

CHAPTER 2

LITERATURE SURVEY

2.1 Chemical and crystal structure of hydroxyapatite

Hydroxyapatite (HAp) is a compound of apatite group, and its chemical formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Hydroxyapatite is a calcium phosphate included hydroxide, and its Ca/P ratio is represented as 1.67. The crystal structure of natural apatite was determined by Naray-Szabo and Mehmel independently in 1930. HAp is hexagonal, space group $P6_3/m$ with cell dimension of $a = 9.423$ and $c = 6.875 \text{ \AA}$. Fig. 2.1 shows the crystal structure of hydroxyapatite projected along c axis (Aoki, 1991)

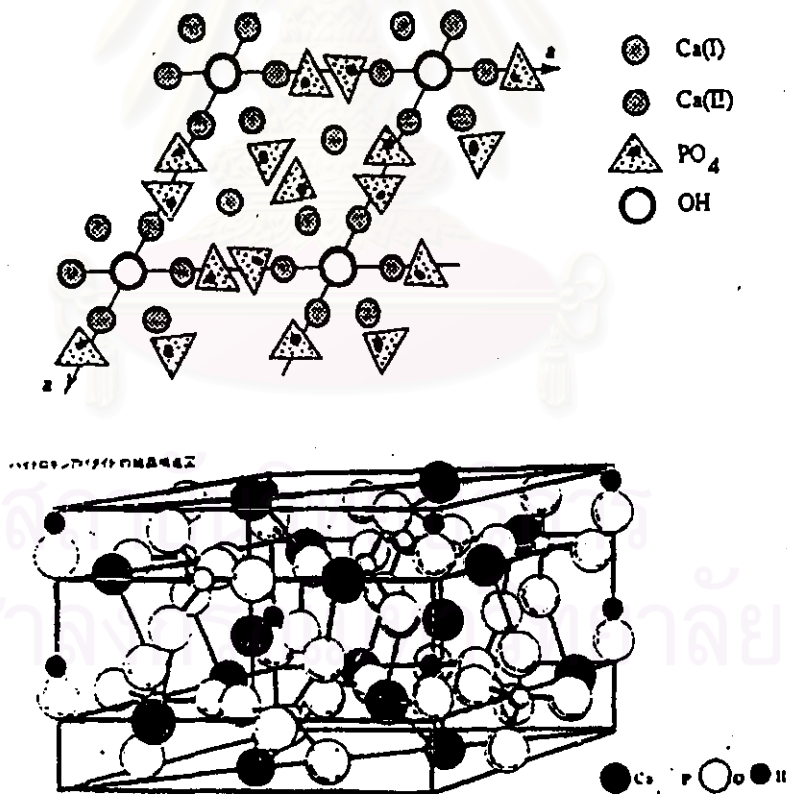


Fig. 2.1 Crystal structure of hydroxyapatite projected along c -axis (upper) and along a axis (bottom)

Some important material properties of hydroxyapatite must be known for the purpose of basic considerations and which are of substantial significance when it comes to constructional design of implant as shown in table 2.1

Table 2.1 Typical values relating to some important properties of hydroxyapatite ceramics

Property	Standard value	Remark
Design density	3.16 g/cm ³	Ideal density, rarely achieved in practical application
Compressive strength	100-200 MPa	
Bending strength	10 MPa max.	for high density material
Young's modulus	100 GPa max.	for high density material
Hardness	500 HV	(Rec standard value)
Thermal expansion	$11 \times 10^{-6} \text{ K}^{-1}$	
Melting point	1650°C	Decomposition
Corrosion resistance		Best for HAp compare to other calcium phosphates when pH value increases

Willmann (1993)

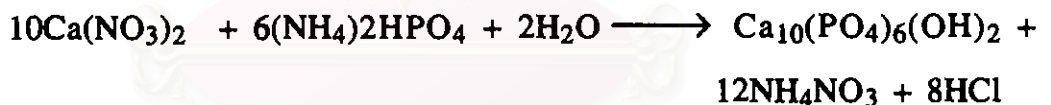
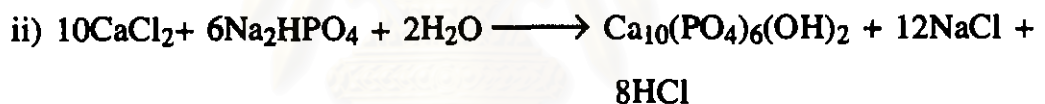
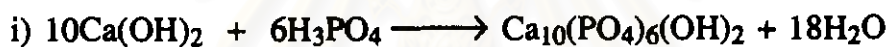
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2.2 Preparation of Hydroxyapatite

There are four methods for preparing apatite compounds: the wet method, dry method, hydrothermal method, alkoxide method (Aoki, 1991)

2.1.1. Wet method

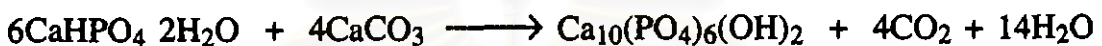
The wet method is available for mass production of hydroxyapatite powder. There are 2 processes for the wet method. One is a process involving a neutral reaction of acid and alkaline solutions. The other involves the reaction of calcium salts and phosphate salts. The chemical formulas for these processes are as follows:



HAP powder wet chemically produced generally possess high surface area and fine particle size. Nonstoichiometry (Ca^{2+} deficiency; $\text{Ca/P} < 1.67$) and low crystallinity are also characteristics of HAP obtained by precipitation synthesis. These are mainly due to the fact that gel amorphous calcium phosphate (ACP) with low Ca/P ratio = 1.50 precipitates as the precursor and that much water is incorporated in ACP. Crystallinity and Ca/P ratio depend on various factor such as pH, aging time and temperature, and the type and concentration of starting materials.

