Chapter 2

Literature review

Alumina substrate [2] is classified as one of the new ceramics. It is also called as advanced ceramics. It consists of aluminum oxide and is classified as the following two categories.

1. Functional ceramic – Substrate, capacitor, ICs packaging, soft and permanent magnet, piezoelectric and optical fiber.

2. Structural ceramic – Cutting tool, bioceramic material and refractory for kiln furniture.

Alumina substrate [3] is used for electronic circuit in general include substrate for thick film with alumina content of 96%, non-glazed substrate for thin film with alumina content of 99.5 and upward, glazed substrate with glass during application.

The desired properties of substrate are low dielectric constant, high electrical resistivity, high thermal conductivity, superior mechanical strength and high dimensional accuracy, produced by pressing or sheet casting.

Sheet casting is divided into extruder method, calender roll and doctor blade method. The doctor blade method is major method used in casting because it easily permits increases in sheet size and high precision in sheet thickness and provides superior dimensional stability.
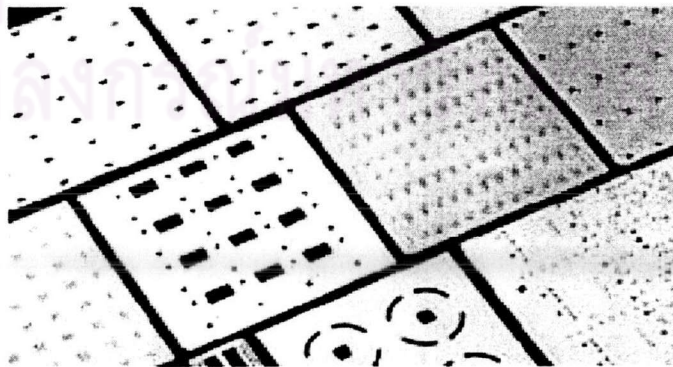

Fig 2.1 Alumina substrate

2.1 Alumina

Alumina is most widely used material for substrates, and is produced from Bayer process. Bayer process [4] begins with bauxite ore. Bauxite is a natural resource consisting of hydrated aluminum oxide, kaolin clay, hydrated iron oxides and titanium dioxide. The bauxite is digested with caustic soda to dissolve aluminum into solution. Other un-dissolved matter is filtered off, and the filtrant solution is precipitated to yield aluminum trihydrate. The trihydrate is calcined to produce alumina as shown in Fig.2.2
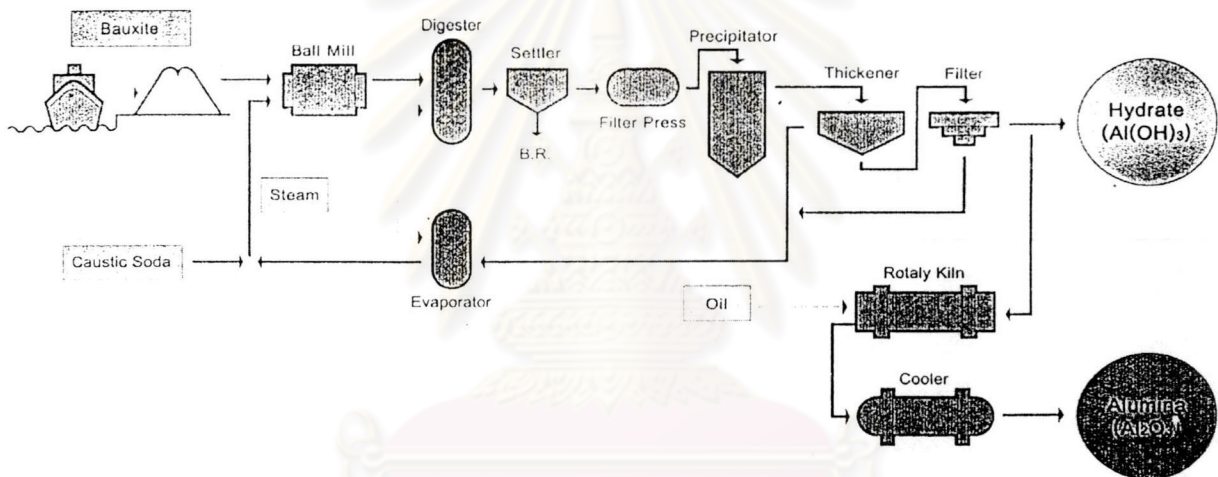

Fig.2.2 Alumina plant block flow diagram [5]

The purity of alumimun trihydrate is very important for the properties of as-received alumina. The alpha alumina is contaminated mostly by silica, iron, titanium and sodium that is added as caustic soda during the digest process. The contaminants are determined in the precipitation step by rate and manner of trihydrate precipitation and absorption of contaminants.

The other technique to increase the purity of alumina is precipitation the trihydrate from specially refined solutions. The precipitation rate can affect indirectly to the calcining conditions and phase purity.

Since trihydrate agglomerates are converted to alpha alumina by rotary calcining, the uniformity of phase conversion is directly affected by agglomerate shape.

Rapid precipitation is produced by the addition of many nucleating sites or seeding can result to trihydrate agglomerate shape and grown by accretion and coalescence lead to irregular cluster which can not be mixed easily in rotary kiln during the calcining step. Otherwise, Slow precipitation from few nucleating sites produces nearly spherical shape agglomerates that are more rapid mixing.

