

Chapter II

Literature Survey

2.1 Hydroxyapatite

Hydroxyapatite is one of the three basic compounds incorporating in bone matrix. It contains at 69% of bone weight. The chemical formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and its Ca/P ratio is represented as 1.67. In general various types of calcium phosphate having different Ca/P ratio from 0.5 to 2.0 can be synthesized. The Crystal structure of HAp is almost isostructure with fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) in which the fluorine atom is replaced by a hydroxyl group.

Hydroxyapatite is in the hexagonal system, space group $P6_3/m$, with the lattice parameter, $a(=b) = 9.432 \text{ \AA}$ and $c = 6.875 \text{ \AA}$ and its structure project along C-axis is shown in Fig 1.1. Each calcium atom is surrounded by 6 oxygen atoms as belong to PO_4 groups and OH group. Calcium atoms form a triangle are normal to the c-axis. The arrangement of OH group surrounded by a calcium triangle along the

c-axis is also characteristic of HAp structure. Phosphate atom surrounded by 4 oxygen atoms form the tetrahedral as a slight distortion.

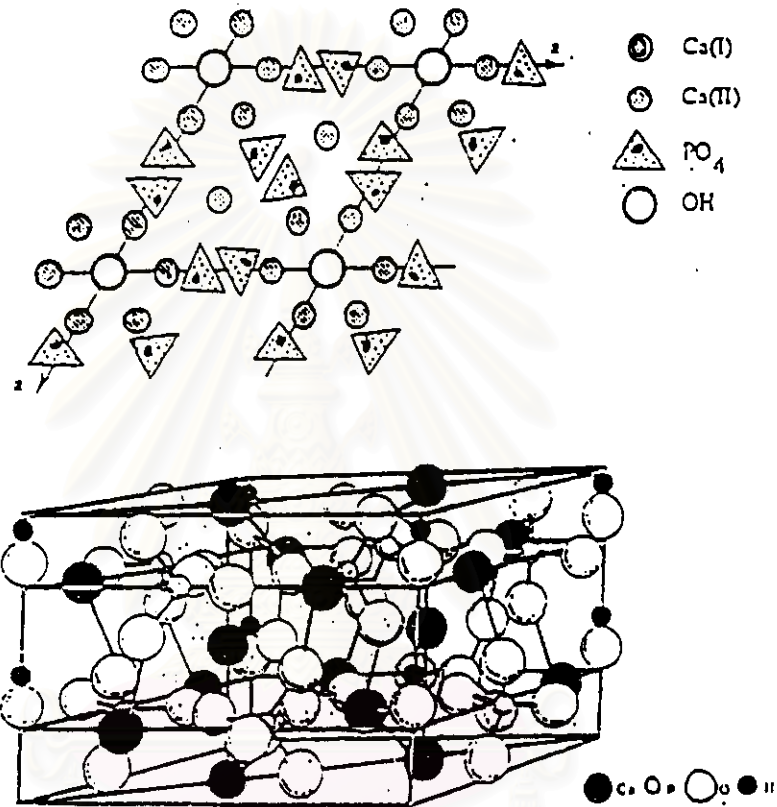


Fig. 2.1 Crystal structure of hydroxyapatite projected along c-axis (upper) and along a-axis (bottom) (Aoki,1991)

The characteristic of an ideal materials for bone substitution is biocompatibility with surrounding tissue. Calcium phosphate ceramic system has been extensively studied since their element components are

presented in bone naturally. Hydroxyapatite and tricalcium phosphate are the two calcium phosphate ceramics most commonly used for bone replacement due to their excellent biocompatibility. It was found that dense and porous sintered HAp and tricalcium phosphate are compatible with bone and expose partially biodegradable or nondegradable by the body fluid after 6 months of implantation (Jarcho et al.,1976). It is possible to arise chemical bonding between bone and the ceramics. Generally, HAp is less biodegradable and more stable than tricalcium phosphate. An implant made of HAp placed in bone will be presented after 3 or 4 years of implantation where as tricalcium phosphate is partially resorbable and will partially disappear in 6 to 15 weeks, depending on its porosity and exact stoichiometry (Lavernia and Schoenung,1991).

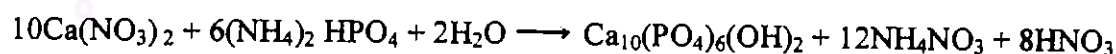
However, the limitation of HAp in its use as its mechanical properties is not sufficient for more demanding load bearing application, such as fracture fixation or spinal fusion.