2.2.2. Dry method

Dry chemical method makes usage of the solid-state reaction between calcium and phosphorous compounds and has the advantage of providing stoichiometric HAp powder ($Ca/P = 1.67$). The synthesis is carried out at high temperature and H_2O vapor must be supplied continuously during thermal treatment as a source of OH^-



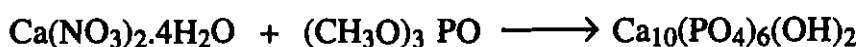
Hydroxyapatite synthesized by the dry method is very fine and the crystallinity is excellent.

2.2.3. Hydrothermal method

As mention above. Hydroxyapatite prepared by the wet method in atmosphere consists of very small crystals with lattice defect. In order to obtain large, perfect single crystals of hydroxyapatite, hydrothermal technique has been promoted. By this technique the mixture and precipitate were heated to higher than room temperature. ie Peroff et al. (1956) succeeded in growing a hydroxyapatite crystal to 0.3 mm. under hydrothermal conditions of $300^\circ C$ and about 85 kg/cm^2

2.2.4. Alkoxide method

This method is available for preparing thin hydroxyapatite film. Example: Calcium nitrate 4-hydrate and trimethyl phosphate were used as starting materials and were dissolved in ethanol or formamide solvents. After the solvent vaporized, the mixture of calcium nitrate 4 hydrate and trimethyl phosphate was heated at $500-1000^\circ C$ to produce well-crystallized hydroxyapatite. The reaction is shown as:



From different method above; in my research, I had synthesis hydroxyapatite by hydrothermal method and the received hydroxyapatite powder was pure phase.

2.3 Strength of porous hydroxyapatite

Studies on the mechanical properties of HAp have progressed with the aim of overcoming brittleness inherent to polycrystalline ceramics and realizing the practical use of HAp as bioactive implant materials. Porous sinters of HAp have the advantage of being completely converted to naturally bone. Such porous materials are generally inferior in tensile strength. Taking account of the advantage when their applicability is restricted to non-stressed region (Kanazawa, 1989)

The mechanical behavior of porous HAp is important in a different sense than dense HAp. The effects of porosity on mechanical properties are remarkable. The porosity-strength relationship of porous HAp is shown in Fig 2.2. In the picture, the result of Peelen et al. (1977) exhibits relatively high compressive strength, bending and impact strengths are also as high as 35 MPa and 0.29 MPa, respectively. This is due to the fact that they have controlled both porosity and pore size. The specimens contain large pores of 150–250 μm . in diameter and micropores of 0.5–1.5 μm . in diameter.

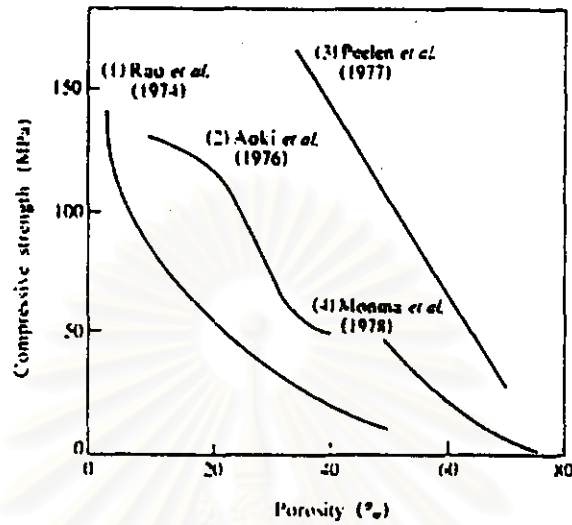


Fig. 2.2. Relation between compressive strength of hydroxyapatite and porosity

Table 2.2. summarizes a variety of equation expressing the relationship

Table 2. Relationship between mechanical strength and porosity

Equation	Porosity(p)	Material*	References
$\sigma_c = 138 \exp(-4.6p/100)$	$p \geq 30$	HAp	Rao <i>et al.</i> (1974)
$\sigma_c = 430 \exp(-4.6p/100)$	$p \leq 80$	HAp	Driessens <i>et al.</i> (1982)
$\sigma_c = -3.7p + 289.3$	$p = 35-70$	HAp	Peelen <i>et al.</i> (1977)
$\sigma_c = -1.5p + 110$	$p = 55-75$	n-HAp	Monma <i>et al.</i> (1978)
$\sigma_b = 2.415 p - 125.1$	$p = 73-95$	HAp	With <i>et al.</i> (1981)
$\sigma_b = 1.50 p - 72.5$	$p = 73-95$	HAp	With <i>et al.</i> (1981)
$\sigma_b = -0.35 p + 28$	$p = 55-75$	n-HAp	With <i>et al.</i> (1978)
$E = 117 (1 - 0.0201 p)$	$p \geq 30$	HAp	With <i>et al.</i> (1981)
$\nu = 22.1 (p/1.8)^3$			
$\nu = 0.281 (1 - 0.006 p)$	$p \geq 30$	HAp	With <i>et al.</i> (1981)
$K_{IC} = 0.0194 p - 0.807$	$p = 73-97$	HAp	With <i>et al.</i> (1981)
$K_{IC} = 0.0154 p - 0.741$	$p = 73-97$	HAp	With <i>et al.</i> (1981)

* HAp: Stoichiometric

* n-HAp: Non-stoichiometric HAp

σ_c : Compressive strength (MPa)

σ_b : Bending strength (MPa)

σ_d : Diametral strength (MPa)

E : Young's modulus (GPa)

ρ : Density (g/cm^3)

ν : Poisson's ratio

K_{IC} : Fracture toughness ($MPa m^{1/2}$)

The introduction of HAp for medical use has opened up new possibilities for hard tissue surgery. However, the material in its current form may only be used for low load bearing applications, this being due to certain limitations, Primary the mechanical properties which are inadequate for load bearing applications. Therefore, the mechanical properties could be improved. Currently a number of methods have been developed to improve the mechanical properties.

