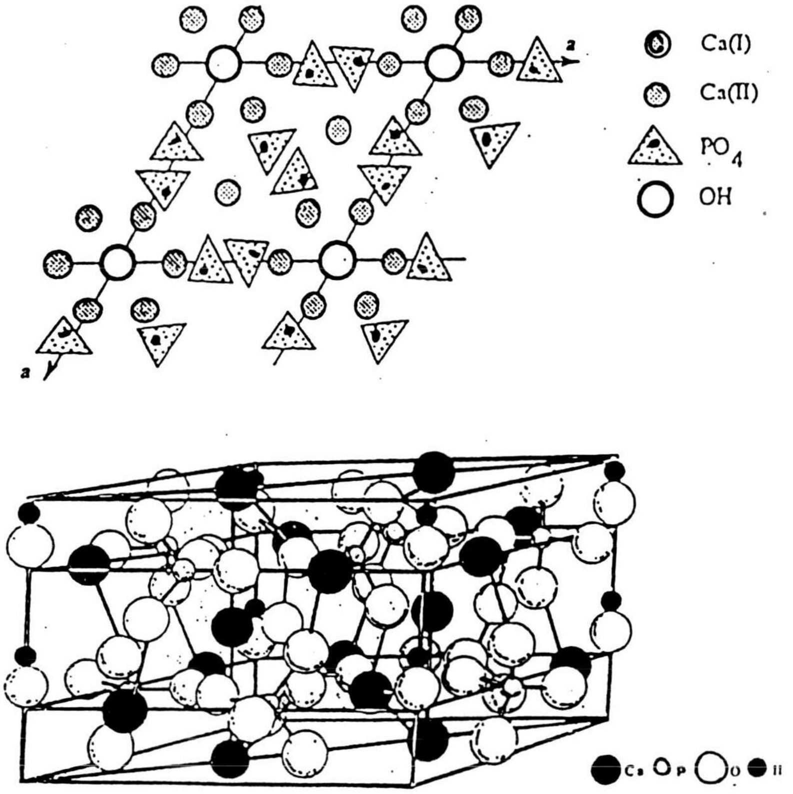

Figure 2.1 Crystal structure of hydroxyapatite projected along the c-axis(upper) and along the a-axis (bottom) (Aoki,1991).

The most popular preparation of synthesized hydroxyapatite is wet chemical method using solution reaction. By this method, the synthesized HAp powders are nonstoichiometric. This has been investigated in detail on HAp. Some interpretations have been proposed as described. At present, the following formula is mainly used for the explanation of the nonstoichiometry.

$$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}nH_2O \; ; \; 0<x<1, \; n=0\text{-}2.5$$

Such proposals are primarily based on the idea of Ca deficiencies. The total electrical charge is assumed to be compensated by the introduction of H^+, giving rise to H_2O molecules replacing OH^-. Besides Ca^{2+}, PO_4^{3-} and OH^-, such ionic species of H_3O^+, $H_4O_4^{4-}$, HPO_4^{2-} can be thought to be incorporated during the wet process. H_3O^+, and $H_4O_4^{4-}$ and HPO_4^{2-} are assumed to substitute Ca^{2+} and PO_4^{3-} on the lattice sites of the HAp structure, respectively. The ionic groups of HPO_4^{2-}, PO_4^{3-} and OH^- have been recognized in HAp precipitates with Ca/P ratios below 1.67 by IR spectroscopy.

During thermal treatment, the ionic group of HPO_4^{2-} has been reported to decompose via pyro-type ($P_2O_7^{4-}$) to PO_4^{3-} in nonstoichiometric HAp. The reactions are

$$HPO_4^{2-} \longrightarrow 1/2\, P_2O_7^{4-} + H_2O\,(g) \quad (600^\circ C),$$

$$P_2O_7^{4-} + OH^- \longrightarrow 2\, PO_4^{3-} + H_2O\,(g) \quad (700^\circ C \text{ to } 800^\circ C).$$