After precipitation, alumium trihydrate is calcined in rotary kiln and adding some mineralizers such as fluorine or chlorine and silica for reducing the sodium content and control grain size and particle shape of final alumina. Furthermore, the trihydrate decomposition is affected to crystal structure by the rearrange of aluminum and closed pack oxygen irons during calcining. The schematic of Bayer process is shown in Fig. 2.3
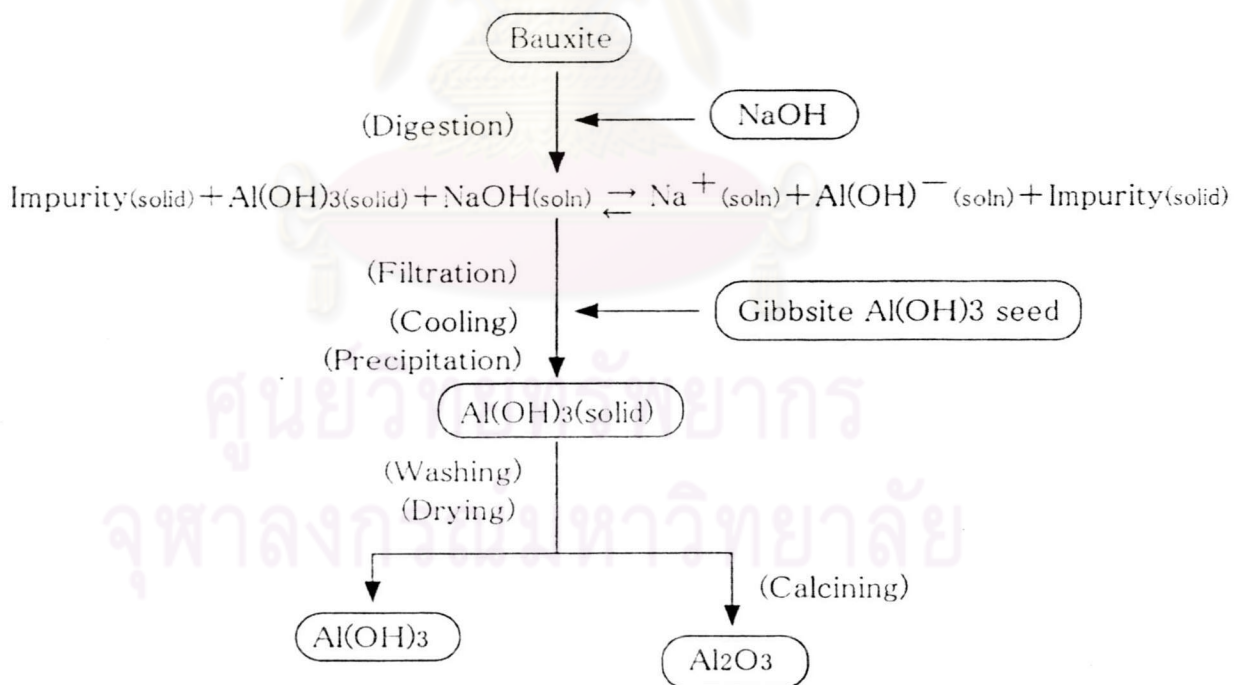
$$Impurity_{(solid)} + Al(OH)_{3(solid)} + NaOH_{(soln)} \rightleftharpoons Na^{+}_{(soln)} + Al(OH)^{-}_{(soln)} + Impurity_{(solid)}$$

Fig.2.3 Schematic diagram of Bayer process [5]

The agglomerate and chemical impurity of alumina powder influence sinterability, electrical characteristics. Therefore, characteristics of alumina powder should be evaluated by the following methods

1. Chemical composition, impurities and crystal structure: X-ray diffraction, X-ray fluorescent analysis, atomic absorption and etc.

2. Particle form, size, size distribution and specific surface area: Observation by microscope, various measurements for particle size distribution, various measurements for specific surface areas.

3. Agglomerate energy and packing property: Various measurements of powder density, contact angle, sedimentation volume, etc.

Following the above characterization, alumina is classified for many applications as shown in Table 2.1

Table 2.1 Classification of aluminas by application [5]

Use	Material	Coarse particle size		Medium particle size	Fine particle size			Low soda			Easily sintered (ordinary soda)			Easily sintered (low soda)		High purity		Filler
		AC-21	A-21	A-26	AM-21	AM-27	AM-28	AL-41~44	AL-M41~M44	ARL-41	AMS-2	AMS-5	AMS-9,12	AES-11,12	AES-21,22S	AL-31	AKP,AKP-G	AL-32,33
Refractory	Electro-fused alumina	◎	◎															
	Sintered alumina			◎	○													
	Insulating file brick	◎		◎	◎						◎	◎	◎	○		◎		
	Unshaped refractory			◎	◎						◎	◎	◎	○	○	◎		
	Spinel			○	○													
	Heat insulater	○	○	○	○													
	Ceramic fiber	◎			○													
Abrasives	Ordinary abrasives				○	○	◎		○		◎							
	Spesial abrasives																◎	
Ceramics	Spark plug							◎	◎									
	IC substrate							◎	◎	◎				○				
	Single crystal																◎	
	Translusent body																◎	
	Glass		○		○	○		○	○							○		
	Cutting tool					○		○	○		○			◎	◎			
	Crucible													◎	◎		◎	
	Medical and dental material													○	○		◎	
	Ordinary alumina porcelain		○	○	○	○		◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	
Others	Glass	○	○	○	○												◎	
	Welding rod		◎															
	Slag-gathering agent		○															
	Levelling sand	◎	○															
	Unmolding facilitator	○	○		○													
	Paint													○	○		○	
	Filler	○			○						○					◎	◎	◎
	Catalyst	○			○			○	○		○	○					○	

2.2 Sintering of alumina

Sintering [6] is essentially a removal of pores between the starting particles and making dense in the compact. The sintering of alumina in this experiment is solid state sintering, which involves the diffusion of material transport. Diffusion consists of movement of atoms or vacancies along a surface or grain boundary or through the volume material.