2.2 Synthesis of Hydroxyapatite

Generally, HAp is prepared by wet method, dry method, hydrothermal method, alkoxide method and flux method (Aoki, 1991).

2.2.1 Wet Method

The wet method using solution reaction is the most popular preparation method to provide the small crystalline or noncrystalline HAp powder. It is composed of 2 kinds of process. One is a process involving a neutral reaction of acid and alkaline solution and the other involve the reaction of calcium salts and phosphate salts. The following chemical formulas are used to describe this method;



It is not easy to determine the exact proportion of $\text{Ca}^{2+} : \text{PO}_4^{3-}$ in the solution in the preparation process. The pH measurement method

used to control the Ca/P mole ratio of HAp since chemical composition and properties of HAp are based on the Ca/P ratio.

2.2.2 Dry Method

The dry method is useful for preparing crystalline HAp by solid state reaction. The following reaction is presented for the examples of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and calcium carbonate as the starting material.



The dry method provides synthesized HAp with a very fine powder and an excellent crystallinity.

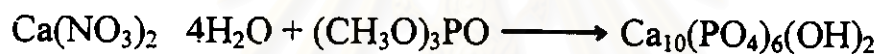
2.2.3 Hydrothermal Method

This method is available for producing perfect single crystals of HAp. The lattice constants of HAp preparing by hydrothermal method depend on the reaction temperature and pressure.

2.2.4 Alkoxide Method

Alkoxide method is used to prepare thin HAp film. Calcium nitrate 4-hydrate and trimethyl phosphate is used as starting materials. These materials are dissolved in solvents, i.e. ethanol or formamide. After the solvent is vaporized, the mixture of calcium nitrate 4-hydrate and trimethyl phosphate is heated at 500-1000°C to produce well-crystallized HAp.

The chemical reaction is represented as follow :



2.2.5 Flux Method

Large single crystal of apatite compounds is obtained using this method. However, pure HAp is not prepared by this method. The boron-containing apatite single crystals using the flux method is described as the following:

The starting materials, HAp, B₂O₃ and CaO, are mixed together. Then the mixture is put in a platinum crucible, heated up to 1200 °C and followed by a controlled cooling rate is after firing, The appearance of

the products is clear and colorless, the obtained crystals are elongated up to 11 mm and up to 0.3 mm thick.

According to the complication of manufacturing techniques either by precipitation from aqueous solutions or hydrothermal treatment, synthetic HAp is expensive. Lorprayoon (1989) has also been successful preparation of 2 kinds of HAp from cattle bone ash. In this method, HAp originated from selected part of cattle bone after organic materials had been removed were calcined at 700 °C, crushed, milled, dried and further powdered (MP-HAp). The chemically treated bone (TP-HAp) was prepared by dissolution the calcined MP with nitric solution and precipitation in NH_4OH solution at pH 10.5. The precipitate was boiled, filtered, washed and dried. By this method, the 2-HAp obtained have low cost comparison to other methods especially the MP product. But the mechanical strength such as compressive strength and flexural strength of MP were found to be 137.7 and 25.7 MPa, respectively. As the low strength, thus MP was limited to load bearing application.

2.3 Strengthening of Hydroxyapatite

Although the structure and composition of HAp are similar to those of bone, there is a difference in the nature of their crystallinities. Polycrystalline HAp is much weaker than bone as a result of the fact that the microstructure of the two materials are quite different. Thus, typical examples of pure sintered HAp do not exhibit sufficient strength and fracture toughness to be suitable as load-bearing biomaterials.

One of the primary restrictions on clinical use of bioceramics is the uncertain lifetime under the complex stress states, slow crack growth, and cyclic fatigue that arise in many clinical applications. Two solutions to these limitations are used as bioactive ceramics as coatings or in composites. Much of the rapid growth in the field of bioactive ceramics is due to development of various composite and coating systems.

Composites have been composed of plastic, carbon, glass or ceramic matrices reinforced with various types of fibers, including carbon, SiC, stainless steel, phosphate glass and ZrO_2 . In most cases the goal is to increase the flexural strength and strain to failure and decrease elastic modulus.

Kondo et al. (1984) increased strength of HAp by adding 5% frits which were prepared from the various compositions of P_2O_5 , CaO, BaO and Al_2O_3 . Frits inhibited grain growth during sintering. The average bending strength of the strongest product was 205.8 MPa.