Hence, nonstoichiometric HAp decomposes via dehydration according to the following path:

$$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}nH_2O$$

$$\xrightarrow{<700^\circ C} Ca_{10-x}(P_2O_7)_x(PO_4)_{6-2x}(OH)_2 + nH_2O\,(g)$$

$$\xrightarrow{700^\circ C - 800^\circ C} (1-x)Ca_{10}(PO_4)_6(OH)_2 + 3xCa_3(PO_4)_2 + xH_2O\,(g).$$

The resultants after thermal treatment are stoichiometric HAp and TCP. At temperature higher than 900°C, further partial dehydration takes place depending on the H_2O vapor pressure as follows,

$$Ca_{10}(PO_4)_6(OH)_2 \longrightarrow Ca_{10}(PO_4)_6(OH)_{2-2y}O_y + yH_2O\ (g)$$

resulting in oxyhydroxyapatite (OHAp) (Kanazawa, 1989).

Clinical Applications of Hydroxyapatite

Among several bioceramic materials used for the repair and reconstruction of diseased or damaged parts of the body, calcium phosphate based ceramics have recieved considerable clinical attention for orthopaedics and dental implants. It has been found that hydroxyapatite and β-tricalcium phosphate (TCP) are extensively used as bone substitutes because of their bioavailability in natural bone. Jarcho and his colleagues have shown that dense and porous sintered hydroxyapatite and tricalcium phosphate are biocompatible with bone and exhibit little or no biodegradation after six-month implantation period (Jarcho et al.,1976). It is possible that there is a chemical bond developing between the bone and the ceramic. The cohesion is so strong that the implant can not be removed without fracturing the surrounding bone (Dennison et al.,1980). It does not seem there is much difference between hydroxyapatite and tricalcium phosphate in biocompatibility with bone except the former allows faster bone growth inside its macropores of about 100 microns in diameter. However, the chemical composition of hydroxyapatite makes it more refractory to bioresorption. Consequently, an implant made of hydroxyapatite placed in bone will be present after three or four years of implantation. On the other hand, tricalcium phosphate placed in bone has partially disappeared in six to fifteen weeks depending on its porosity and stoichiometry (Lavernia and Schoenung,1991). However there has been some controversy between the degradation behaviors of hydroxyapatite and that of tricalcium phosphate. It is generally accepted that hydroxyapatite is more stable and less biodegradable than tricalcium phosphate which is more reactive and elicits a layer foreign body response when being implanted.

Hydroxyapatite has been reported to have superior biocompatibility with skin tissue as well as with gingiva (Aoki et al.,1989). In addition both dense and porous hydroxyapatite in the form of granule have been employed successfully in orthopaedics, dentistry including facial plastic surgery (Willmann,1993). Other applications of hydroxyapatite also include skin treatment, gum treatment, jawbone reconstruction, ear and nose bone repair and spinal surgery. Furthermore, many bioceramic composites based on hydroxyapatite have been synthesised to be used for repair of large bone defects (McIntyre et al.,1991).

Strengthening of Hydroxyapatite

In view of the mechanical properties of brittle polycrystalline materials as well as hydroxyapatite depending on porosity rather than grain size. It is evident that the strength of those materials is decreased rapidly as porosity increases. This relationship between the strength and porosity can be represented in the Ryskewitch equation (Hench,1991) as below:

$$\sigma = \sigma_o e^{-cp}$$

where σ = strength

σ_o = strength at zero porosity

c = constant

p = porosity

There are several studies on the mechanical properties of hydroxyapatites in the literatures. Rao and Boehm (1974) realised that compressive strength of hydroxyapatite was greatly influenced by porosity. Jacho et al. (1976) showed that the strength of dense polycrystalline hydroxyapatite resulted from precipitation was increased after being sintered at 950°-1250°C for 1 h. The higher compressive strength and tensile strength of such a material were obtained at the values of 917 MPa and 196 MPa respectively. However the strength has also been found to be dependent on different forming methods. Duff et al. (1980) cited that compressive and tensile strength of hydroxyapatite were decreased in the range of 59-265 MPa and 4-11 MPa recpectively when it was formed by hydraulic pressing. Hydroxyapatite ,on the other hand, has the strength of 207-275 MPa when isotatic pressing is used (Rao and Boehm,1974). It has also been demonstrated that the application of hydraulic pressing followed by isostatic pressing on the hydroxyapatite can raise the compressive strength up to 320-464 MPa. Furthermore,the strength can increase up to 350-502 MPa when the surface of hydroxyapatite is well-polished(Aoki et al., 1979). Alternately, the forming of hydroxyapatite by extrusion method has implemented the strength in the range of 81-325 MPa as well as the flexural strength in the range of 32-102 MPa (Sombuthawee,1981).

