Chapter 2

Literature Survey

2.1 Hydroxyapatite

Hydroxyapatite(HA,HAp) is a ceramic compound of apatite group, crystallizing in hexagonal system (space group $P6_3/m$ with cell dimensions of a = 9.423 and c = 6.875 Å). It is a calcium phosphate including hydroxide which chemical formula is $Ca_{10}(PO_4)_6(OH)_2$ and its Ca/P ratio is represented as 1.67. However, the hydroxyapatite structure is held within a rather wide range of nonstoichiometric compositions. Calcium-deficient or partially dehydrated (OH-deficient) apatite is generally known. The degree of its nonstoichiometry depends on the method of preparation.

Hydroxyapatite has been commonly used as a substitue material for damaged teeth or bone over the past few decades because of its crystallographical similarity to various calcified tissue of vertebrates. The excellent biocompatibility of this material has been widely documented in the dental as well as the orthopedic literatures (Groot, 1983; Ueno et al., 1987; Callis et al., 1988). Even in cases where the hydroxy-

apatite construct has failed,an extremely benign cellular response was found at the microscopic level (Lavernia and Schoenung, 1991). Jarcho et al. (1976) confirmed that dense hydroxyapatite was compatible with bone and exhibited little or no biodegradation after long period of implantation.

Dennison (1980,quoted in Boretos,1985) was one of the first to propose that a chemical bond was developed between the bone and the ceramic, and the union was usually so strong that the implant can not be removed without fracturing surrounding bone.
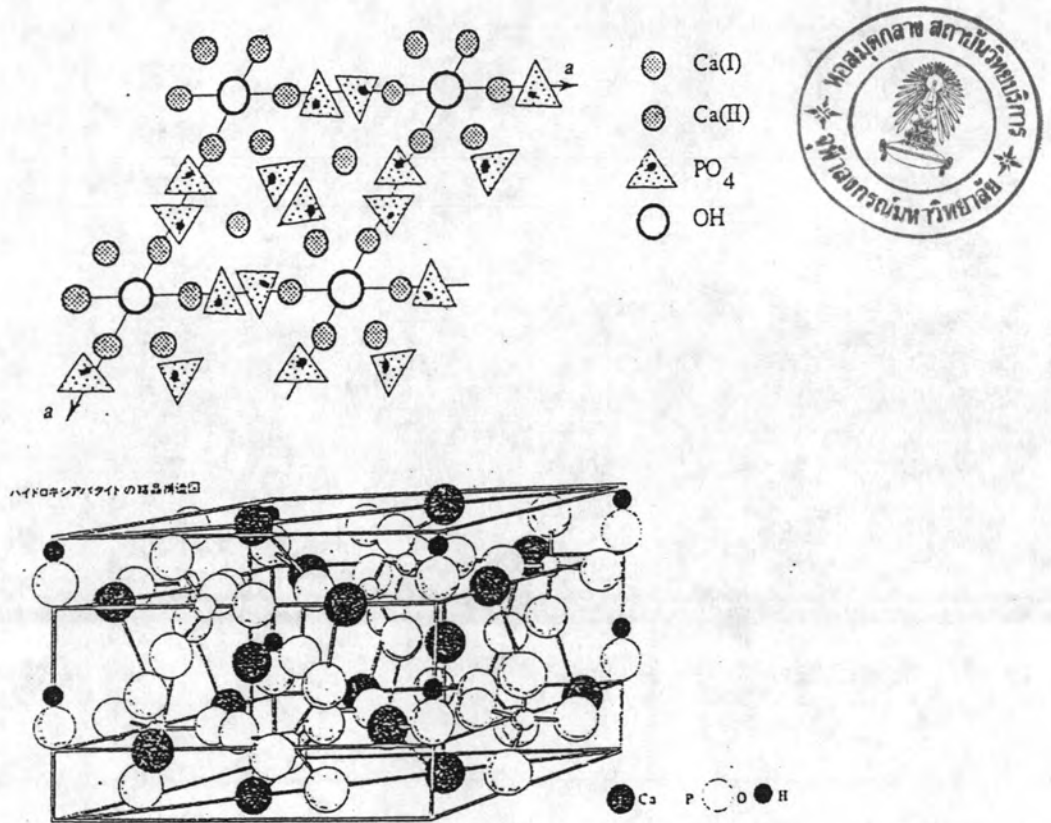
Figure 1. Crystal structure of hydroxyapatite
projected along c-axis(upper) and
along a-axis(bottom).
(Aoki, 1991)

2.2 Strengthening of Hydroxyapatite

The strength of brittle polycrystalline materials, as well as hydroxyapatite, depends on porosity and grain size. As the porosity increases the strength of the material decreases rapidly as indicated by the Ryskewitch equation (Hench, 1991)

$$\sigma = \sigma_0\, e^{-cp}$$

where is strength, σ_0 is strength at zero porosity, c is constant and p is porosity. Rao and Boehm (AoKi, 1991) reported that compressive strengths of apatite have an exponential dependence on porosity.The flexural strengths of apatite, measured in Aoki's works (1991), tended to depend on porosity rather than grain size.