Tormala et al., 1991 developed tough porous hydroxyapatite (MA) blocks for bone surgical applications by reinforcing porous HAp blocks with fibrous polylactide composite. Coral-based and sintered HA types were examined.

Tencer et al, 1992 Increased the mechanical strength of porous coralline hydroxyapatite by dip coating with di-lactic polylactic acid (OL-PLA). The result showed that coated specimen were on average 3.76 times as strong as uncoated implant, were 30% stiffer and adsorbed about 100% more energy in compressive failure.

Knowles and Bonfield, 1993 Utilizing of the types $x\text{Na}_2\text{O}(1-x)\text{P}_2\text{O}_5$ and $x\text{CaO}(1-x)\text{P}_2\text{O}_5$ (where $x = 0.2, 0.3$ and 0.5), a systematic study of the effect of increasing network modifying oxides in glasses were made on the mechanical properties of a glass reinforce hydroxyapatite, at glass additions of 2.5 and 5.0 wt%. For the soda type glass, considerable differences between the effects of 2.5 and 5.0 wt% additions were seen. At 5.0 wt%, the increased amount of liquid phase present promotes an increased level of phase inversion to alpha and beta tricalcium phosphate. At 2.5 wt%, a larger percentage of HAp remains stable at higher temperatures. Furthermore, the effect of the composition may be seen. As the mol% of net work forming oxide increases, (ie, the Ca/P ratio moves toward 1.67, the ratio for HAp) the HAp remains

more stable. This is seen in the maintenance of both the HAp phase and also the enhanced mechanical properties.

Knowles, 1994 Produced a ceramic with enhanced mechanical properties, obtained by using phosphate based glasses as a sintering aid. In this paper the effect of the network modifying oxide type on the stability of hydroxyapatite at high temperature is reported. Three glasses were produced of composition $x\text{Al}_2\text{O}_3(1-x)\text{P}_2\text{O}_5$, $x\text{Na}_2\text{O}(1-x)\text{P}_2\text{O}_5$, and $x\text{CaO}(1-x)\text{P}_2\text{O}_5$ (coded A 3P, N3P and C3P, respectively, where $x= 0.3$ mol). The glasses were added at the 5.0 wt% level and the HAp-glass materials fired between 1200–1350°C. There was no statistically significant increase in flexural strength (FS) with increasing firing temperature, the N3P type glass, however, showed a reduction in FS at the higher temperatures. The young's modulus (E) values showed no statistically significant increase with increasing firing temperature; the N3P type glass showed a significant drop in E at higher temperatures. The young's modulus values for HAp-glass compositions were found to be lower than those measured for HAp without glass additions complex changes in phase structure and in the ratio of phase transformation were observed but no correlation was found between the phase changes and the mechanical properties.

Ota et al, 1997 used high-strength calcium metaphosphate fibers, which are expected to show good biocompatibility, are extracted from crystallized products of ultraphosphate glasses by aqueous leaching. Porous ceramics with skeletons of β $\text{Ca}(\text{PO}_3)_2$ fibers for biomedical usage are prepared by the sintering of fibers. In the present work, porous ceramics having a large porosity of ~70% were obtained the compressive test of these porous ceramic showed that large strain of 0.2–0.3 are requisite for their fracture; the calcium

phosphate porous ceramics in this work show much higher flexibility than conventional ceramics. The present work discusses the influence of the preparation conditions of the porous ceramics on their compressive strength behavior.

2.4. Slip and slip rheology

The suspension of powder in the liquid constitutes the slip. Unfortunately, the rheology of concentrated suspensions of fine powder is not a simple function of that of the suspension vehicle or of the ratio of the component. The preparation of the slip is a physico-chemical process. Thus the critical aspects of the technique must ultimately be examined.

2.4.1. Theory of slips

It is evident from an examination of the requirement that most properties relate to rheological factors. Thus rheological control is of great importance in slip casting.

The first approach to the rheology of suspension is purely physical. The well known Einstein equation for relative viscosity, $\eta = \eta_0(1+2.5V)$, where η is the suspension viscosity, η_0 is the liquid viscosity, and V is the volume fraction solids, is inapplicable since the assumption on which it is based do not obtain in concentrated casting slips. The empirical approach of Arrhenius, Du Claux and Wollman, and Baker has been applied to ceramic suspensions by Norton et al. It was found that the relation

$$\eta = (1-V)\eta_0 + K_1V + K_2V^3 \quad (2.1)$$

where K_1 and K_2 are empirical constants, held over a wide range of concentration for monodisperse kaolinite suspensions. The last term predominates at the high concentrations of solid used in slip casting. It must be stressed, however, that such an equation only relates the viscosity of monodisperse suspension to the concentration of solids under-fixed chemical conditions. The significant viscosity variations that occur when the ionic atmosphere of suspension is changed cannot be predicted from the equation. For instance, the apparent viscosity of an alumina casting slip of specific gravity 2.8 changes from 65 centipoises at pH 4.5 to approximately 3,000 centipoises at pH 6.5. Changing the specific gravity 2.6 to 2.8 at pH 4.5 only doubles the viscosity; at pH 6.5 the change is about tenfold. The changes in viscosity with density variation depend on the ionic atmosphere. These observations serve to emphasize the need to understand rheology in chemical as well as physical terms.