In addition, the enhancement of the strength of hydroxyapatite has been observed by addition of 5 % frits prepared from the various compositions of P_2O_5 and CaO, BaO and Al_2O_3. It was shown that the average bending strength of the strongest sintered hydroxyapatite was increased to 205.8 MPa due to the retardation of these frits in grain growth during sintering(Kondo et al., 1984). An attempt in strenthening polycrystalline hydroxyapatite by means of surface ion-exchange has also made by treatment with strontium chloride in the solid state resulting in the formation of chloroapatite on the surface. In consequence, flexural strength of hydroxyapatite has been found to be incresing of about 22 %(to 79 MN/m^2). The measurement of the mechanical properties of other related materials such as HAp-TCP, strontium substituted hydroxyapatite and titanium dioxide-hydroxyapatite composite ceramics have been conducted (Aoki,1991). It has been understood that the flexural strength of these ceramics is directly proportional to grain size. Furthermore, the effects of various additives on flexural and compressive strength of sintered hydroxyapatite has been observed as shown in Fig. 2.2 and 2.3.

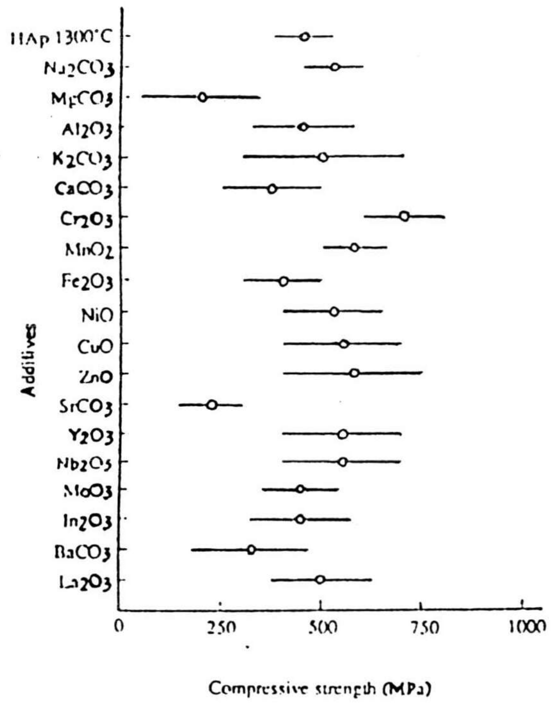

Fig. 2.2 Effects of additives on compressive strength.

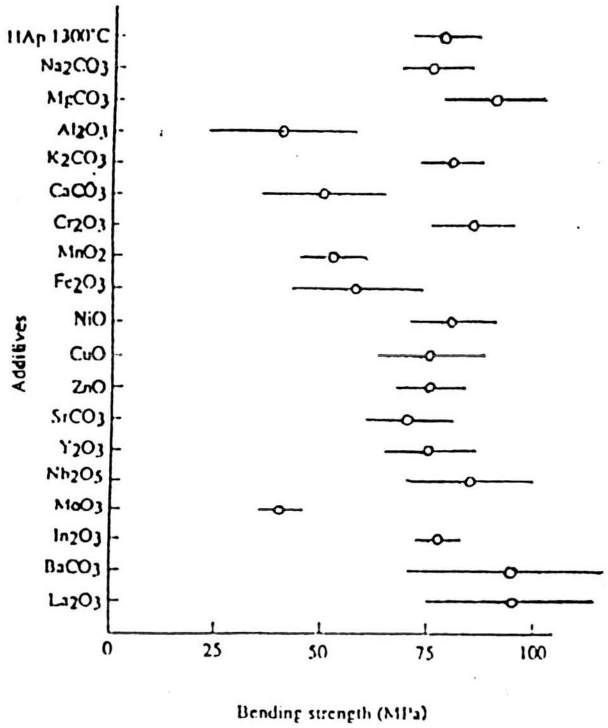

Fig. 2.3 Effects of additives on bending strength.