The driving force [7] for solid state sintering is the difference in free energy or chemical potential between the free surfaces of particles and the point of contact between adjacent particles. The equation is derived from mechanism of transport of material by lattice diffusion from the line of contact between two particles to neck region. The schematic of solid state sintering is shown in Fig.2.4
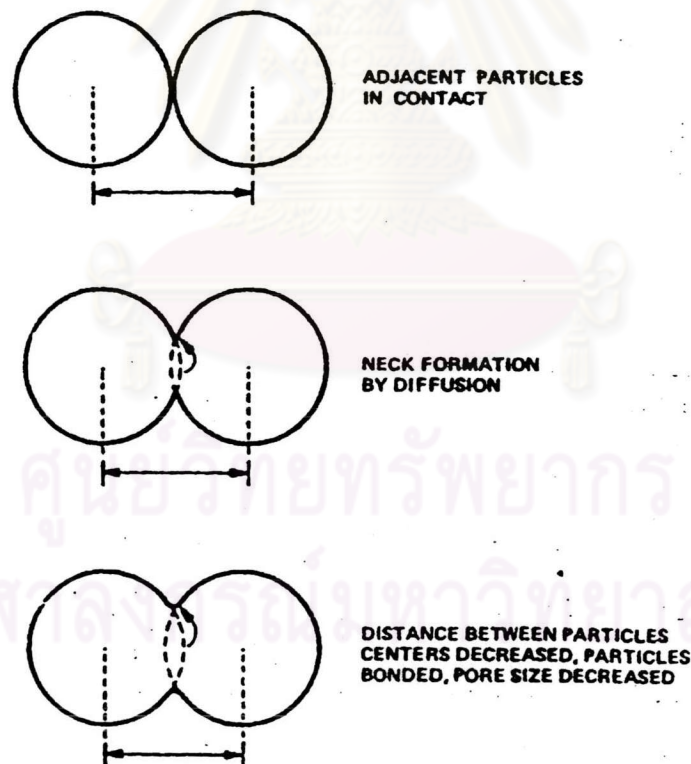
ADJACENT PARTICLES
IN CONTACT

NECK FORMATION
BY DIFFUSION

DISTANCE BETWEEN PARTICLES
CENTERS DECREASED, PARTICLES
BONDED, PORE SIZE DECREASED

Fig. 2.4 Schematic diagram of solid state sintering [7]

$$\frac{\Delta L}{L_0} = \left[\frac{20\gamma a^3 D^{*\,2/5}}{\Gamma 2\,kT} r^{-6/5} t^{2/5} \right] \qquad (2.1)$$

Where $\Delta L/L_0$ is the linear shrinkage (equivalent to the sintering rate), γ the surface energy, a^3 the atomic volume of diffusing vacancy, $D^{\cdot}$ the self-diffusion coefficient, k the Boltzmann constant, T the temperature, r the particle radius (assuming equal size spherical starting particles), and t is time.

Equations for other volume diffusion mechanisms of sintering are similar. In each case the rate of shrinkage increases with increasing temperature and with decreasing particle radius and decreases with time.

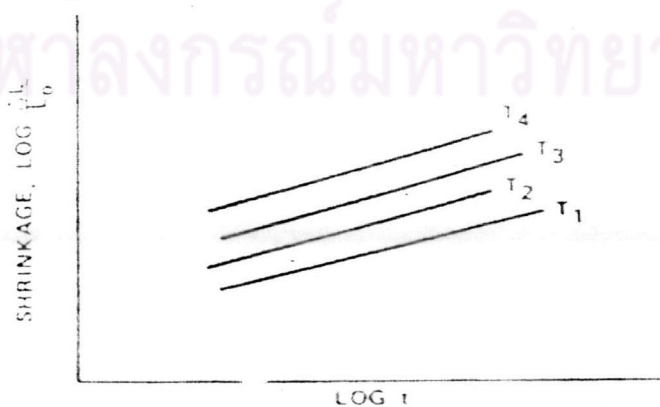Fig.2.5 Sintering rate curve of the effect of temperature and time

Fig.2.6 Log plot of the effect of temperature and time

Fig.2.5 illustrates the effect of temperature and time. Fig.2.6 shows the log plot of the same data. The slope of the log $\Delta L/L_0$ versus log t line is approximately two fifths for solid state sintering.

It is apparent from the examination of equation 2.1 and Fig.2.5 and 2.6 that control of temperature and particle size extremely important, but the control of time is less important.

Finer-particle size powder can be sintered more rapidly and at a lower temperature than coarser powder. Not apparent in the equation, but highly important to the final properties, are the uniformity of particle packing, the particle shape, and the particle size distribution. If particle packing is not uniform in the green product, it will be very difficult to eliminate all the porosity during sintering. Agglomerates are a common source of non-uniformity, Non-uniformity can also result during shape forming due to gas entrapment, particle segregation, lamination.

Particle shape can also be important. Too high a concentration of elongated or flattened particles can result in bridging during forming, producing a large or irregularly shaped pore that is difficult to remove during sintering.

Particle size distribution is also critical. Particles that are all of one size do not pack efficiently. They form compacts with large pores and high volume percentage of porosity. Unless very uniform close packing was achieved during compacting will undergo a high percentage of shrinkage and yet will retain significant porosity. For very fine particle (500 $^{\circ}$A) this may be acceptable and may result in very uniform properties.