Jarcho et al. (1976) measured the compressive and flexural strengths of dense polycrystalline hydroxyapatite obtained by heating gelatin precipitated from $Ca(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$. The high compressive strength (917 MN/m^2) resulted from fine grain size and high purity of the starting hydroxyapatite, from forming process (filtration) and from strength testing that the length of test specimen was shorter than which in standard testing.

Sombuthawee, Monroe and Rausch (1981) attempted to strenghten polycrystalline hydroxyapatite by means of surface ion-exchange. Flexural strength increase of about

22 %(to 79 MN/m^2), occured when sintered calcium hydroxyapatite was reacted with SrCl$_2$ in the solid state, resulting in formation of chlorapatite in the surface of product.

Kondo et al.(1984) measured the flexural strength of sintered hydroxyapatite added with frit (various compositions of P$_2$O$_5$, CaO, BaO and Al$_2$O$_3$). The aim of frit addition was to retard grain growth during sintering. The everage flexural strength of the strongest product was 205.8 MPa.

Aoki(1991) measured mechanical properties of sintered hydroxyapatite, hydroxyapatite-tricalcium phosphate ceramics, strontium-substituted hydroxyapatite and titanium dioxide-hydroxyapatite composite ceramics at various compositions and temperatures and indicated the relation between flexural strength and grain size. Furthermore, he showed the effect of various additives on flexural and compressive strength of sintered hydroxyapatite (Fig. 2).
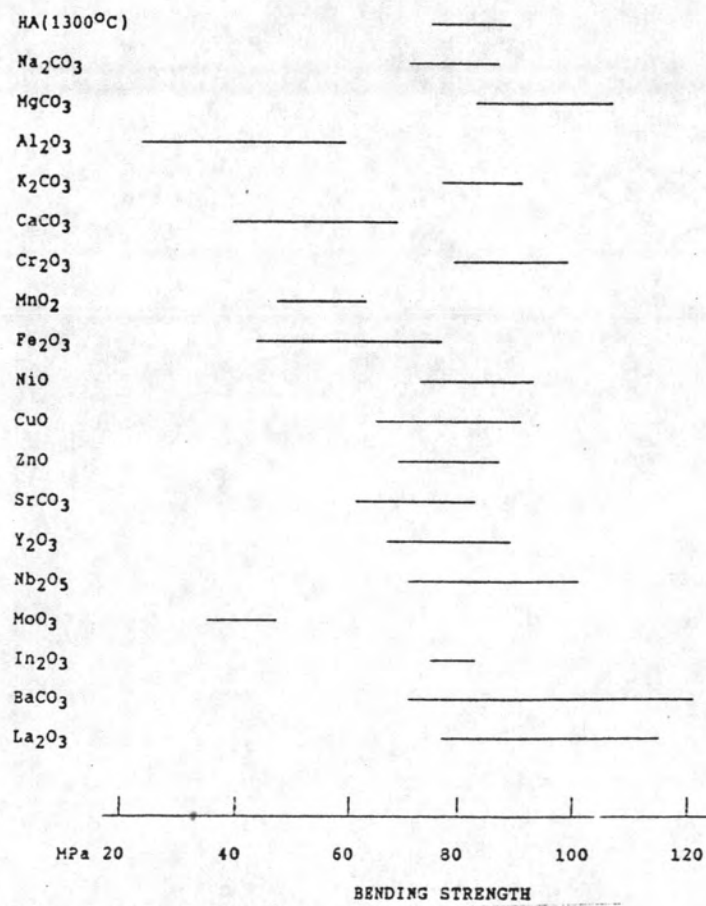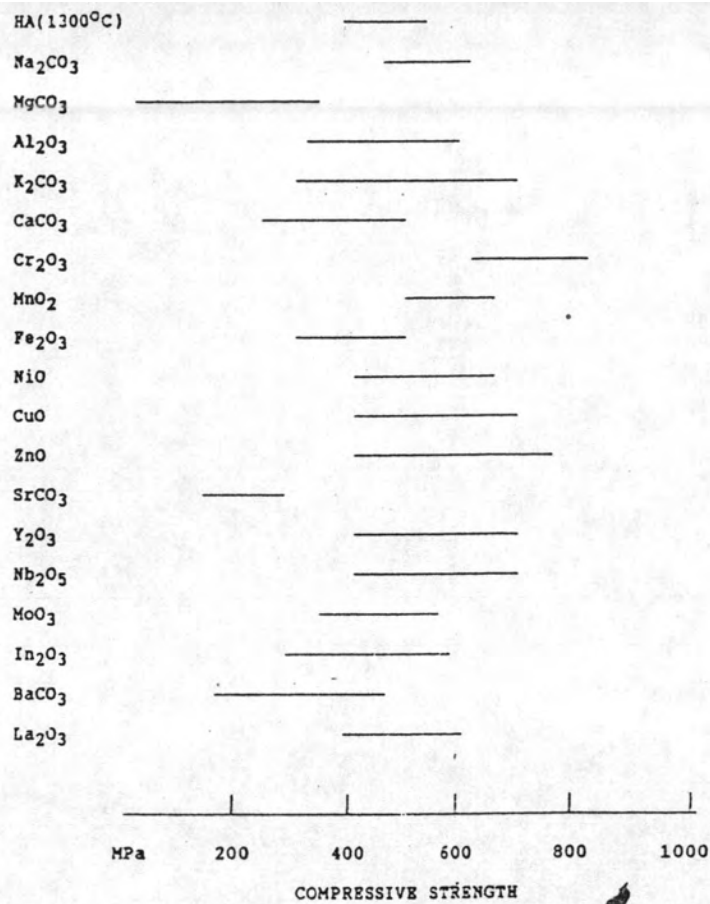
Figure 2. Effects of additives on compressive and
bending strength of sintered hydroxyapatite