A plausible theory advanced to explain the chemical aspects of the rheology of aqueous slips has its origins in the concept of the Helmholtz double layer. Surfaces absorb ions from the electrolyte, but the overall neutrality is maintained by a diffuse layer of counter ions that surround the charged surface. Viscosity changes are explained in terms of the balance of attraction and repulsion forces at the Particle's surface

The potential difference (ζ) across this layer may be derived by treating the interface as two plates of condenser. Thus ζ is given by the expression:

$$\zeta = (4\pi e d)/D \quad (2.2)$$

where e = charge on particle

d = thickness of double layer

D = dielectric constant of the medium.

If the potential is high the particles will repel each other and mutual interference will be at a minimum. A stable, fluid suspension results. When the particles are uncharged, or have a low ζ potential, approach is easier and coagulation possible through attraction by van der Waals forces.

An examination of the expression for ζ reveals the condition necessary for changing this potential at will. Most significant are the changes that can be made in the thickness of the diffuse layer. For instance, if counter ions are chosen that have large standoff distances, then ζ is increased, and hence fluidity and stability promoted. ζ may be increased by adding suitable electrolytes, but it should be noted that the contrary effect may result if excessive additions are made. This reversal is caused by the crowding of the counter ions reducing the effective thickness (d) of diffuse layer. (Pierre, 1968)

2.4.2 Rheology of slips

It is important not only to have a slip that has minimum viscosity, but one in which the rheological properties are suitable for casting. The flow properties of slips are usually illustrated by graphs showing the shearing stress as a function of the rate of shear. For liquid such a curve is usually a straight line having its origin at zero. Suspensions of solid in liquids particularly at the concentrations involved in slip casting, rarely show such behavior. Instead, considerable nonlinearity and hysteresis are observed. The three main features of this nonlinearity are yield point, thixotropy and dilatency .

Yield point is an abrupt change of slope of the curve. Thixotropy is a decrease of viscosity with increasing strain rate. The opposite of this , a decrease of viscosity with increase in strain rate, is called dilatency. All three of these phenomena, singly or in combination, are usually encountered in practical applications of slip casting. The degree to which these occur varies considerably and a good slip is one in which these factors are minimized. A highly dilatent slip cannot be poured nor will it fill small detail of a mold. A slip that is thixotropic will have high permeability of the cast layer, which lead to high casting rate and low density (Wirrall,1963). A high yield point will inhibit good draining characteristics. It has been shown by Moore (1959) that yield point is influenced strongly by the amount and type of deflocculating agent. A properly deflocculated slip will exhibit a very low yield point. Dilatency occurs over relatively narrow range of liquid contents. It is accentuated by the presence of a substantial fraction of colloidal particles.

Dilatent slips usually have insufficient liquid content. Berzley (1965) described many features of dilatency and how it is formed in china clay suspensions.

Thixotropy is often encountered in casting slips. It is thought to be a characteristic of suspensions of particles having irregular shape. The control of thixotropy is largely a matter of proper liquid content and optimum deflocculation. Moore has emphasized the necessity of making viscosity measurements at very low shear rates. Here the effect of thixotropy is most pronounced and it also approximates the conditions under which slip is poured into a mold. Mehta and Langston (1963) have suggested a control test for casting slips in which shear stress measurements are made at two different shear rates. By calculating the negative shear rate intercept, a measure of the state of deflocculation may be determined. The slope calculated from such data characterizes the state of dilution of a slip. A comparison of these values with those at a known "good" slip allows one to decide whether to liquid or deffocculant. (Cowan,1978)

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2.5. The method of producing porous materials

2.5.1. Repiamineform process

In this method, the porous microstructure found in skeleton of some reef corals can be reproduced in a variety of materials (eg. Al_2O_3 , TiO_2 , hydroxyapatite silver, Co-Cr-Mo alloys and polymers) fit for hard-tissue implantation and prosthetic application.

The advantage of manufacturing porous biomaterials by this method is the pores and intercommunicating pores with controlled diameter dimensions can be achieved. But not all species of coral have interconnected porosity in their skeletons. Only the genera *Porites* and *Goniopora* have been used extensively to make medical implants because they have this attribute. The replica moulds from these coral can be used only one time. Therefore, it was the waste and expensive process.

White et al, 1972 prepared porous structure by duplicating the microstructure of carbonate skeletal component in ceramic, metal or polymer materials such as methacrylate, titanium and sintered alumina. Pore structure of marine invertebrate skeleton-materials such as echinoid, spine and corals, which are difficult or impossible to create artificially, can thus be copied in useful materials. Of immediate interest is the possibility of using these replicated microstructures in the fabrication of orthopedic devices. By means of this technique prosthetic materials having a controlled pore microstructure for optimum strength and tissue ingrowth may be obtained.