However, more commonly available powder has arranged particle sizes in submicron upward. Better overall packing can be achieved during compaction, but isolated pores due to bridging and agglomerates are usually quite large and result either in porosity or a large grain size after sintering.

2.3 Influence of additives

2.3.1 Effect of MgO

Magnesium oxide [8] is a solid solution additive in the sintering of alumina. Magnesia is added to increase the densification rate during sintering directly through enhancing the diffusion coefficient, the pore mobility directly through surface diffusion, On the other hand, MgO decrease the rate of grain growth during sintering through lowering the surface diffusion.

Magnesium oxide [9] also the causes of grain boundary roughening that leads to prevention of abnormal grain growth of pure alumina. The grain boundary [18] is very important in the sintering process that can act either as sinks or as diffusion paths for lattice vacancies. Thus the configuration of the grain boundaries will have an important effect on the rate of sintering. Grain growth during sintering changes the configuration of grain boundaries relate to the pores and thus may markedly increase the shrinkage rate as the grain size decreases Impurity additions will increase the sintering rate if they increase diffusion rate, but may also decrease sintering rate s by impeding grain boundary movement.
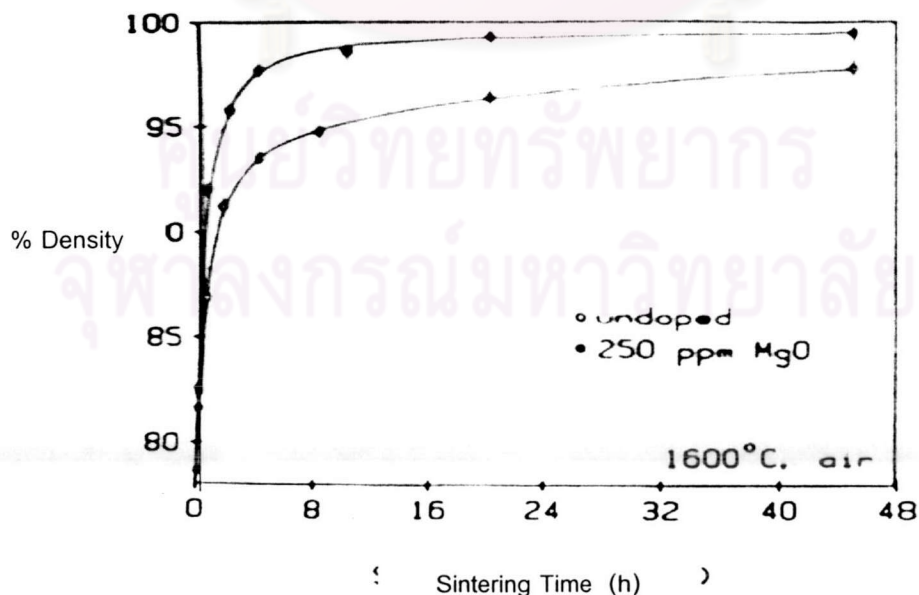

Fig.2.7 Sintered density for undoped and 250 ppm-MgO doped alumina as a function of sintering time at 1600 °C [8]

Fig.2.7 shows that MgO can increase the densification rate of alumina. The densification rate ($^\circ\rho$) depends on the diffusion coefficient responsible for densification as shown by the sintering model (2.2)

$$^\circ\rho \ = \ CD/G^n \tag{2.2}$$

Where C is a constant and D is the relevant diffusion coefficient, G is the grain size exponent, n is 3 for lattice diffusion-controlled densification and n is 4 for grain boundary diffusion controlled densification.

2.3.2 Effect of ZrO_2

Zirconia is grain growth inhibitor in alumina sintering. It is used for preventing abnormal grain growth during sintering, which allows pores to be swallowed to limit end-point densities, and for limiting grain size to achieve higher strengths.

Inhibition of grain growth by inclusion has generally been on refinements of Zener's original concept [10], in which the inclusion residing at the grain boundary produces a dragging force due to the lower free energy of the junction/inclusion system when the inclusion resides at the junction.

In the alumina sintering with dopant of ≤ 2.5 vol% ZrO_2 were strongly bimodal at temperature $\geq 1600\ ^\circ C$, whereas grain growth control (normal grain growth) was achieved for ZrO_2 contents ≥ 5 vol%. Microstructure of composites exhibited controlled grain growth (≥ 5 vol% ZrO_2). Fracture surface observations showed that the ZrO_2 grains were primarily located at 4-grain junctions.

Abnormal grain growth [1] occurred when the inclusion distribution was not sufficiently uniform to hinder the growth of all Al_2O_3 grains. This condition was observed for compositions containing ≤ 2.5 vol% ZrO_2, where the inclusions did not fill all 4-grain junctions. For this condition, the grain size was inversely proportional to the volume fraction of the inclusions. Grain growth control (no abnormal grain growth) was achieved when a majority (or all) 4-grain junctions contained a ZrO_2 inclusion, For this condition, the grain size was inversely proportional to the volume fraction of the inclusions.

2.4 Forming of thin ceramics

The process of forming thin ceramic has been developed and patented following the demand in the electronic industry, divided into 2 major processes.

1. Extrusion

2. Tape casting or doctor blade

For the process, parameters and detail in each process are described in this chapter.

2.4.1 Extrusion

Extrusion [11] is a plastic forming method by the shaping of cross section of a cohesive plastic material by forcing it through a rigid die. The properties of materials are flow ability and wet strength, which are considered in this process. Products formed by extrusion include structural refractory products such as hollow furnace tube, honeycomb catalyst supports, transparent alumina tube for lamp, magnetic ceramics, electrical porcelain insulators, tile product and flat substrate. Extrusion is also used to produce a de-aired plastic material of controlled volume for pressing or jiggering operation.