2.3 Strengthening by compressive surface stresses

Ceramic materials are characteristically brittle and their use is limited by relative weakness in tension and under impact stress. Various procedures have been devised to use the high intrinsic strength of brittle ceramics materials, and the most common of these involves developing a compressive surface stresses with a compensating tensile stresses in the interior of the body.

Compressive surface stresses have been used to strengthen ceramics since antiquity (Kirchner, 1979). Most pottery and china ware are glazed with glazes that have lower expansion coefficients than those of the bodies which they are applied.As the materials are cooled to room temperature after glazing, the body tends to contract more than the glaze, placing the glaze in compression and the body in tension.

Warshaw (1957, quoted in Kirchner, 1979) used the differential shrinkage of two different alumina porcelain bodies to form compressive surface layers but the strengths of the original ceramic bodies and the degree of improvement achieved were unimpressive.

Burton, Brubaker and Russell (1967) formed two-layer laminated ceramics, using three vitrified whiteware bodies having different thermal expansion coefficients, leading to tensile and compressive stresses in the layers and measured flexural strengths and impact resistances of the laminates. Substantial improvements in both properties were observed when the compressive layers were subjected to tensile force due to the externally applied loads. Even so, the resulting bodies were not very strong in comparison with readily available fine-grained oxide ceramics.

Moody (1969) used B_4C coatings to strengthen titanium carbide bodies. B_4C has lower thermal expansion coefficient than titanium carbide ($56 \times 10^{-7} \, {}^{o}C^{-1}$ vs $80 \times 10^{-7} \, {}^{o}C^{-1}$). B_4C powder was applied to the surface and sintered. A 50% increase in strength to 10,300 psi was observed.

In some works of Kirchner et al. (1970-1971) many materials were strengthen by compressive surface stress induction. Zircon porcelain was strengthened by up to 40% (to 41,400 psi) using CVD-Si_3N_4 coatings. The thermal expansion coefficient of Si_3N_4 is lower than that of zircon porcelain($26.31 \times 10^{-7} \, {}^{o}C^{-1}$ vs $41.10 \times 10^{-7} \, {}^{o}C^{-1}$). Hot pressed SiC could be strengthen slightly by nitriding CVD-Si coatings to form Si_3N_4 by 18% to 49,830 psi.

In glass-ceramics, Duke et al. (1968) reported that glasses in the $Na_2O-BaO-Al_2O_3-SiO_2$ system nucleated with TiO_2 were strengthen by glazing with lower expansion coefficient glaze, resulting in moduli of rupture up to five time that of the initial glass-ceramic.