2.5.2. Polymeric sponge method.

Porous ceramics can be fabricated by immersing open-celled sponge in ceramic slurry and removing excess slurry from sponge. Impregnated sponge is evaporated volatile slurry constituents. After that, sponge is fired at high temperature to verify ceramics.

Ching and Sorrell, 1993 Fabricated porous silicon nitride of controlled pore size and permeability using polyurethane foam for generating network in porous body and polymethylmethacrylate (PMMA) beads in producing pore in structure. Polyurethane foam with slurries of silicon powder and polymethylmethacrylate (PMMA) bead in size range $\sim 150\text{--}500\ \mu\text{m}$. After drying were nitrated over 28 hours at temperature up to 1450°C . Porous silicon nitride product has the apparent porosities in the range $\sim 44\text{--}66\%$. The compressive and tensile strength was in range $\sim 10\text{--}50\ \text{MPa}$ and $3\text{--}10\ \text{MPa}$ respectively.

2.5.3. Foaming method

Forming porous ceramics, chemical mixture containing the desired ceramic component plus a variety of organic foaming agent (such as H_2O_2) is treated to evolve a gas which creates bubbles in the material and causes it to foam. Then porous material is dried and fired at high temperature.

The foaming has advantages such as certain shapes, compositions and densities, small-pore-sized, closed-cell foam and open cell in structure be obtained. But we can't control the distribution of these pores.

The research about producing porous hydroxyapatite by foaming method in Chulalongkorn University

Pakapinyo and Borisuit, 1992 Forming porous hydroxyapatite by mixing hydroxyapatite from cattle bone ash with H_2O_2 and making slurry. After controlling viscosity, slurry was heated at $55-60^\circ C$. H_2O_2 was dissociated to oxygen in slurry. Then slurry was poured into plaster mould. After drying and mould releasing, green body was fired at high temperature (900 in air and $1100^\circ C$, $1250^\circ C$ in H_2O ambient). Final product was porous hydroxyapatite that had densities $0.88-1.25 \text{ g/cm}^3$, porosity $60-74\%$. Pore size was $150-250 \mu\text{m}$. suitable for bone ingrowth.

2.5.4. Volatilize matter

Fabricated porous materials by mixing ceramic powder with organic matter such as polymethylmethacrylate (PMMA), naphthalene, after fabrication and sintering at high temperature. Organic matter was burnt out and left the porous within ceramic body. Pore size and porosity can be controlled by amount and size of organic matter.

Research about making porous hydroxyapatite by volatilize matter in Chulalongkorn University

Chanda and Thongbai, 1991 Prepared porous hydroxyapatite from cattle bone mixing with, different amount ($0, 20, 40, 60, 80\%$) naphthalene as pore forming agent and sodium carboxy methyl cellulose as binder. Granulation and fabrication to preform. After that, sintering in H_2O ambient. The Product received had different porosity.

And other research about making porous hydroxyapatite by volatilize matter is

Ching and McCertney, 1993 produced porous silicon nitride by mixing polymethylmethacrylate (PMMA) bead in the size range $\sim 150\text{--}425\ \mu\text{m}$ with silicon powder. Additive such as steric acid and ethylene glycol. After that, the sample was nitrified over 28 h. at temperature up to 1450°C . From microstructure analysis of product showed dense array of spherical pores of diameter approximately twice the original bead size, which probably resulted from expansion during heat cycle. Some permeability was achieved owing to the presence of channels between the pores, which probably resulted from polymer volatilisation. The bulk densities and apparent porosities showed converse linear trends as a function of bead content. Both the compressive and tensile strength were very low ($\leq 20\ \text{MPa}$) as a result of the high porosities, defective microstructures, low temperature binder loss and pressing lamination.

2.5.5. Extrusion

Extrusion is used extensively for fabrication green body with elongated shapes that has a constant cross section. A plastic mix of ceramic powder and organic additive (ie, volatile organic matter / binder) is placed in an evacuated cylinder, where it is kneaded to remove air and to achieve uniform consistency. The mix is then typically carried by an auger and force through a desirable die. After extrusion, green body was burnt out binder/ organic matter and sintered. The drawback of this method is defect such as lamination, void and tearing may be developed in product.

Prodan, Comanescu and Popescu, 1987 Produced porous bodies from aluminium hydrate, calcine alumina. Admixture of kaolinite and acetic acid, polyvinyl alcohol and starch made it possible to obtain pastes mouldable by extrusion. Naphthalene was used as pore supplier. After sintering, these porous ceramics were used for carrier of oxidation catalysts. The closed relationship between reactivity, apparent porosity and pore distribution of ceramic carrier fired at 1500°C and 1600°C . The optimum value of these properties are investigated.

2.5.6. Hot isostatic pressing (HIP)

HIP is normally used to densify powder compacts or presintered materials and to remove volumetric defaults of foundry materials. Powder compacts encapsulated in glass or metallic container, or sinter materials with closed pore are sintered under high-pressure gases. These materials are densified by the effects of high temperature and high pressure, on the other hand, HIP, when used for obtaining porous materials, is a sintering process in which powder compacts or partially sintered bodies are treated under high-pressure gases at high temperature without encapsulation. In this method, the surface of open pores are exposed to high pressure gases at high temperature (Nanko et al, 1996)

HIPed Porous material have excellent properties such as higher open porosity, smooth pore surface (ie, lower specific surface area) and narrow pore size distribution than conventionally sintered materials. But HIP has relative large initial cost of installation and long time necessary to develop and establish a total process.