Strengthening by Compressive Surface Stress

Since the use of ceramic materials are limited due to relative weakness in tension and impact stress, various ceramic processing have been developed to overcome such problems and to increase intrinsic strength of brittle ceramic materials. The most common procedure employed in the ceramic production is compressive surface stresses including the compensation of tensile stresses in the interior of the body.

Compressive surface stresses have been utilised to strengthen ceramics for several decades. Most pottery and chinawares are coated with glazes having lower thermal expansion coefficients. While the ceramics are slowly cooled to room temperature after glazing, the body tends to contract more than the glaze, causing the glaze in compression and body in tension.

The formation of compressive surface layers by the differential shrinkage of two different alumina porcelain bodies was demonstrated by Warshaw(1957). But the strength of the original ceramic bodies was improved only insignificantly.

However, Brubaker and Russell (1967) used three vitrified whiteware bodies with different thermal expansion coefficients, leading to tensile and compressive stresses in the layers and then measured flexure strength and impact resistance of the laminates. It was found that both properties were substantially increased and the compressive layers were subjected to tensile forces due to the externally applied loads. Later, the application of low expansion glazes to strengthen an alumina body has been suscessful. An 40% increase in flexural strength of 96% alumina body has been observed when it is coated with the glaze of various compositions of SiO_2, PbO, Al_2O_3, B_2O_3, CaO and others with a lower thermal expansion coefficient of $5.3 \times 10^{-6}\ K^{-1}$ compared to that of the 96% alumina body ($6.5 \times 10^{-6} K^{-1}$) (Kirchner et al.,1968).

In the meantime, Duke et al. (1968) reported that the strength of glass ceramic in the Na_2O-BaO-Al_2O_3-SiO_2 system nucleated with titanium oxide was better improved by glazing with a lower thermal expansion coefficient glaze, resulting in the moduli of rupture as great as five times that of the initial glass-ceramic.

Similarly, the significant enhancement of the strength on a titanium carbide body by B_4C coatings has been reported (Moody,1969). Since B_4C has lower thermal expansion coefficient than titanium carbide ($5.6 \times 10^{-6}\ K^{-1}$ vs $8.0 \times 10^{-6} K^{-1}$),its strength is increased by 50%.

Other applications of compressive surface stresses has also been introduced to zircon porcelain using CVD-Si_3N_4 coatings. The strength of zircon porcelain can be raised up to 40% because the thermal expansion coefficient of Si_3N_4 is lower than that of zircon porcelain ($2.6 \times 10^{-6} K^{-1}$ vs $4.1 \times 10^{-6}\ K^{-1}$ (Kirchner et al.,1970). From the recent work of Kochawattana (1993) involving the investigation on the strength of hydroxyapatite prepared from chemically treated cattle bone ash, it has been evident that the maximum compressive strength of 146 MPa is obtained as being coated with the same material having a different thermal expansion coefficient of 4.7% but the strength is only increased about 5% compared with an uncoated material.

As mention earlier, compressive surface stresses has been developed as a result of differential thermal expansion between the coating and the body on cooling. While cooling continues, the higher expansion body continues to contract and the compressive stress induced in the surface is compensated by an equivalent tensile stress in the body. The magnitude of these stresses can be calculated using the below equation on the basis of assumption that (Duke et al., 1968)

1. Both surface layer and the body are isotropic and elastic.
2. The temperature distribution is uniform.
3. The elastic moduli and the Poison's ratio are the same for coating and body and ,
4. The radial and circumferential stresses are very small with respect to axial stresses , then

$$\sigma_s = -(\alpha_1 - \alpha_2)\,\Delta T \,.\, \frac{E}{1-\nu} \,.\, \frac{A_1}{A}$$

$$\sigma_b = -(\alpha_1 - \alpha_2)\,\Delta T \,.\, \frac{E}{1-\nu} \,.\, \frac{A_2}{A}$$

where σ_s and σ_b = stress in surface layer and body, respectively.

α_1 and α_2 = linear expansion coefficient for the body and coating respectively.