Stress in surface layer develops as a result of a differential thermal expansion between the coating and the body as they cool from the setting temperature down to room temperature. As cooling continues, the higher-expansion body continues to contract and the compressive stress,which is induced in the surface, is compensated by an equivalent tensile stress in the body.
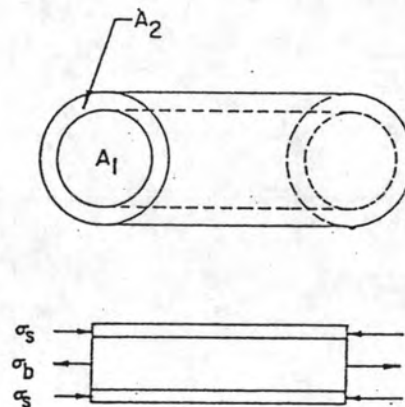

Figure 3. Schematic of stresses in a cylinder coated with a compression coating. (Duke et al., 1968)

The magnitude of these stresses can be estimated as follows: In a cylinder (see fig. 3), if we assume that

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 ratios are the same for coating and body and,

4) the radial and circumferential stresses are very small with respect to the axial stresses, then

$$6s = -(\alpha_1 - \alpha_2)\, \Delta T \, \frac{E}{1-\sqrt{}} \, \frac{A_1}{A}$$

$$6b = -(\alpha_1 - \alpha_2)\, \Delta T \, \frac{E}{1-\sqrt{}} \, \frac{A_2}{A}$$

$6s$ and $6b$ = stresses in surface layer and body, respectively.

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

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

E = Young's modulus.

= Poisson's ratio.

A, A_1 and A_2 = cross-sectional areas of the cylinder, body and coating, respectively.

The condition at the surface has a vital bearing on the mechanical strength of the materials. Since ceramic materials break easily in tension, this surface compression, as well as the initial body strength, must be overcome before occures. The presence of compressive stresses may prevent surface flaws from acting to cause failure when the body is stressed.

If suitable conditions are not taken during the heating and cooling of the product, the resulting strains and stresses set up in the product may cause crazing or peeling.

Because ceramics are less able to withstand tensile force than compressive force, when thermal expansion of coating is only slightly greater that of the body, the surface layer fails in tension with crazing being the result. In contrast, when the difference between the thermal contraction of body is much higher than that of the coating, excessive compression is generated in the coating. This can be greater than the strength of adhesion between surface layer and body and there is then a stress-relieving fracture at the interface known as peeling. However, the materials can be strengthen, when the conditions are adjusted.
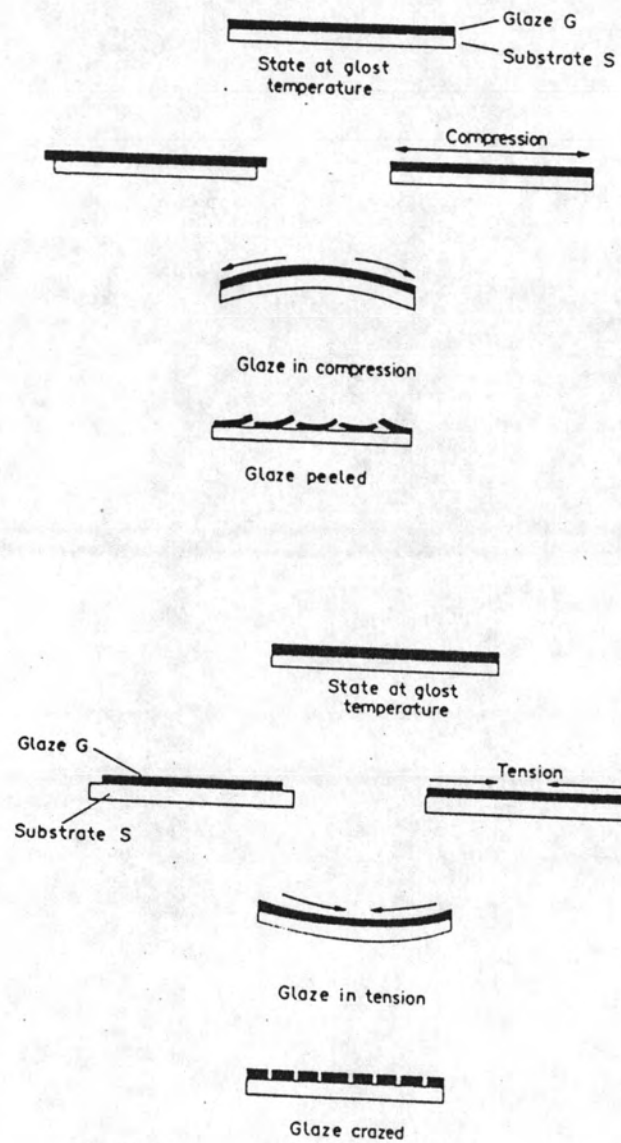
figure 4. Crazing and peeling in ceramic coatings.