Perera et al., 1992 produced stronger porous alumina by HIP without encapsulation compared with pressureless sintered. The results have been shown that HIPed alumina is stronger than sintered alumina for same open porosity.

2.5.7. Tape casting

Process consists of suspending finely divided inorganic powder in aqueous or nonaqueous liquid systems comprised of solvent plasticizers, binder and organic matter to form a slurry that is cast onto a moving carrier surface. The slurry passes beneath the knife edge of a blade that levels the slurry into a layer of controlled thickness as the carrier surface advances along a supporting table when the solvent evaporate, the fine solid particles coalesce into a relatively dense, flexible sheet that may be store on take up reels or stripped from the carrier in a continuous sequence. After that, burnt out the organic additive and sintered. We will get thin film with high porosity.

Arita and Castano, 1995 Prepared hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) ceramic sheet with a wide range of porosities (up to 62%). The process is based on the reaction between dicalcium phosphate (CaHPO_4) and calcium carbonate (CaCO_3). When mixed for obtaining hydroxyapatite Ca/P ratio, this proves to be a reliable new method for obtaining hydroxyapatite. Moreover, CaCO_3 serve as a gas-forming agent (due to the evolution of carbon dioxide and water during the reaction), which leads to the development of highly porous microstructures. Alternatively, CaHPO_4 and CaCO_3 can be reacted by calcining at 1000°C to produce pure hydroxyapatite powders. When processed in a similar way, a dense ceramic results. By mixing 50 vol% of

CaCO_3 and CaHPO_4 with precalcined powders, hydroxyapatite with an intermediate porosity was obtained. Moreover, it should be possible to achieve porosity control by mixing different amounts of uncalcined and precalcined powders. All of these powders are colloidally processed using tape casting to produce. Thin sheets 150–200 μm thick. This technique can be used to make laminates, with or without porosity gradients, up to several millimetres thick.

2.5.8. Hydrothermal hot pressing

Hydrothermal hot pressing technique is a possible processing for producing a ceramic body at relative low temperatures. the compression of sample under hydrothermal condition accelerates densification organic materials. The technique is applied to solidified many kinds of materials such as glass, silicate, titanium, calcium carbonate, hydroxyapatite and so on. It's known that water of crystallisation in starting materials is slowly lose at low temperature and the solidification of HAp can be acheived

Ioku, et al.,1992 prepared porous hydroxyapatite ceramics by hydrothermal hot pressing. The hydroxyapatite ceramics prepared by mixing $\text{Ca}(\text{OH})_2$ powder and $(\text{NH}_4)_2 \text{HPO}_4$ powder with HAp stoichiometricly (Ca/P= 1.67) showed about 50% density of porous structure with 45% open porosity. Scanning electron microscope indicated that open.pore size was 100–500 μm which was larger than 100 μm . We may expect ingrowth of bone tissue. The hydroxyapatite ceramics sintered at 1000°C for 3 h. After hydrothermal hot pressing at 300°C had about 55% density .The open porosity scarcely decreased by sintering. The value of compressive strength was about 150 MPa

Yanagisawa, Ioku and Yamasaki 1994 Porous silica ceramics with homogeneous pore distribution were prepared by hydrothermal hot pressing of silica gels. The recovered porous ceramics had high mechanical strength with large pore volumes. The ceramics prepared at 300°C and 20 MPa for 1 hr. with 17.2 mass% water showed the following properties; high compressive strength (60 MPa), low bulk density (0.68 g/cm³) large pore volume (0.98 cm³/g) and uniform pore distribution with average pore size 65 nm. The average pore diameter of the ceramics was controlled from 25 to 100 nm. by selecting hydrothermal hot pressing condition and starting materials silica gels . The formation mechanism of large pores in the silica ceramics could be elucidated by capillary effects.

Hosoi et al., 1996 Developed a new processing technique for preparing hydroxyapatite (HAp) ceramics using the hydrothermal hot pressing (HHP) method. Powder mixed dibasic calcium phosphate dihydrate and calcium hydroxide mixed with a Ca/P ratio of 1.67 was treated at 150°C and 40 MPa. The HHP method with the selection of the powder enabled the HAp solidified at low temperature. The resulting HAp had a tensile strength of approximately 10 MPa. Furthermore, the HAp ceramics possessed a lamellar microstructure and high porosity.

2.5.9. Microwave (hybrid) heating

Microwave (0.3–300 GHz) lie between radiowave frequencies (RF) and infrared (IR) frequencies in the electromagnetic radiation spectrum. Microwave can be reflected, absorbed and/or transmitted by materials. Reflection and adsorption require interaction of the microwaves with materials; transmission is the result of partial reflection and incomplete adsorption. During interaction energy in the form of heat is generated in materials primarily through absorption. Gases, liquid and solids can interact with microwaves and be heated. Under certain condition, gases can be excited by microwaves to form plasma that are also useful for Processing. Materials reflect and adsorb heat to various degrees depending on their composition, structure, temperature and the frequency of the microwaves.

Park, J. H. and Ahn, Z.S. (1994) used Microwaves (Hybrid) Heating (MHH) to oxidize Al–Al₂O₃ powder mixture and sinter the oxidized alumina to produce low shrinkage porous alumina. Compared with conventional fast firing, MHH gave fast oxidation rate due to the surface ohmic current on Al powder. Porous alumina with low thickness change +1% and bulk density (2.78 g/cm³) was produced. SEM analysis was used to explain the oxidation and sintering behavior of Al₂O₃ powder mixture.