Kasuga (1990) created the strongest composite achieved from apatite-wollastonite (A/W) glass-ceramic containing a dispersion of tetragonal zirconia, which had a bending strength and fracture toughness of 703 MPa and $4 \text{ MPa}\cdot\text{m}^{1/2}$, respectively.

Murase et al. (1991) investigated the mechanical properties and biocompatibility of the carbon fibre reinforced ceramics composite materials, which were reinforced by PAN (polyacrylonitrile) and pitch carbon fibre. The results observed are shown in Table 2.1.

Table 2.1 Mechanical properties

	Bone	C-SN	C-MU	Alumina	Zirconia	HAp
Flexural strength (MPa)	115-168	600-690	610-850	206-370	900-1200	113-196
Elastic modulus (GPa)	15.8	280-310	210-220	364	140-200	-
Fracture toughness (MPa.m ^{1/2})	2.2-4.6	28.1-28.8	16.6-18.0	3.1-5.5	5.7-9.6	0.96-1.16

Bone: cortical bone, C-SN: carbon fibres reinforced silicon nitride

C-MU: carbon fibres reinforced mullite

Aoki (1991) measured the mechanical properties of sintered HAp mixed with the additives. The mixture was pressed in a stainless steel mold at a pressure of 100 MPa, heated in air at 1300 °C for one hour. The effects of additives on the flexural and compressive strengths of sintered HAp were shown in Fig.2.2 and Fig.2.3.