(Taylor and bull, 1986)

2.4 Ceramic Processing

Ceramics have been produced for centuries. The earliest ceramic articles were made from naturally occuring raw materials. Early civilizations found that clay became plastic when water was added and could be molded into shapes. The shape could then be dried in the sun and hardened in a high-temperature fire. The word "ceramic" comes from the Greek word "keramos", which translates roughly as "burnt stuff" (Richerson, 1982).

2.4.1 Powder Preparation

During the past 60 years, scientists and engineers had acquired a much better understanding of ceramic materials and their processing and had found that naturally occuring minerals could be refined or new composition synthesized to achieve unique properties.

The preparation of synthetic powders from solution is the most common process, and is often called the wet chemical powder preparation technique (McColm and Clark, 1988). Starting materials are milled, dissolved in acids, water, alkalis or molten salts at suitable pH, pressures and temperatures. At this stage actions can be taken to control purity, and, particle size and shape by such methods as electrolysis, precipitation or crystal-lization. Then salt of desired powder or desired powder, derived from the reaction, will be separated from the

solution by such methods as filtration or evaporation. Salt of desired powder will also be calcined (heat treated) to produce desired powder.

Experimentally, it is well known that the strength of polycrystalline ceramics increases with decreasing particle size. If starting materials are not available with the optimum particle size distribution, the method called powder sizing must be used. In this research, screening and ball milling were used.

2.4.1.1 Screening

For this method, the powder is poured onto a single screen having the selected size openings or on a series of screens, each subsequently with smaller openings. The particles are separated into size ranges, the particles larger than the screen openings remain on the screen and smaller particles pass through until they reach a screen with holes too small to pass through. Screen sizes are classified according to the number of openings per linear inch and are referred to as mesh sizes. A 16 mesh screen has 16 equally spaced opennings per linear inch; a 325 mesh screen has 325. Table 1 compares the mesh size of standard screens with the actual size of the openings.

" Mesh " sieve designation	Sieve opening	
	mm	in.
4	4.76	0.187
6	3.36	0.132
10	2.00	0.0787
12	1.68	0.0661
16	1.19	0.0469
20	0.84	0.0331
40	0.42	0.0165
80	0.177	0.0070
120	0.125	0.0049
170	0.088	0.0035
200	0.074	0.0029
230	0.063	0.0025
270	0.053	0.0021
325	0.044	0.0017
400	0.037	0.0015

Source : ASTM E11, <u>Annual Book of ASTM Standards</u>, American Society for Testing and Materials,Philadephia,1970.

Table 1. ASTM standard screen sizes.

2.4.1.2 Ball Milling

The desired particle size distribution usually cannot be achieved simply by screening. Ball milling is one of most widely used. Ball milling consists of placing the powders to be ground (the charge) in a closed container with grinding media (balls, short cylinders or rods) and rotating the container around its axis so that the media cascade. The powder particles move between the much larger media and between the media and the wall of the mill and are effectively broken into successively smaller particles.

During milling, several particles are simultineously and repeatedly subjected to stress application in the milling zone (Somasundaran,1978). With each stress application, several fractures occur in each particle.The fracture of a particle involves the propagation of cracks that are present or initiated in the particle. The stresses required for fracture is given by the Griffith relationship:

$$\varsigma = \sqrt{\frac{2\ E\gamma}{L}}$$

E   =   Young's modulus

γ =   Fracture energy

L   =   Crack length

ς =   Stresses required for fracture

For brittle materials, γ is between 10^3 and 10^4 erg/cm^2. With plastic deformation, γ is much greater than 10^4 erg/cm^2. When a particle is repeatedly fractured, each new particle (fragment) tends to be stronger. The distribution of cracks and the interaction among them during propagation will essentially determine the size distribution of the particles obtained during fracture of each particle.

Milling can be conducted either dry or wet. Wet milling (milling with addition of dispersive liquid such as water or some organic liquids.) is usually more efficient than dry milling. Cushioning effects due to the presence of a bed of fines will be less during wet milling than during dry milling, since the fine particles tend to remain suspended in the liquid.

Variables of operation include the size and angular velocity of the mill, the size of the grinding media relative to the size of the feed powder, the loading of the mill, the relative volumes of the grinding media and feed powder, the physical characteristics of the grinding media, agglomeration of feed or product, and, in wet milling, the viscosity of the slurry during milling.