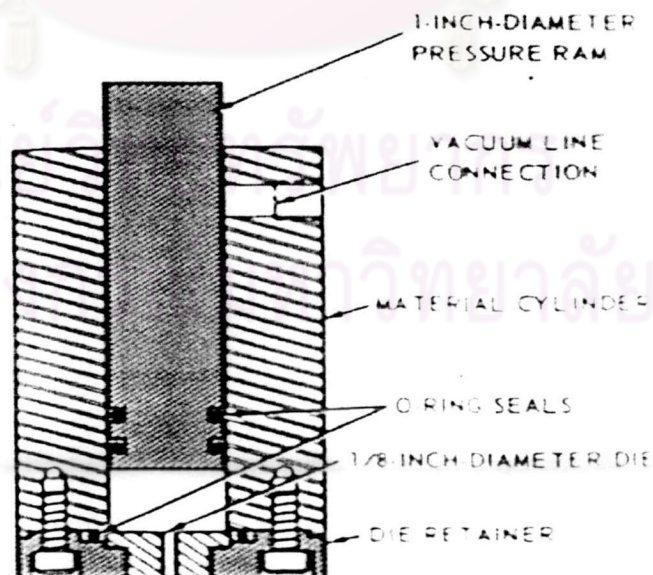One sample of extrusion device is shown in Fig.2.8

Fig.2.8 Extrusion device [12]

2.4.1.1 Formulation principles [13]

The formulation of this process is designed for making the consistency of batch relate to the plasticity and wet strength of material which depend on the mechanical properties of particulate-solvent system and mechanical properties of binder phase

A) Powder

The important parameter is starting powder. For non-plastic ceramic powder (largely all non-clay powders), a particle size is considered parameter above 5 μm may present problems in batch formulation. The powder in water has a low degree of flocculation due to weak van der Waals forces. At high solids loadings this may lead to dilatancy. For powders with particle size distribution below 1 μm, extrusion problems are generally not so severe. The attraction between the particles is higher and the permeability is lower.

In general, a flocculated system is preferred to a dispersed system if the mechanical properties of particle-solvent system are providing the plasticity and wet strength to the system. A flocculated system has higher strength at a given solids loading and has a longer working range for systems that depend on the mechanical properties of the solid phase. A fully dispersed system may be preferred if the mechanical properties of the binder are providing the plasticity and wet strength for the system.

B) Additives

Additives include binders, viscosity modifiers, dispersant, flocculants and lubricants. Binders have at least 2 roles in this process

1. Enhance the wet body and dry strength

2. Thicken the solvent phase

They may also act as dispersant or flocculants and lubricants. Typical binders are listed in Table 2.2 and 2.3.

The most popular binder for extrusion included Methylcellulose, polyethylene oxide, polyvinyl alcohol, sodium carboxy methylcellulose (also known as cellulose gum), alginate, ethyl cellulose. The characterization of binder that should be considered is rheology, burnout behavior and green strength properties. Most binders are available in a variety of viscosity grade The high viscosity grade is composed of high molecular weight and exhibit viscoelastic behavior, may be advantageous if a high springback, which is a term used to describe the elastic rebound of a material after subjected to pressure during forming operation. It is not desired phenomena in extrusion, die pressing and pressure casting.

Complete binder burnout is critical to the manufacture of high quality ceramics. In air there is generally no problem except for sodium that the residue remaining after burning may affect the following process and properties.

Table 2.2 Aqueous binders for extrusion [13]

Binder type	Viscosity grade[b]	Electrochemical Type	Biodegradable
Gum arabic	VL	Anionic	Yes
Lignosulphonates	VL	Anionic	Yes
Dextrins	VL to L	Non-ionic	Yes
Poly(vinyl pyrrollidone)	VL to L	Non-ionic	No
Poly(vinyl alcohol)	VL to M	Non-ionic	No
Acrylates	VL to M	Anionic	No
Starch	L to H	Non-ionic	Yes
Poly(ethylene imine)	L to H	Cationic	No
Methylcellulose	L to H	Anionic	Yes
Polyacrylamide	L to VH	Non-ionic	No
Sodium carboxy-methylcellulose	M to VH	Anionic	Yes
Poly(ethylene oxide)	M to VH	Non-ionic	No
Alginates	M to VH	Anionic	Yes
Natural gums	H to VH	Varies	Yes

`Adapted from [3].
[b]Viscosity grades are defined as the concentration of binder in aqueous solution required to give a solution viscosity of 2 Pa s.

Very low	(VL)	> 10 wt%
Low	(L)	3 to 10 wt%
Medium	(M)	1 to 3 wt%
High	(H)	0.3 to 1 wt%
Very high	(VH)	< 0.3 wt%

Table 2.3 Non-Aqueous binders for extrusion [13]

Type	Solubility	Manufacturers
Acrylics (PMMA, PMA, PBMA, PEMA)	Ketones, alcohols, glycol ethers, and some hydrocarbons	DuPont, Rohm and Haas, Polyvinyl Chemical Industries
Butyral (PVB)	Wide	Monsanto
Cellulosics (ethyl, methyl, acetate, butyrate)	Wide (some are water soluble)	Dow, Eastman Kodak, Hercules
Poly (ethylene oxide) (PEO)	Water and polar organics (can also act as a dispersant)	Union Carbide
Pyrrollidones (PVP)	Water and polar organics	GAF Corp., BASF
Styrene (PS)	Ketones and hydrocarbons	Monsanto, Dow, Mobil, Shell B.\SF, ICI
Pitch	Hydrocarbons (used mainly with carbon black for graphite extrusion)	Ashland Oil Co.
Silicone resins	Not soluble (used as 'precursor binder' in silica and alumina, refractories)	General Electric Dow Corning
Waxes, oils, gums, resins	Various	Various (an excellent reference is Industrial Waxes, H. Bennet, Chemical Publishing, Inc., 1975)

In this experiment, methylcellulose derivative is considered to be the binder. It is polymer, which is prepared by the reaction of methyl chloride and propylene oxide with cellulose in the presence of sodium hydroxide following the requirement of performance by vary the degree of substitution and molecular weight.