ΔT = temperature difference between the setting point of the coating and the temperature where the stresses is measured.

E = Young' s modulus.

ν = Poison' s ratio

A, A1 and A2 = cross-sectional areas of the cylinder, body and coating, respectively.

From the above equation, it has been seen that σ_s and σ_b are dependent upon α_1 and α_2. In 1989 Ravaglioli et al. cited that HAp possessed α approximately $11\times10^{-6}\,K^{-1}$. Afterwards Aoki (1991) showed the value of for HAp was $13.7\times10^{-6}\,K^{-1}$ whereas Kochawattana (1993) gained the value of $12.389\text{-}13.792\times10^{-6}\,K^{-1}$. The discrepency of the value has resulted from different preperation methods of HAp. Consequently, the coating of HAp having the higher value of α with HAp having low value of α may therefore induce the compressive surface stresses that increase the strength of the material.

Furthermore, optimum conditions at the surface should be taken into account before the mechanical strength of a material is measured. Since the ceramic materials are easily broken in tension, thus, the presence of compressive stresses can prevent surface flaws developing cracks as the body is stressed . In an inappropiate condition, the resulting stresses occurring inside the body can cause crazing or peeling at the surface of a product Generally, ceramic materials are capable of withstanding compressive force rather than tensile force when a coating has a thermal expansion coefficient similar to that of the body, the surface layer fails in tension, crazing occurs. In contrast, if a thermal expansion coefficient of the body is much higher than that of the coating, excessive compression will be generated in the coating. This causes a stress-relieving fracture at the interface known as peeling. However, the material can be strengthened, when the conditions are adjusted. Both phenomena of crazing and peeling can be illustrated in Fig. 2.4 .

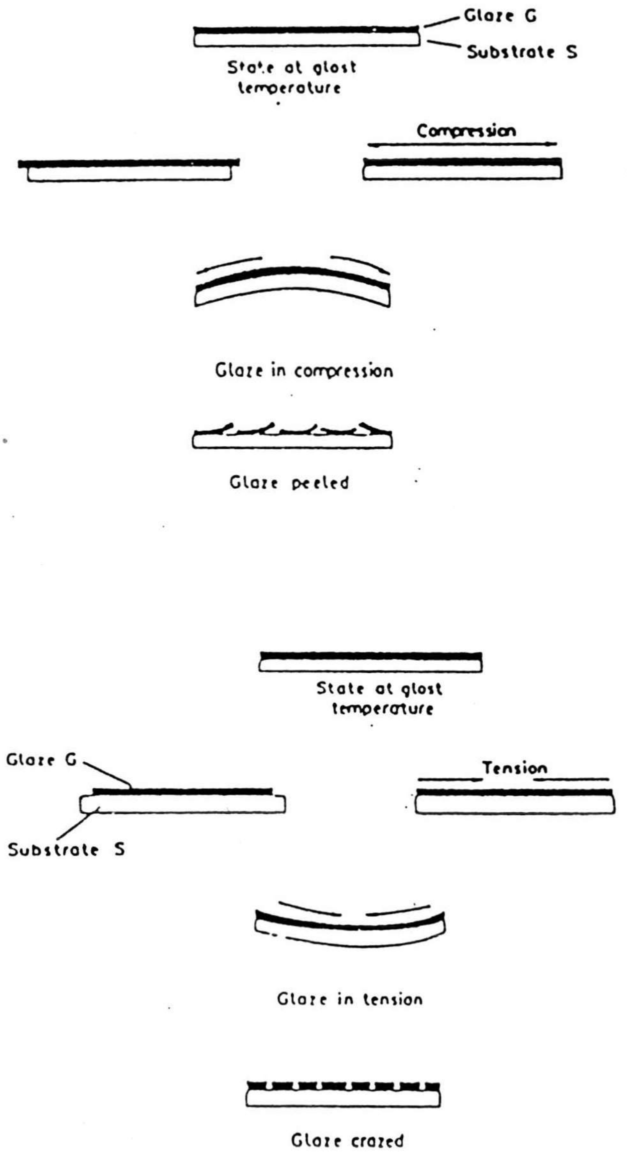

Fig. 2.4 Crazing and peeling in ceramic coating (Taylor and Bull,1986).