In many cases, ball mills are used for mixing and deagglomeration.

2.4.2 Granulation

After powder preparation, the following important step is forming. If seleted forming method is pressing, extrusion or injection molding such powder may cause problems. Fine particles (<1 μm diameter) have poor pourability and are usually dusty. The solution to this problem is to granulate the powder in order to achieve good pouring (free-flowing) characteristics. Granulation is a method used to produce a satisfactory pre-pressing material consisting of controlled agglomerate sizes. The controlled agglomerates are called granules. These granules should be broken down by the relatively low pressures in the early steps of pressing to produce high density. Size of granules is also important because high packing density can not be formed with uniformly fine particles but with coarser particles allowing the finer particles to fill the interistices between them (Kingery, Bowen and Uhlmann, 1991). For this reason, two granule sizes (with suitable size difference) should be produced to improve the strength of green body.

The following methods have been found satisfactory for granulate formation of ceramic powders ranging from clays to submicron SiC :
(McColm and Clark, 1988)

1. Spray-drying

2. Greenbody crushing and sieving

3. Enrich mixing

Spray-drying : A pressure of 50-300 kPa is applied to small drops of powder slurry (concentrated powder solution) which are thereby atomized to a fine spray. The droplets are uniform in size, in range 100-500 μm and are rapidly dried by hot gas. It is energetically expensive and is not suitable for the preparation of small amounts of powder.

Greenbody crushing and sieving: This method is accomplished by pressing the powder into compacts that are chopped or crushed and then screened to obtain the desired granules. However,a wide range of powder particle size now exits, and even though good pourability is achieved, sintering inevitably produces exaggerated grain growth and unsatisfactory microstructures.

Enrich mixing : The powders are mixed when up to 12% moisture is added. A common improvement is to add up to 6 % of water-soluble binder material during tumbling (moisture contents used in granulating tile and high alumina bodies containing clay are commonly in the range of 20-36 vol% (8-14 wt%) (Reed,1989). The damp or plastic material is then forced through orifices of the desired size or screened. The resulting granules are usually harder and more dense than spray-dried granules and irregular in shape. They do not flow as readily, but do tend to pack to a lower volume.

2.4.3 Forming

Forming is the process which transforms the unconsolidated system of feed material into a coherant, consolidated body having particular shape. The selection of a ceramic-formaing technique for a particular product is very dependent on the size, shape, and dimensional tolerances of the product, the requisite microstructure characteristics and levels of reproducibility required, and capital investment and productivity considerations. Products obtained from forming process are called green body or compact body. Major forming techniques are summarized in table 2.

Forming method used in this research was uniaxial pressing. Pressing is accomplished by placing the powder or prepared granules into mold and applying pressure to achieve compaction. For uniaxial pressing, compaction occurs when pressure is applied along a single axial direction. Most pressure are either mechanical or hydraulic. Mechanical presses typically have a higher production rate. Three types of mechanical presses are widely used in ceramic industries, single-stroke, rotary and toggle presses.

Hydraulic presses transmit pressure via a fluid against a piston.They are usually operated to a set pressure, so that the size and characteristics of the pressed component are determined by the nature of the feed powder, the amount of die fill, and the pressure applied.

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Pressing

     Uniaxial pressing

     Isostatic pressing

     Hot pressing

     Hot Isostatic pressing


Casting

     Slip casting

     Soluble-mold casting

     Nontradition casting


Plastic Forming

     Extrusion

     Injection molding


Others

     Flame spray

     Green machining

     etc.
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Table 2.   Major techniques of forming process.

Hydraulic presses are suitable for Lab-scale operation because they have a much lower cycle rate than mechanical presses.

2.4.4 Coating

Coating, in ceramic field, is applied to greenbody, calcined body or sintered body for many purposes such as : to provide a decorative attraction; to provide special effect (electrical, optical, chemical effects), to protect body from severe environment, to increase strength, etc.

Several techniques used for coating are:

1. Dipping
2. Spraying
3. Sedimentation and tapes
4. Curtain coating
5. Trailing
6. Paste
7. Pressing
8. Pouring
9. Painting and Brushing
10. Electrophoresis
11. Flame spraying
12. Sol-gel coating

13. Silk screen

14. Self-coating

15. Fluidized bed

etc.

Dipping, the commonest technique, was selected in this research. Dipping is a simple, efficient and quick technique requiring no special equipment, although success with the way depends upon experience.