2.6. Pore evolution during densification

The evolution of pore network during densification is difficult to quantify. At the first approach, and a common one is to determine the average pore diameter as it appears in a polished cross section of compact. The characterization require serial sectioning and polishing as well as advanced image analysis and quantitative stereology methods. Work by Rhines and DeHoff (1983) has characterized the change in the pore network as a topological decay process in which a pore network as shown in Fig 2.3 changes by the collapse of pore channels and the reforming of a new network of lower connectivity, as sketch in Fig 2.3(b). The major feature of the pore changes during the intermediate stage of densification can be seen that the pores get fewer and larger. Such an evolution is universally observed in sintering powder compacts.

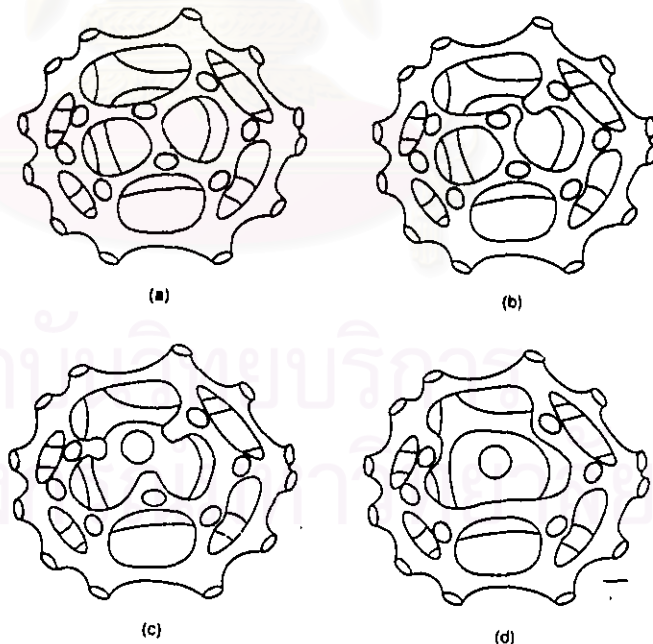


Fig. 2.3 Sequence of pore channel collapse in a porous sintering solid. The sequential collapse can be envisioned as the coarsening process leaving a larger pore network as well a isolated pores : Evan and Jonghe 1992

Without dealing with all the details of the geometrical changes that the real pore structure reveals, it remains useful to define a relationship that describes coarsening in a way that can be related to the sintering rate equation that were developed. Qualitatively, Coarsening of the pore structure can result from (1) densification itself and (2) nondensifying processes, such as evaporation / condensation or surface diffusion. The coarsening relationship must be expected to have the same form as the grain growth equation

$$G^n = G_0^n + K (t-t_0) \quad (2.3)$$

Thus the average distance between the pores is taken to be equal to the grain size G ; We could propose to write, under isothermal conditions,

$$G^n = G_0^n + \left[A \exp (-E_d/kT) + B \exp (-E_s/kT) \right] (t-t_0) \quad (2.4)$$

Where A and B are system-specific constants ; E_d is the activation energy of the diffusional transport of atoms, which is responsible for densification, and E_s is the activation energy characteristic of the nondensifying transport processes that contribute to coarsening. That coarsening can proceed even when there are only negligible densify changes occurring in the sample (ie., when A is near zero).

Since sintering is often carried out in nonisothermal condition. We could rewrite equation (2.4) in a more general form which the instantaneous grain size may be obtained for any time and temperature history:

$$G^n (T, t) = G_0^{n+1} A \int_0^t \exp(-E_d / kT) dt + B \int_0^t \exp(E_s / kT) dt \quad (2.5)$$

You will note that equation (2.4) is recovered from equation (2.5) under isothermal conditions ($T = \text{constant}$). The value of $G(T, t)$ can then be obtained by numerical integration once a temperature-time-relationship has been established. One of the most useful, yet simplest relationships would be a constant heating rate, for which

$$T(t) = \beta t + T_0 \quad (2.6)$$

and

$$dt = dT / \beta \quad (2.7)$$

when densification rate is

$$\epsilon_p = (k_b / G^3) \Sigma \phi^2 \quad (2.8)$$

ϵ_p = the uniaxial strain rate of the sintering solid

Σ = the sintering stress for densification,

k_b = the temperature - dependent kinetic factor associated with grain boundary diffusion.

ϕ = function of degree of densification

Substitution of equation (2.7) into (2.5) then shows that for a constant heating rate, The mean grain size G will be inversely proportional to the heating rate when $G \gg G_0$. Note also that for a given compact, for which A, B, E_d and E_s are fixed, the right hand side of equation (2.5) will be only a function of temperature. The corresponding densification rate follows from inserting equation (2.5) in expression for the densification rate equation (2.8)

Which would then read.

$$\dot{\epsilon}_p(T,t) = -K_0 \left[A \exp(E_d/kT)/G(T,t)^n \right] \Sigma \phi^2 \quad (2.9)$$

where $G(T,t)$ is given by equation (2.5)

and Σ is the sintering stress

An example of some densification data collected during constant-heating rate sintering of ZnO shown in Fig 2.3 , together with a numerical evaluation based on equations (2.5) and (2.4)