Ceramic Processing

For the purpose of the manufacture of fine ceramic products, the process of ceramic production must be well-controlled and well-performed. At the same time ceramic processing technology is also required to achieve better product performance and reliability. The ceramic processing is divided stepwise as follows:

1. Powder preperation

The most common process of powder preperation is the direct synthesis from solution. It is so called the wet chemical method. In the process, a starting material is crushed by milling and dissolves in either water , acids or alkalis as well as in molten salt. The solution is also maintained at certain temperatures or pressures and at appropiate pH. The separation of a product can be fulfilled by means of filtration and evaporation. A product will be varied with different particle size and purity according to the methods of preperation e.g. electrolysis , precipitation and crystallisation. Nevertheless, the properties of the final ceramic products are virtually dependent upon the purity and particle size of the starting material used. In the other word, a controlled optimum particle size distribution is required to gain maximum mechanical strength. Some impurities of the material have affected to a certain extent the strength and sintering temperature while the particle size can outstandingly influence on forming and product strength as well as reactivity. Small particle size is also very significant for densification of a compacted powder at high temperatures. Very small particles with high surface area produce high surface free energy to be bound firmly with other particles. Consequently, a desired product with small particles of approximate 1μm or less can be controlled to have relative density closed to thereotical one. (Richerson, 1982).

2. Powder sizing

The particle size distribution is a main factor in the process of ceramic production. Normally raw materials are not available with the optimum particle size. However, appropiate particle sizes can be achieved by several different techniques before the forming will be proceeded. The two important techniques for particle size distribution are :

2.1 Screening

This technique is a convenient method of particle sizing. At first, the powder is screened either onto a single sieve having selected size opening or onto a series of sieves having successive smaller openings. The smaller particles can be seperated by pouring through the sieve until they reach a screen with too smaller holes while the larger ones still remain on the sieve. The sieve size are classified according to the number of openings per linear inch and are referred in mesh. For example a 16 mesh sieve has 16 equally spaced opening per linear inch. The mesh size of standard screens can be used in comparison with the actual size of the openings. (see Appendix A)

2.2 Attrition milling

Attrition milling can be employed in the transformation of one particle size into another. An attrition mill as illustrated in Fig. 2.5 is a cylindical container in which contains a rotor and milling balls or grinding media. This method offers better working performance than does a ball milling because the milling time is shorter and fine particle is achieved in the range of submicrons. Furthermore, the attrition milling results in less contamination in the powder than does the ball milling and easily be conducted in either dry or wet conditions as well as in vacuum or inert atmosphere.

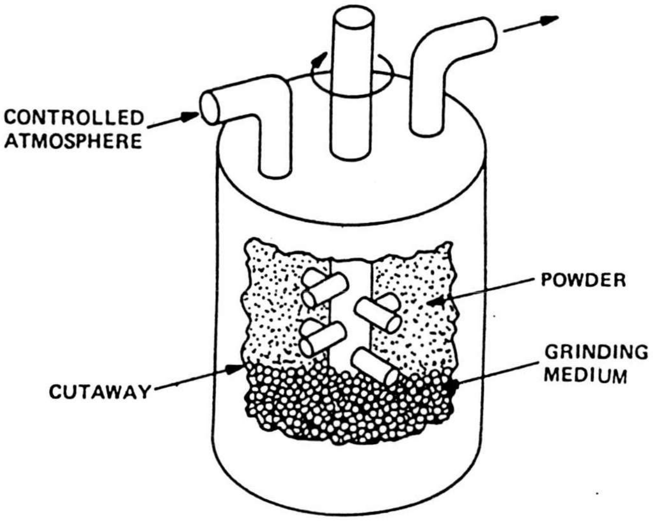

Figure 2.5 Schematic of an attrition mill (Richerson,1982).

3. Granulation

Before the forming is performed, the granulation of a desired powder is another approach to acquire better flow property of the powder. Although very small particle size is importance for fine material, such particles do not flow very well when the die is filled. In order to overcome such a problem granulation is a method used to produce a satisfactory prepacked powder that consists of controlled agglomerate sizes or granules and to reduce the volume of the material during pressing, extrusion or injection molding. However, granule size is important in the shape forming of a product because high density packing of the material can not be obtained with uniformly fine particle but with the coarser particles allowing the finer ones to fill up the interstitial spaces between them can result in denser packing (Kingery, Bowen and Uhlmann, 1991).