Dipping is the operation where the body (greenbody, calcined or sintered compact body)is immersed in the coating slip, withdraw, allow to drain (in drain casting) and dry. the amout of coating taken up depends upon the state of the body, the rheological properties of the slip and the time of immersion and also depends on the nature of body's porosity.

Coating slip is prepared by mixing the batch composition with water added. Viscosity of coating slip depends on nature and particle size of composition and amount of water. In many cases, additives such as binder and deflocculant are necessary for rheology control.

2.4.5 Sintering

After surface finishing or coating, greenbodies are densified by firing in a variety of klins and furnaces with desired temperatures and times. The densification of a particulate ceramic compact during firing is technically referred to as sintering. Sintering is the process whereby a heat treatment is used to convert a powder compact into a dense polycrystalline solid. Sintering is essentially a removal of pores between the particles (accompanied by shrinkage of the component), combined with growth together and strong bonding between adjacent particles.

Thermodynamically, sintering is an irreversible process in which the free energy decrease is brough about by a decrease in surface area. Sintering does not commonly begin until the temperature in the furnace exceeds one-half or two-thirds the melting temperature, which is sufficient to cause significant atomic diffusion for solid state sintering or significant diffusion and vicous flow when a liquid phase is present or produced by a chemical reaction. Material changes on heating prior to sintering may include drying, the decomposition of organic binders, the vaporization of chemically combined water from the surfaces of particle and from within inorganic phases contaning water of crystallization, the pyrolysis of particulate organic materials introduced with the raw materials or as con-

tamination during processing, changes in the oxidation states of some transition metal and rare-earth ions, and the decomposition of carbonates, sulfates etc. introduced as additives or as a constituent of the raw materials. (Reed, 1989).

Modelling of sintering behaviour can lead to several mechanisms and ways to estimate their rates that are conflicting in predictions. However, understanding of these mechanisms is the most reliable way to interpret sintering behaviour and then to proceed to the design of optimum experimental conditions. Models have been constructed from observing the characteristic phenomena as the change from green compact to dense body proceeds (fig.5) (McColm and Clark, 1988).

Sintering process can be defined into three stages as follows:

1. The initial stage :

   - With time, there is an increase in inter-particle contact area.

   - Sharp re-entrant angles at the points of contact are rounded off.

   - In many cases the powder particle centres approach each other at this stage, but in not quite as many cases the particle centres do not move. The first happening is detected as a start of densification of the compact.

2. The intermediate stage :
   - Nearly all pores are interconnected, but with time they decrease in volume.
   - At longer times, the pores become broken into isolated pores.
3. The Final stage :
   - Grains grow and grain-boundary area decreases.
   - Isolated pores decrease in volume, giving the final increase in density.

The sintering variables that can be used to influence the material movement mechanism are :

1) Temperature
2) Time at chosen temperature
3) Powder particle size and shape
4) The composition of the system with particular reference to the atmosphere and to additives either in solid solution or as a sinter mix
5) pressure

In this research, no liquid phase was produced during sintering temperature which called solid-state sintering. Solid-state sintering involves material transport by diffusion. Diffusion can consist of movement of atoms or vacancies along a surface or grain boundary or through the volume of the material. The driving force for solid-state sintering is the difference