Methylcellulose [14] is widely used as binder in ceramic fabrication such as injection molding, pressing, isostatic pressing and especially in extrusion with beneficial properties such as water soluble, surface active (wetting of ceramic powder), nonionic (no interact with dispersants and emulsifiers), water retention, clean and predictable burnout ($> 225\,^{\circ}C$), lubricity, nontoxic and thermal gelation.

2.4.1.2 Mixing

Mixing [13] is the most critical step in extrusion batch formulation and affect to the forming, handling, firing and in the final part. The purpose of mixing is to produce a uniform extrusion batch with many methods including brute force, filter pressing and some form of slurry mixing followed by drying.

The brute force approach typically, uses a high intensity mixer such as sigma blade or muller mixer or plug mill. The dry powder and binder solution is loaded into the mixer and the extreme mechanical action forces the powder and binder together. The poor mixing often leads to dilatant flow behavior by the binder resides within agglomerates and affect to solid loading of the system.

The filter pressing is used in whiteware industry by the mixing of slurry with high solid loading. And the last method is based on drying of a fluid suspension by mixing the powder and solvent in a mixer or ball mill and then transfer to high intensity mixer with binder and then raise the solid loading by vacuum or heat.

2.4.1.3 Extrusion process

The extruder is a machine that forces material through a die by applied pressure. There are two basic types:

Piston extruder consists of a barrel, a piston and die. It is inherent batch process, after the extrusion mix is loaded into the barrel and press through the die. The defects are generated at the extruder during pressing process. Typically, piston is used for technical ceramic for lab trial.

Auger extruder is more complicated equipment and inherently continuous process. It can incorporate a mixing stage with a forming stage. Typically, there is a pug mill or other mixer such as sigma blade mixer associate with extruder. The potential capacity of an auger extruder is enormous and can be as high as 100 tons/hour. Therefore, it is used in industry.

In the present [11], the patented process for substrate forming, square entry die system that can form the material at the thickness down to 0.2 mm is used.

The flow mechanic of extrusion bodies is described by plastic rheological model as shown in Fig.2.9
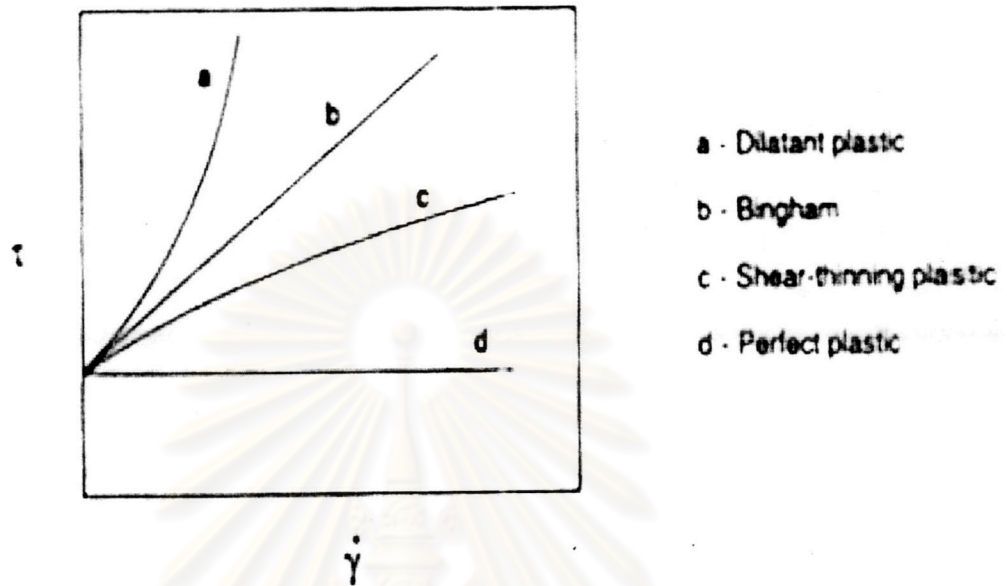

a - Dilatant plastic

b - Bingham

c - Shear-thinning plastic

d - Perfect plastic

Fig.2.9 Plastic rheological model [13]

The Bingham [13] plastic body is widely observed experimentally, and provides a useful starting point for many theoretical analyses. The shear thinning and dilatant plastic bodies are refinement on Bingham model. The shear thinning is often observed for bodies in which the particles are anisotropic or high viscosity binder phase. In case of the anisotropic particles that the higher degree of shear, the greater alignment of the particle and lower the resistance of flow of a body. For the high viscosity, there will be a strong decrease in the viscosity of binder solution with increasing shear rate. The dilatant plastic is observed at high solid loading and also poor mixing.

2.4.1.4 Extrusion defect [11]

The important defect in sheet extrusion process is classified as follows :

1. Insufficient strength

The yield strength of extruded sheet depends on liquid content, content of binder and colloidal particle.

2. Crack and lamination [15]

Crack and laminations are caused by differential springback and differential drying shrinkage.