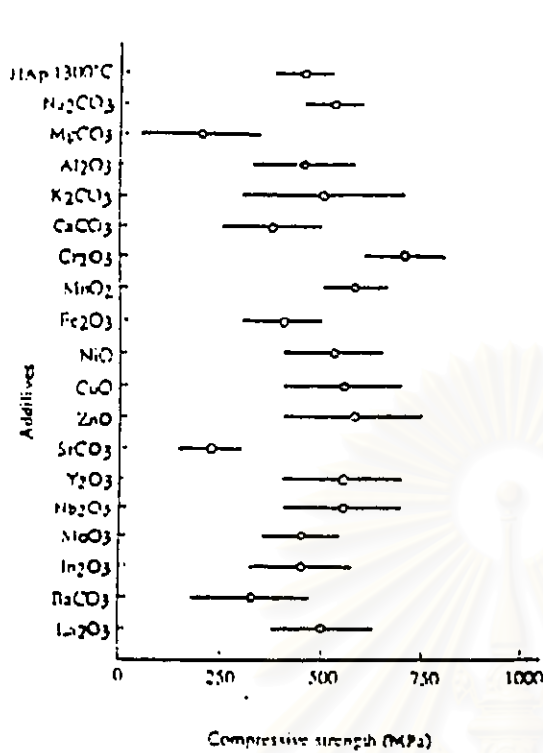


Fig.2.2 Effect of additives on
compressive strength

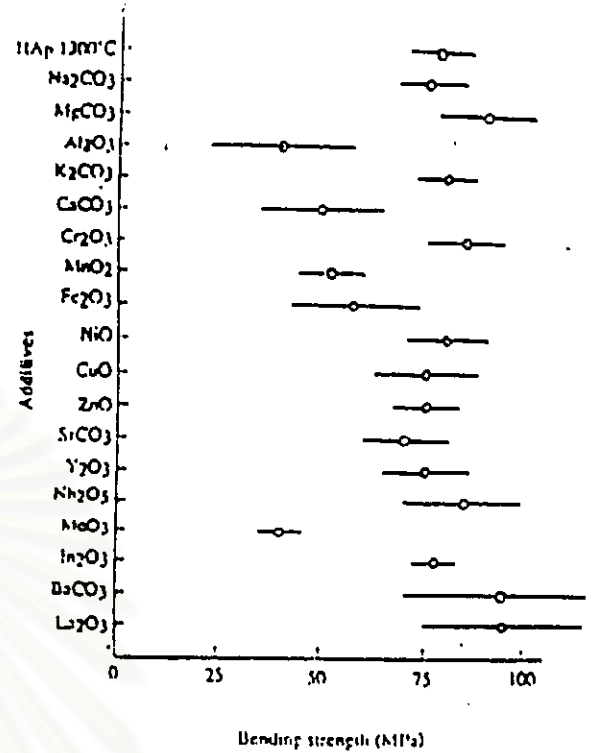
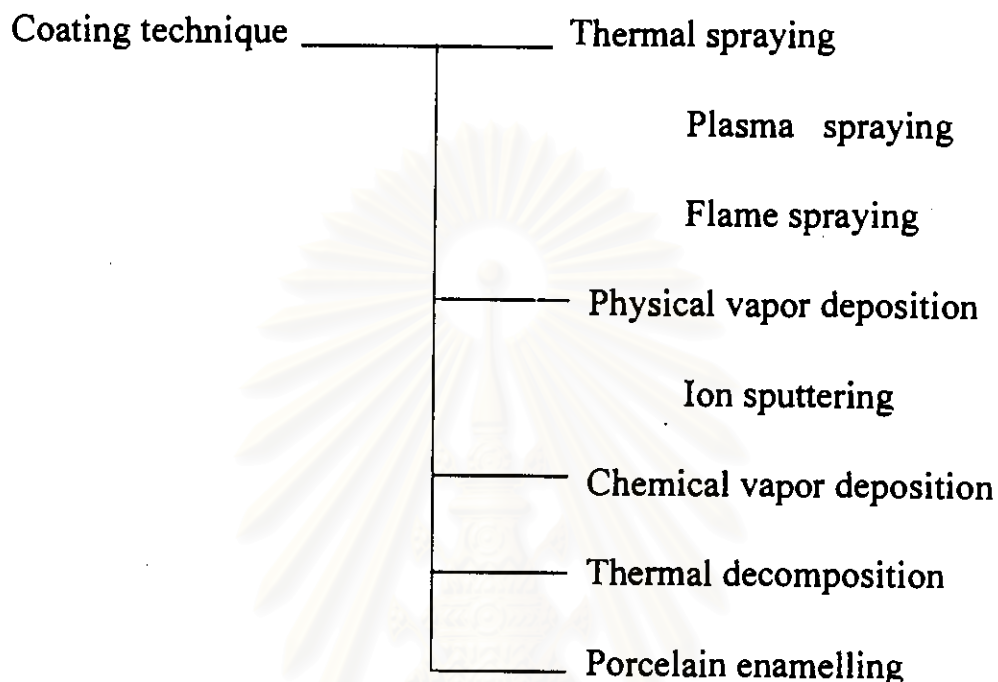


Fig 2.3 Effects of additives
on flexural strength

Coating is a wide method for improving some drawback of HAp. HAp was coated on the porous metal surface for fixation of orthopedic protheses in accordance with the excellent toughness of the metal, typical metal, titanium has fracture toughness about $40 \text{ Kg}^{1/2}/\text{cm}^2$. A number of technique for HAp coating are summarized in Table 2.2.

Table 2.2 Various techniques of coating HAp onto metals



Compressive surface stresses is one of the technique using for enhancing the strength of ceramic since antiquity. Various procedures have been devised to use the high intrinsic strength of brittle ceramic materials, but the most common of these involves developing a surface compressive stress with a compensating tensile stress in the interior of the body. Since ceramic materials break easily in tension, this surface compression, as well as the initial body strength, must be overcome before failure occurs. One means of providing this surface compression

is glazing (Kirchner, 1979). Most pottery and chinawares are coated with glazes having lower thermal expansion coefficients than the bodies.

Stress in surface layer develops as a result of a differential thermal expansion between the coating and the body as they are cooled 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. The magnitude of these stresses can be estimated as follows (Duke et al., 1968):

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

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

where

σ_s and σ_b denote stresses in surface layer and body, respectively

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

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

E is Young's modulus.

ν is the Poisson's ratio.

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

In the assumption that;

- 1) both surface layer and the body are isotropic and elastic
- 2) the temperature distribution is uniform
- 3) the elastic moduli and the Poisson'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.

Warshaw (1957) 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 were unimpressive.

Brubaker and Russell (1967), formed two-layer laminated ceramics using three vitrified whiteware bodies with different thermal

expansion coefficients, leading to tensile and compressive stresses in the layers and measured flexural strengths and impact resistances of the laminates. Both properties were observed when the compressive layers were subjected to tensile forces due to the externally applied loads.

Duke et al. (1968) reported that glass in the $\text{Na}_2\text{O}-\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system nucleated with titanium oxide were strengthened by glazing with lower expansion coefficient glaze, resulting in moduli of rupture up to five times that of the initial glass-ceramics.

Moody (1969) increased the strength on a titanium carbide body by coating with B_4C which had lower thermal expansion coefficient than titanium carbide ($5.6 \times 10^{-6} \text{ K}^{-1}$ vs $8.0 \times 10^{-6} \text{ K}^{-1}$), its strength was increased by 50%.