Cold pressed   Initial-intermediate   Final stage
sinter

Viscous flow sinter
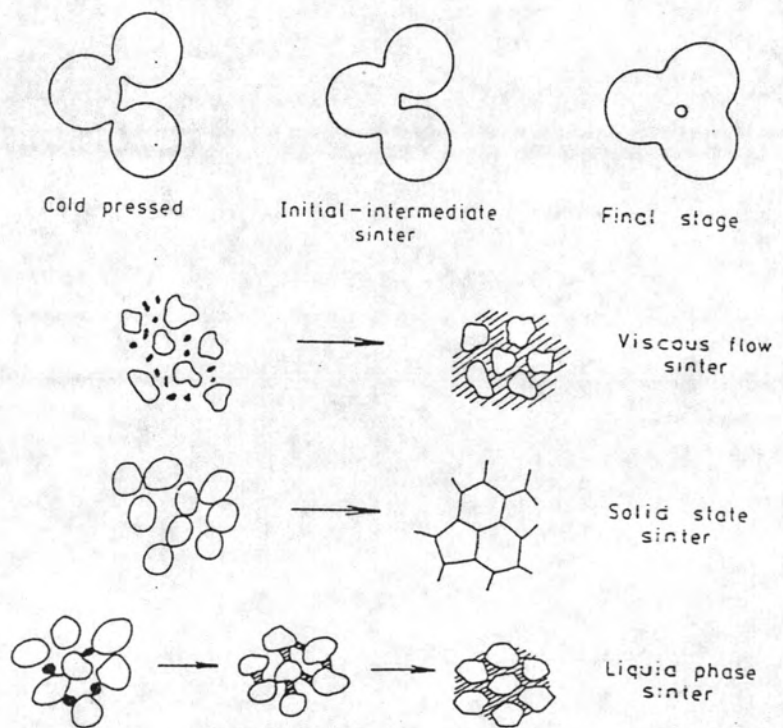
Solid state sinter

Liquid phase sinter

Figure 5. Schematic representation of the stage of
sintering and the types of sinter process.
(McColm and Clark, 1988)

in free energy or chemical potential between the free surfaces of particles and the points of contact between adjacent particles.

Microstructural changes observed in the three stages of solid-state sintering are summerized in table 3.
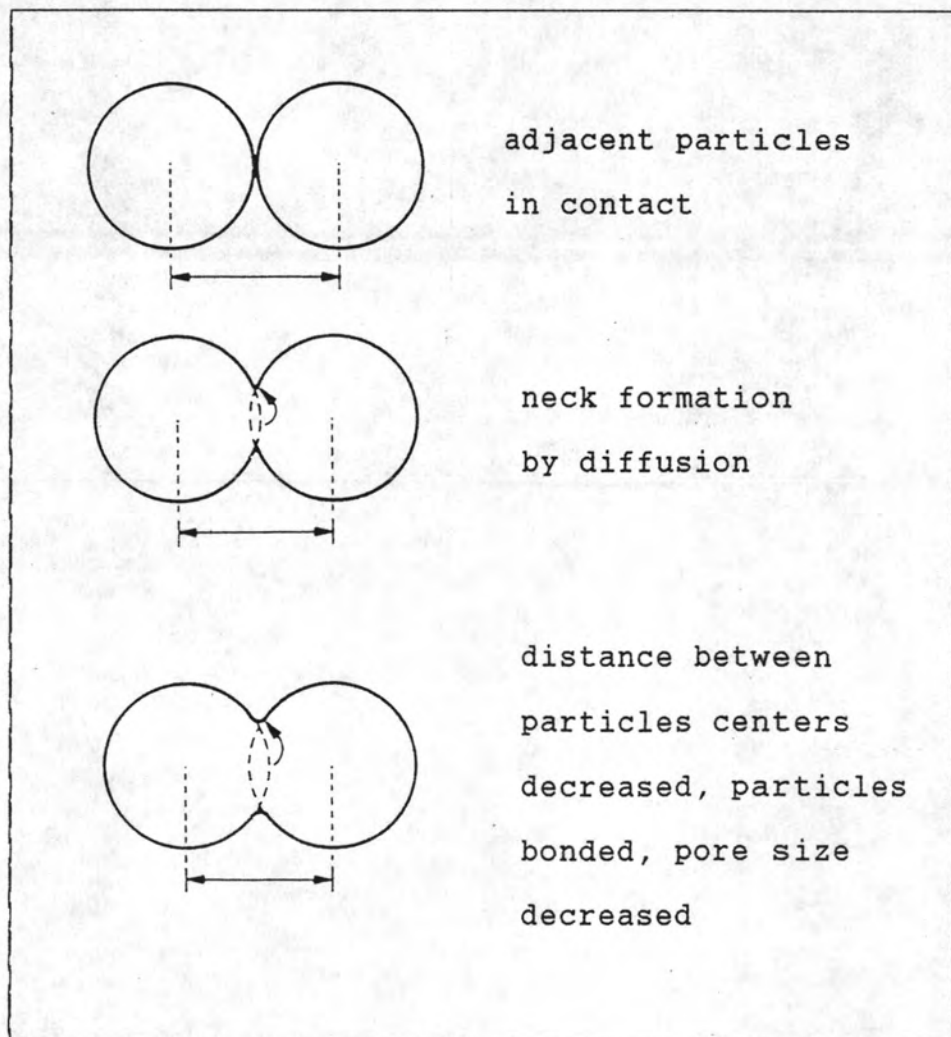

adjacent particles
in contact

neck formation
by diffusion

distance between
particles centers
decreased, particles
bonded, pore size
decreased

Figure 6. Schematic of solid-state material transport.

(Richerson, 1982)

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 %
Intermidiate	- 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 - Pores 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 grains shrink relatively slowly

Table 3. Microstructural changes observed in solid-state sintering. (Reed, 1989)