3. Blister

It causes by the air in the body dissolved in the liquid under pressure due to the incomplete de-airing.

4. Periodic surface lamination

It occurs from the poorly lubricated die under high extrusion pressure.

5. Curing

It causes from dimensional distortion due to differential drying shrinkage.

2.4.2 Tape casting

Tape casting [16] is also known as doctor blade and knife coating that is well known in many industries, including paper, plastic and paint manufacturing. It has been used for forming large-area, thin, flat ceramic or metallic parts by casting the slip on the moving carrier behind doctor blade, which used for control the flatness and wet thickness. Other variables that come into consider include reservoir depth, speed of carrier movement, viscosity of slip and shape of doctor blade. The wet film of slip passes into a drying chamber, and the solvents are evaporated from the surface, leaving a dry tape on the carrier surface.

Tape casting [17] is also used in development project because small quantities can be processed easily and better than extrusion and dry pressing those have some limitation in making very large area, thin and flat part.
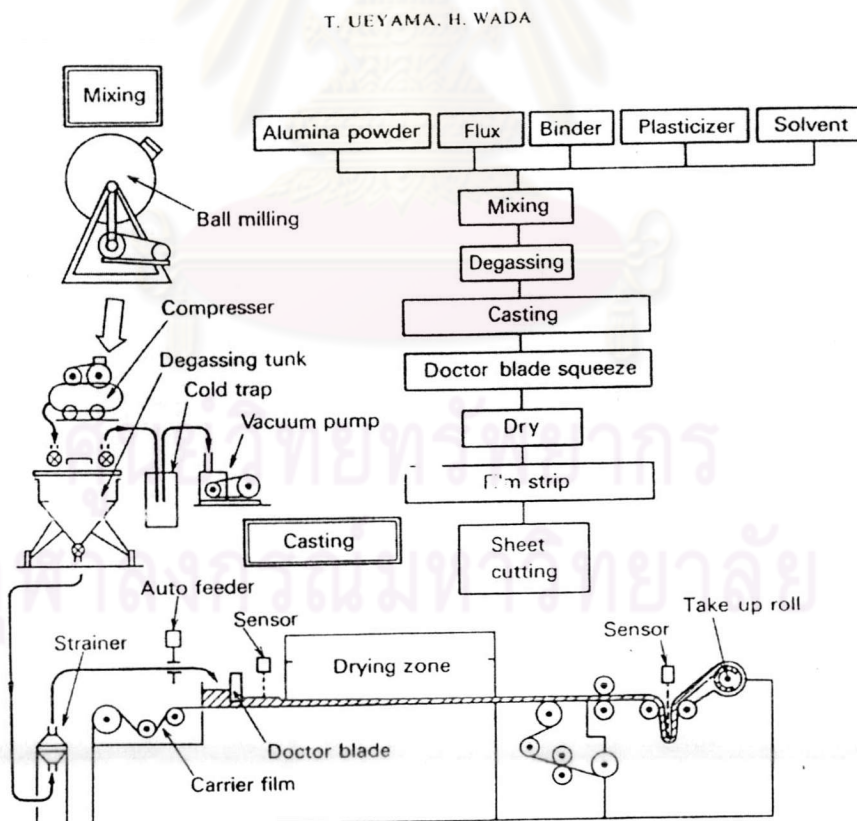
T. UEYAMA, H. WADA

Fig.2.10 Schematic diagram of the manufacturing process of green sheet by doctor blade [3]

<u>2.4.2.1 Materials for tape casting process</u> [16]

A) Powders

Powders are the most important ingredients in batch formulation for tape casting. After binder removal and final consolidation, the powders are the only portion of the batch left, and define the properties of the part produced.

In the process, it is essential that the starting powders be well characterized. The important parameters to monitor in all powders are the average particle size distribution, surface area, impurities and powder density.

1. Particle size distribution and shape

The particle size distribution and particle shape are important parameter for the properties of tape. They are related to particle packing of green tape during fabrication process and also important for dispersion milling which purpose for breaking down the agglomerates to achieve very excellent densification.

2. Surface area

The surface area of powder is a measure of its size, shape and the presence of voids that open to the surface. It is determined by BET technique using the adsorption of a monolayer of a gas such as nitrogen on the powder surface. The surface area of powder is also important in the term of the interaction with organic additives such as surfactant and binders. Processing chemicals are usually added as weight per weight of powder and are the best associated with the area that they have to interact with to prvide the proper dispersion, lubrication or binding quantities. The particular true of tape casting in the total powder area is directly proportional to the amount of organics. The surface area is significantly affect the sintering temperature versus fired density relationship.

B) Solvents

The solvent is used to distribute powder and the other ingredient homogeneously throughout the slip to create a uniform mixture. Other ingredients to be distributed may include binder, plasticizer, lubricant, release agent, flattening agent, thixotrope, wetting agent, dispersant and etc.

The organic solvent is widely used and called as solvent-base casting as oppose to aqueous or water-based casting. Over the years organic solvents have become the standard solvents of choice for tape casting slip such as ethanol, methanol, toluene, methyl ethyl ketone and etc.

The criteria for selection of solvent is considered following that the solvents should have good balance between drying rate, cost, safety and environmental considerations, miscibility in other solvents and dissolving power of additives and also non-adverse affect with the powder.

In some of slip preparation, homogenizer is recommended to avoid the skin formation during drying. Ex. Cyclohexanone.