Kirchner et al. (1970) used CVD- Si_3N_4 coating to strengthen zircon porcelain up to 40%. The thermal expansion coefficient of Si_3N_4 is lower than that of zircon porcelain ($5.6 \times 10^{-6} \text{ K}^{-1}$ vs $8.0 \times 10^{-6} \text{ K}^{-1}$).

Kochawattana (1993) attempted to strengthen hydroxyapatite prepared from chemically treated cattle bone ash by means of inducing compressive surface stress with the slip of same material but having a different thermal expansion coefficient of 4.7%. The strength was increased about 5%.

Kositamongkol (1995) prepared coating slips having different coefficients of thermal expansion by proportioning two different hydroxyapatite powders. After coating on the HAp substrate, it was found that the flexural strength of the sintered specimens decreased by 19-27 % due to the inadequate difference in thermal expansion coefficient.

2.4 Forming

Forming is the process in which a powder material is consolidated into a coherent and compact body having a particular geometry and uniform structure. 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. Forming method in the relation of water content and pressure was shown in Fig. 2.4.

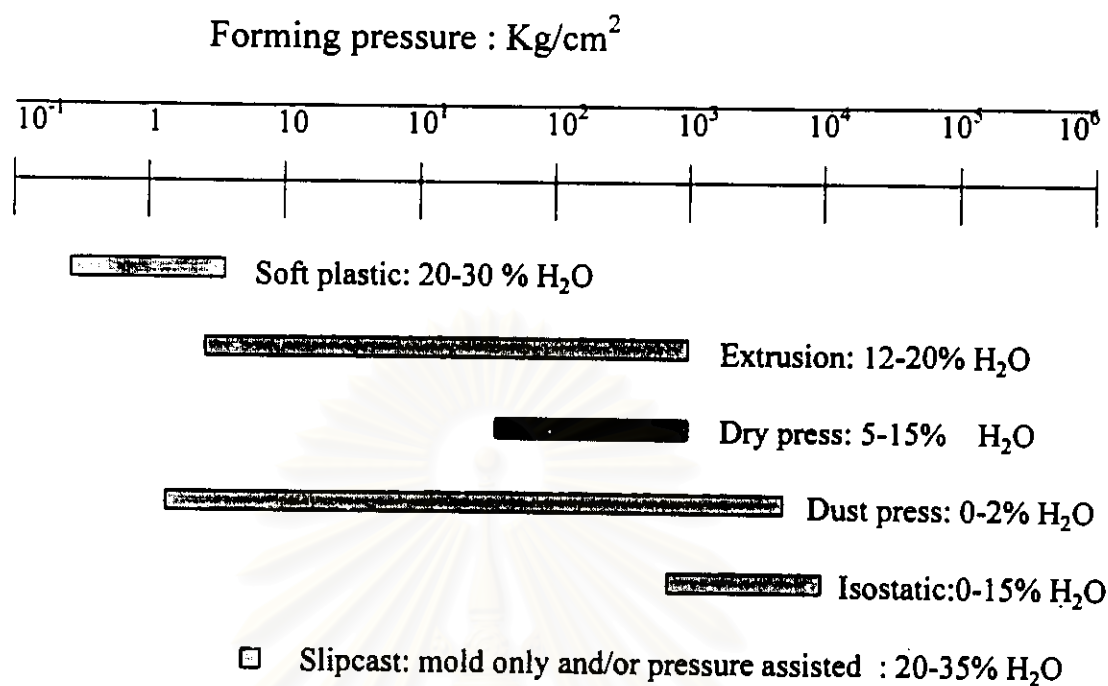


Fig.2.4 The relationship of pressure and water content for the various types of forming.

Extrusion is a popular process for shaping an object by pushing a material through an opening the size and shape of the cross section of the object. This process is suitable for the samples with high symmetry such as rods, tubes, honeycomb structures and channels. Extruder is comprised of two basic types; the piston and auger (Janney, 1995).

The piston extruder is very simple in construction. It consists of a barrel, a piston, and a die (Fig.2.5). There is a minimal amount of wear (and hence minimal amount of contamination) because the design

inherently minimizes the amount of contact between the extrusion mix and the extruder. The piston extruder is an inherently batched process, after the extrusion mixture is loaded into the barrel, no more can be added until the extrusion press run is finished.