4. Forming

Forming is the process in which a powder material is consolidated into a coherent and compacted body having a particular geometry and uniform microstructure. In general, the selection of a forming method for a desirable product counts on the dimension, shape and microstructural characteristics of a product as well as level of reproducibility. The largest number of polycrystalline ceramic products are usually formed by pressing. It is the simutaneous compaction and shaping of a powder or granular material which are premixed with suitable binder and lubricants and then are confined in a rigid die or flexible mould using applied pressures. Product obtained from forming process are called green body or compacted body. The most extensively practiced forming process is uniaxial pressing in which the compaction takes place as pressure is applied along a single axial direction Other techniques for powder consolidation and shape forming can be summerized in Table 2.1.

Table 2.1 Techniques for consolidation of powder into a particular shape.

Pressing	Plastic forming
Uniaxial pressing	Extrusion
Isostatic pressing	Injection molding
Hot pressing	
Hot isostatic pressing	
Casting	Others
Slip casting	Frame spray
Soluble-mold casting	Green machining
Nontradition casting	etc.

5. Coating

Coating is a useful method by which a glazing is applied in a thin film onto a green body or calcined body or sintered body, for many specific purposes. The major advantages of coating are that:

1. It provides a decorative attraction in different styles as required.
2. It causes special effect in various aspects including electrical, optical and chemical effects.
3. It can protect a body from drastic environments e.g. sunlight, moisture and various chemicals.
4. The strength of a product is improved.

There are several methods to be used for applying coatings the body including spraying, fountaining, dipping, slingering, spattering, srcreening and so on. One of these common methods is spraying that can be widely employed in many applications because the thickness of a coating is uniform and excellent smoothness is given. The basic principle of the spraying method is concerned with controlled of the slurry or slip coating and the direct flow of the droplets onto a surface. On impact, the droplets deform and coalesce into a thick film. The thickness of a coating is dependent on the spray geometry controlled by the design of a nozzle, solid content of the slurry, working distant between a sprayer and surface and spraying time as well as the flow of droplets. The slurry must be thoroughly screened before being pumped to the nozzle. A smaller nozzle tends to produce a narrow distribution of droplet size and a more controlled spray. Furthermore, the slurry should be psudoplastic to permit flow through the nozzle but to resist running due to gravity, air currents and mechanical vibrations of the film on the product. The strength and viscosity of the film can be increase a little by the adsorption of the droplets into a product and gelation of a liquid on the surface.

6. Sintering

After surface finishing or coating, greenbody is densified by firing in a variety of kilns or furnaces with desired temperature and times. The densification of a particular ceramic compact during firing is technically referred to as sintering. Sintering is a process whereby heat treatment is used to convert a powder compact into a dense polycrystalline solid. This process is essentially required for a removal of pores between particles in order to make adjacent particles combined each other through the formation of strong bonding.

Thermodynamically, sintering is an irreversible process in which there is a decrease in free energy due to the reduction of surface area. Sintering temperature is usually operated not below two-thirds of the melting temperature, which is sufficient for material transport by diffusion in the solid state. Diffusion can occur by movement of atoms or vacancies along a surface or grain boundary or through the volume of the material.

Surface diffusion is general transport mechanism that can result in surface smoothness, particle joining and pore rounding, but it does not produce volume shrinkage. On the other hand, volume diffusion, whether along grain boundary or through lattice dislocation, does result in shrinkage as illustrated in Fig 2.6.

In addition to solid-state sintering, other transformation may involve during presintering process such as the decomposition of organic binder and inorganic carbonates, the vaporization of water of crystallization and the pyrolysis of inorganic impurities as well as changes in the oxidation states of some transition metal and rare-earth ions (Reed, 1989).