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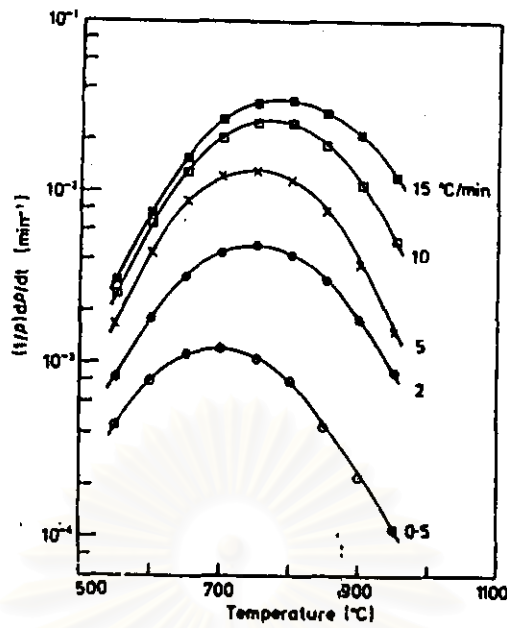


Fig. 2.4 (a) Densification strain rate versus temperature in a constant - heating rate experiment for a ZnO powder compact. The heating rates were between 0.5 and 15°C / min

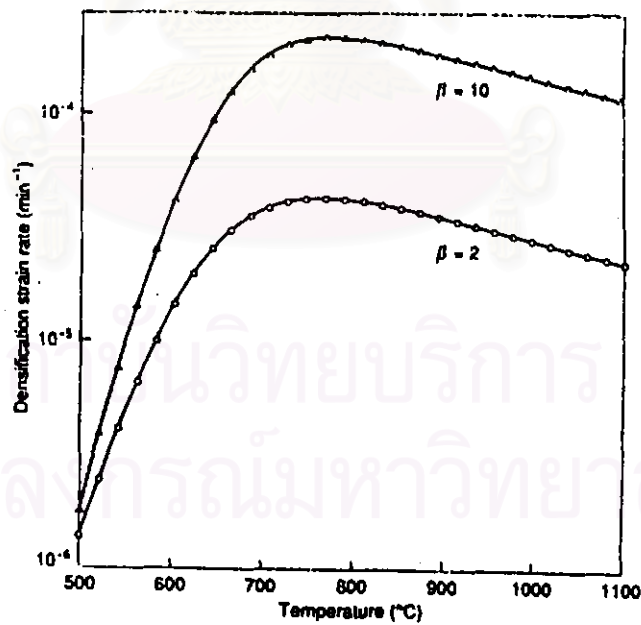


Fig. 2.4(b) Calculated densification strain rate as function of temperature for two different heating rates, versus temperature. β is heating rate in °C / min

The actual density at time t and temperature T follows after some algebra (Chu, 1990) from integration of equation (2.9) for the known $T-t$ relationship. In a constant-heating rate experiment, when G has grown significantly larger than G_0 , the densification rate then becomes proportional to the heating rate, β , as follows from equation (2.5), (2.7) and (2.4) and to a function of temperature while the density become only a function of temperature and does not depend on the heating rate. This interesting result is borne out by experiment, as shown for ZnO in Fig 2.4

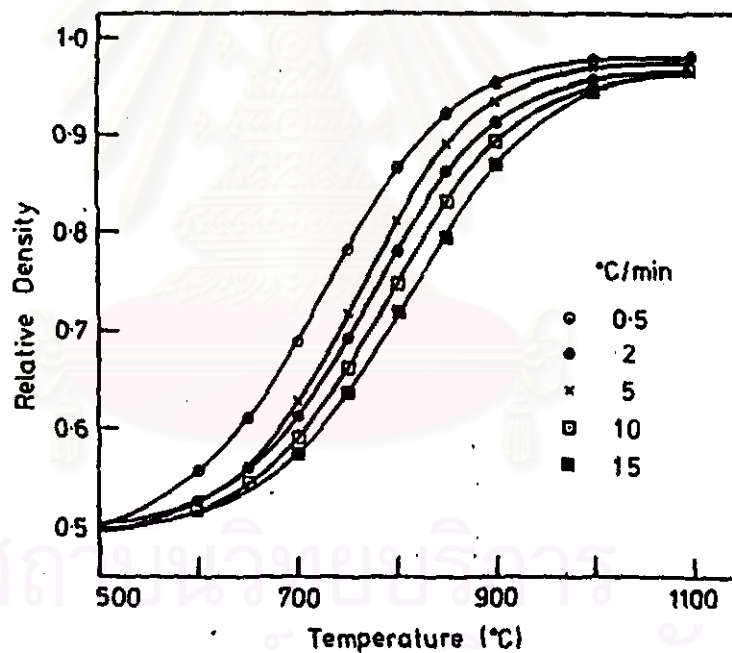


Fig 2.5. Density increments versus temperature at different heating rates for ZnO. The incremental sintered density is not strongly dependent on heating rate.

The activation energy for the nondensifying processes , E_s , is usually significantly lower (a factor of 2 or more) than E_d , and the coarsening rate can therefore be manipulated relative to the densification rate by changing the time - temperature schedule. This permits an important means of controlling the microstructure of a sintered compact. If a coarse microstructure is desired, sintering would have to be carried out at lower temperatures. For obtaining a fine microstructure, one would need to heat up as rapidly as possible to a high temperature. The control of the microstructure by adjusting the sintering temperature such that the densification rate is changed relative to the heating rate is sometimes called **ratio-controlled sintering**. Combinations of low temperature coarsening up to some intermediate sintered density , followed by a high-temperature completion of the densification process can also be used effectively in manipulating the microstructure of sintered ceramics (Dejonghe et al., 1988, Chu, 1990)



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