This occurred mainly during the reduction of the extrudate from the barrel section on the die part. The piston extruder is typically used for making technical ceramics and lab trials.

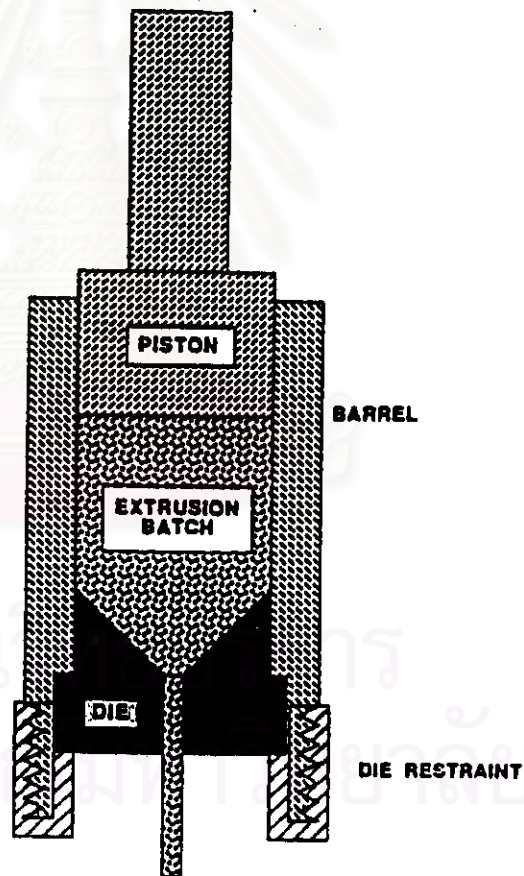


Fig.2.5 Piston extruder

In contrast with the process mentioned above, the auger extruder consists of complicated pieces of equipment (Fig 2.6). Flow is not required for this type, forward movement depends on friction between the extrudate material and the barrel lining to restrain the extruded materials from turning with the auger. The extrudate must either slide on the surface of the auger or shear at intermediate surface between the auger surface and the interior barrel surface to move forward. Auger extruder is inherently a continuous process. It can incorporate a mixing stage with the forming stage. Auger extruders are routinely used in the heavy clay, refractories, and whitewares industries. In addition, they are sometimes used in technical ceramics applications such as capacitors and thermocouple tubing.

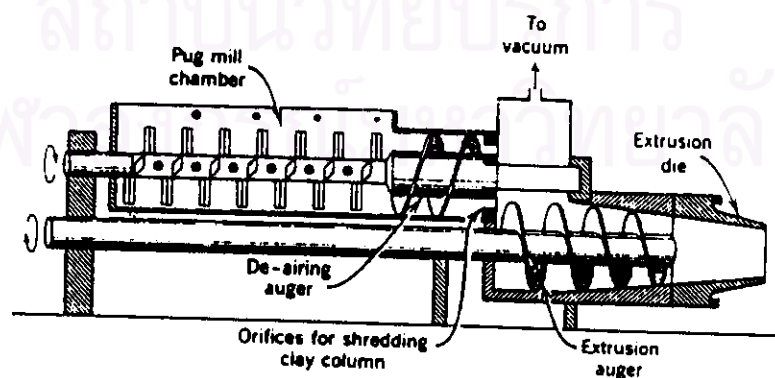


Fig.2.6 Vacuum auger extruder

2.5 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 combine with each other through the formation of strong binding.

Thermodynamic of sintering is an irreversible process in which there is a decrease in free energy due to decreasing in surface area. Sintering begins to occur at one-half or two-thirds of the melting temperature, which is sufficient for material transport by diffusion in the solid state.

The driving force for sintering is the reduction of the free energy, ΔG_T of the system.

$$\Delta G_T = \Delta G_V + \Delta G_b + \Delta G_s$$

where ΔG_V , ΔG_b and ΔG_s represent the change in free energy associated with the volume, boundaries and surfaces of the grains, respectively. 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 one results in shrinkage as shown in Fig.2.7.