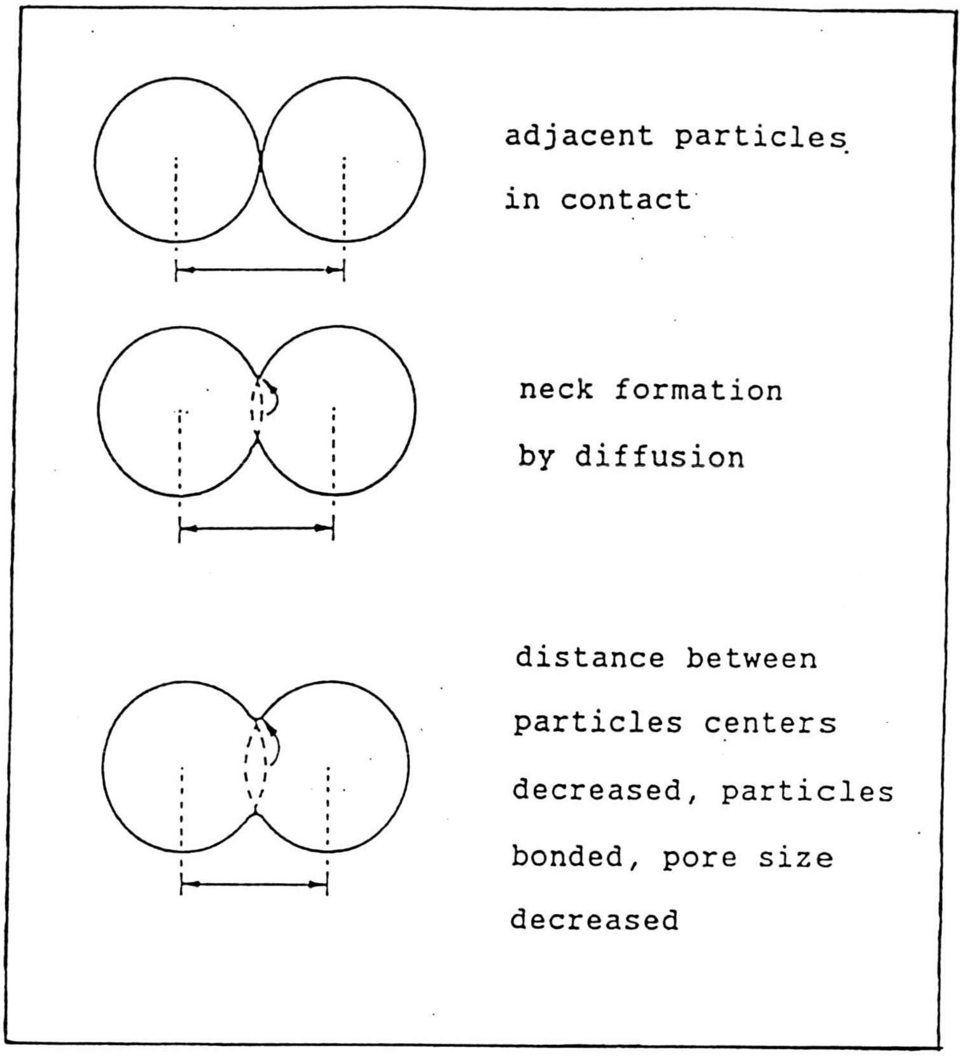

Figure 2.6 Schematic of solid-state material transport(Richerson,1982).

Mechanisms for sintering process may be split into three stags, the initial, the intermediate and the final stage. Observations of microstructural change in each stag can be shown in Table 2.2

Table 2.2 Microstructural changes observed in solid-state sintering (Reed, 1989).

Stage	Observation
Initial	- Surface smoothing of particles
	- Grain boundaries form, neck growth
	- Rounding of interconnected, open pores
	- Diffusion of active, segregated dopants
	- Porosity decreases <12%
Intermediate	- Shrinkage of open pores intersecting grain boundaries
	- Mean porosity decreases significantly
	- Slow grain growth
	(Differential pore shrinkage, grain growth in heterogeneous material)
Final (1)	- Closed pores containing kiln gas form when density is ≈92% (>85% in heterogeneous material)
	- Closed pores intersect grain boundaries
	- Pore shrink to a limited size or disappear
	- Pore larger than grains shrink relatively slowly
Final (2)	- Grains of much larger size appear rapidly
	- Pores within larger grain shrink relatively slowly