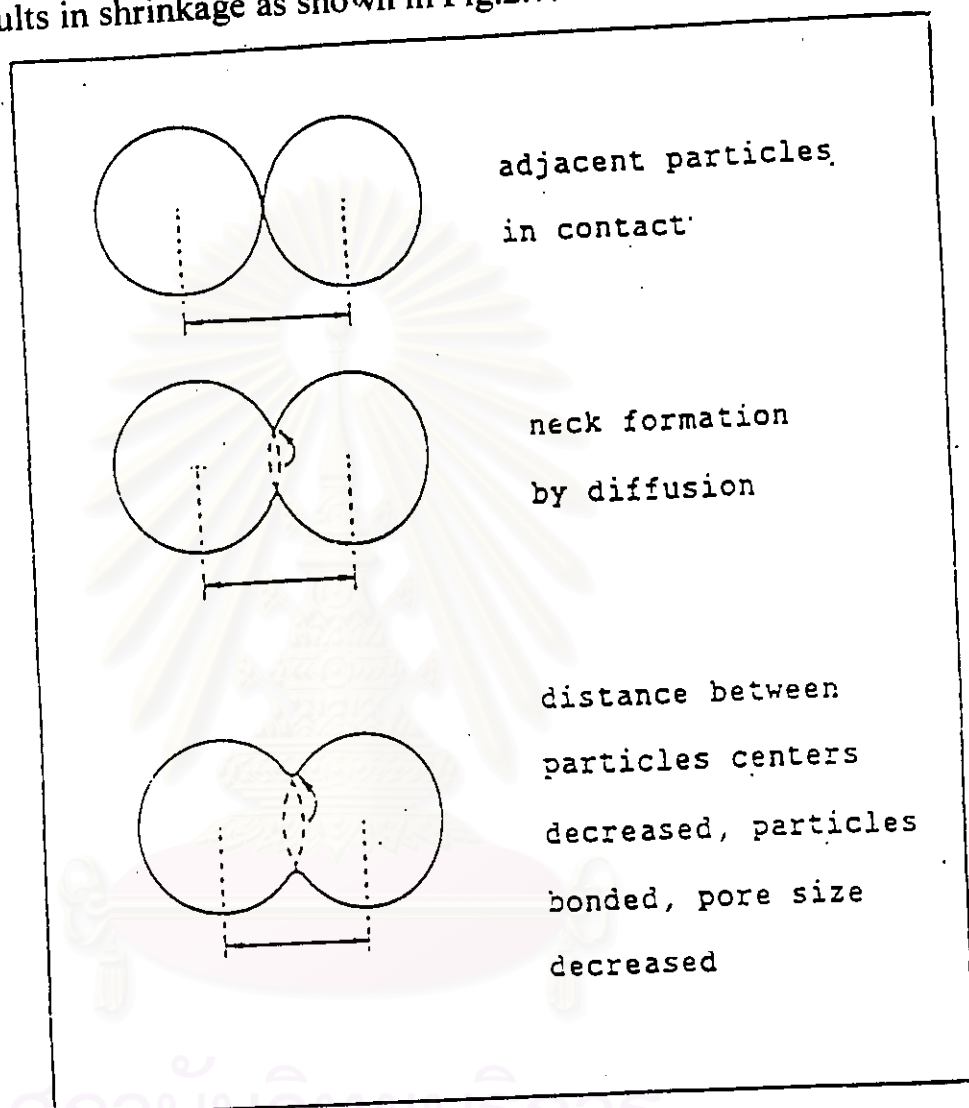


Fig.2.7 Schematic of solid-state material transport (Richerson, 1982)

Microstructure characteristics or changes observed in these stages of particle are listed in Table 2.3.

Table 2.3 Microstructural changes observed in solid-state sintering
(Reed, 1989)

Stage	Observation
Initial	<ul style="list-style-type: none"> - Surface smoothing of particles - Grain boundaries form, neck growth - Rounding of interconnected, open pores - Diffusion of active, segregated dopants - Porosity decrease < 12 %
Intermediate	<ul style="list-style-type: none"> - Shrinkage of open pores intersecting grain boundaries - Mean porosity decrease significantly - Slow grain growth (differential pore shrinkage, grain growth in heterogeneous material)
Final (1)	<ul style="list-style-type: none"> - Closed pores containing kiln gas form when density is $\approx 92\%$ ($> 85\%$ 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)	<ul style="list-style-type: none"> - Grains of much larger size appear rapidly - Pores within larger grains shrink relative slowly

2.6 Calcium Phosphate Glass

The great bulk of inorganic glass is silicate glass. This glass can be produced commercially to contain silica 70% or more by weight. The term "glass" used without qualification usually means such a glass. The glass used here is concerned specifically with "phosphate glass" with a phosphorus rather than silicon base. Structural characteristics of phosphate glass are different from silicate glass. Some properties and crystallization behavior are unique for phosphate glass, originating from these characteristics. Recently phosphate glass and glass-ceramics have been extensively attracted and concentrated on their application as biomaterials.

2.6.1 Structure of Phosphate Glass

Note that because the PO_4 tetrahedral has a double-bonded oxygen atom as part of the tetrahedral (in order to satisfy the +5 valence state of phosphorus), only three bonds are available for joining tetrahedral together. This results in a planar relation among phosphate tetrahedral as shown below:



Fig.2.8 Forms planar chains of tetrahedral

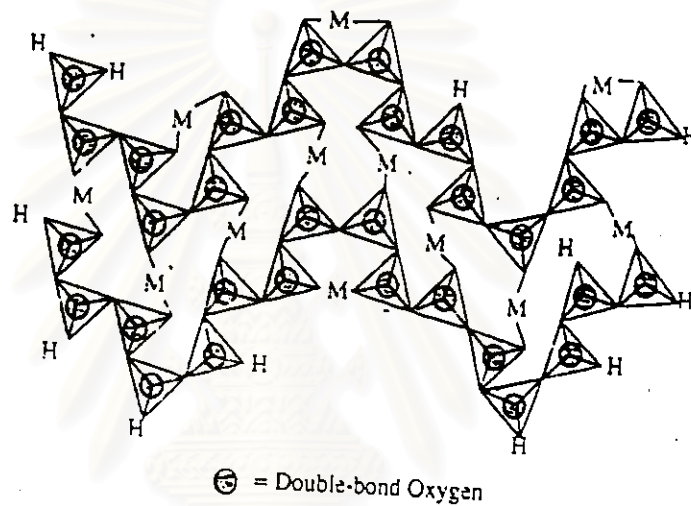


Fig.2.9 Phosphate chains cross-linked by divalent cations

Note that some of the hydroxyl groups is "terminal" by mean of these groups terminate at chain end whereas the other groups be "non-terminal" are resident on the sides of the chain. A basic difference between the classes of glass, silicate and non silicate, is that non-bridging oxygens. Hydroxyl groups almost never present in silicate glass while in nonsilicate glass or phosphate base glass, it is occurred commonly.

It has been shown that the structure consists of long PO_4 chain in a calcium sodium metaphosphate

2.6.2 Biomedical Applications of CP Glass

CP glass has been applied to medical markets including joint prostheses, bone cement, and bone repair as a result of the only one compatible materials with the constituents of bone, i.e. calcium hydroxyapatite and collagen.

The possible applications in joint prostheses involving to the strong adherent glass coating on metal prostheses and joints to render the metal surfaces biocompatible and manufacture of tough glass-ceramic prosthetic joint use and design would depend on inherent strength of the glass-ceramic. Dental implants and repair fall into subperiosteal and endosteal uses (Ropp, 1992). The use of CP glass and glass-ceramic crown for dental implantation appears to be feasible since the sufficient strength and hardness, however, the chemical durability of that glass composition was not observed. The application in fibre and fibre optics has been also used including fibre optic cables and domestic lighting. The polymeric glass can be drawn from the melt. The transmission

properties of polymeric glass are these better than quartz at the critical wavelengths of 0.85-1.06 μ . however, these wavelengths are those critical only to silicates glass, not polymeric phosphate glass.

CP glass is used as bone cement in many application such as Osteogenic cement for fixation of bone joint implants, repair of bone defects and injuries, facial reconstruction including maxillo-facial repair. and repair of periodontal disease effects. A grout made from ground glass may be superior to any material now used in the marketplace. A grout would need the procedure to achieve the end-usage as follows:

1. Be plastic and workable so as to conform to all irregular shapes and cavities.
2. Set rapidly to a rigid solid within one hour, to possess a sufficient modulus 2×10^6 psi for repair of dental caries and repair of periodontal disease effects in the bones of the mouth.
3. Have the ability to induce bone growth for more secure implantation.
4. Have long term life in the body with regard to biocompatibility, load bearing and impact loading.

From the past studies , CP glass is compatible with the surrounding tissues that it has attracted much attention as coating to

modify to some mechanical property of HAp. It can be selected in such a way that it has the appropriate thermal expansion coefficient by adding Na_2O . The coating process of HAp in molten glass will exhibit free stress before reaching setting point was reached, CP glass was readily flows and covers completely on the specimens. At the setting point temperature, the difference of thermal expansion between CP glass and HAp will affect the induction of compressive surface stress.



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