C) Defloculants and dispersants

Defloculant is an additive that works in the system to keep particle apart. The role of a defloculant in the tape casting slip is fivefold

1. To separate the primary particles so the binder can coat them individually.
2. To increase solids loading in the powder suspension in order to maintain viscosity after binder addition.
3. To decrease the amount of solvent in the powder suspension in the term of saving cost, dry the slip faster with less shrinkage.
4. To burn out cleanly.

The purpose of the dispersant is to disperse primary particles and hold them in a homogeneous suspension by two methods, steric stabilization (separation of particles by coating on one particle that prohibit the another particle contact with it) and electrostatic stabilization as shown in Fig.2.11.
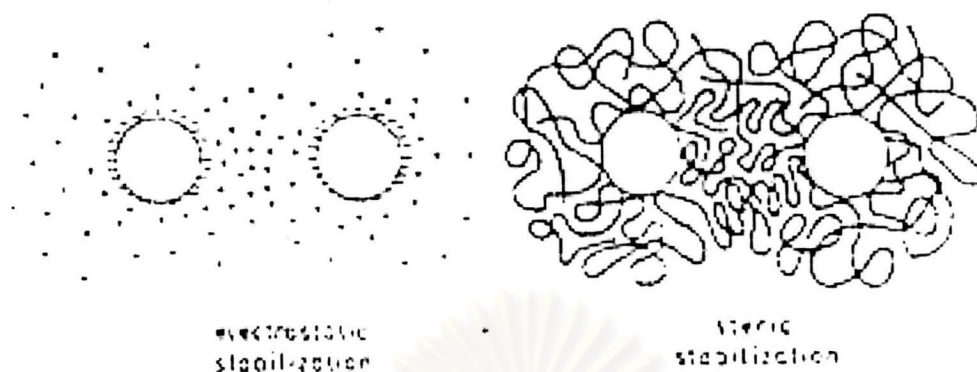
electrostatic
stabilization

steric
stabilization

Fig.2.11 Mechanism of particles dispersion in tape casting slip [2]

(Left- electrostatic - stabilization), (Right - Steric stabilization)

They also act to avoid the air entrapment inside the agglomerates. Specimen achieves higher pack density by the well settle of slip. The dispersants and defloculants are shown in Table.2.4.

Table 2.4 List of Dispesants/Defloculants used for tape casting [16]

Some Reported Dispersants/Deflocculants used for Tape Casting	
Polyisobutylene[48]	pH adjustments
Linoleic acid[48]	Sodium silicate
Oleic acid	Dibutyl amine
Citric acid	Substituted imidazolines[47]
Stearic acid	Sulfanates
Lanolin fatty acids[47]	Aliphatic hydrocarbons[47]
Salts of polyacrylic acids	2-amino-2-methyl-1-propanol[47]
Salts of methacrylic acids	Polyethylene glycol[47]
Blown menhaden fish oil	Polyvinyl butyral[47]
Corn oil	Sodium sulfosuccinates[47]
Safflower oil	Ethoxylate[47]
Linseed oil	Phosphate ester[47]
Glycerol trioleate	Glycerol tristearate
Synthetic waxy esters	Many proprietary chemicals

D) Binders

The binders are used in production of green ceramic tape that probably the most important processing additives of the system. The binder has the greatest effect on such green tape properties as strength, flexibilty, plasticity, laminatability, durability, toughness, printability and smoothness.

From the above, the binder is very important ingredient in tape casting slip. Therefore the binder should be considered following these factors, solubility, viscosity, cost, strength, T_g or ability to modifiy T_g, Firing atmosphere of powder, ash residue, burnout temperature and by-product. The group of binders that is most widely used is Vinyl, Acrylics and Cellulose as shown in Table 2.5.

Table 2.5 List of binders used in tape casting [16]

Reported Binders Used for Tape Casting

VINYL	CELLULOSE
Polyvinyl alcohol	Cellulose acetate—Butyrate
Polyvinyl butyral	Nitrocellulose
Polyvinyl chloride	Methyl cellulose
Vinyl chloride—Acetate	Ethyl cellulose
	Hydroxyethyl cellulose
ACRYLIC	Hydroxypropyl methyl cellulose
Polyacrylate esters	
Polymethyl methacrylate	
Polyethyl methacrylate	

OTHER	AQUEOUS BINDERS
Petroleum resins	Polyvinyl alcohol
Polyethylene	Celluloses:
Ethylene oxide polymer	Ethyl, methyl, hydroxyethyl
Polypropylene carbonate	hydroxypropyl methyl, above
Polytetrafluoroetylene (PTFE)	Emulsions of:
Poly-alpha-methyl styrene	Acrylics, latex
Poly isobutylene	Polypropylene carbonate
Atactic poly(propylene)/Poly(butene)	PVB, waxes
Polyurethane	

D) Plasticizers

The purpose of the plasticizer is to enable the tape to be bent, without crack. Most of the polymeric binders used for forming tape will form a relatively strong, stiff and brittle sheet if no plasticizer is used. Later forming and assembly needs require the ability to punch, cut, roll, or laminate the dry tape. The role of plasticizer is to allow a hole to be punched in the tape without shattering or cracking the tape. The plastcizers are classified into 2 types following the different mechanism.

1. To soften the binder polymer chain allowing them to stretch under applied force

2. Act as lubricant in the tape matrix.

The plastcizers used in tape casting are shown in Table 2.6.

Table 2.6 List of plasticizers used in tape casting [16]

Reported Plasticizers Used for Tape Casting

PHTHALATES
n-Butyl (dibutyl)
Dioctyl
Butyl benzyl
Mixed esters
Dimethyl

GLYCOLS
(poly)Ethylene
Polyalkylene
(poly)Propylene
Triethylene
Dipropylglycol dibenzoate

OTHER
Ethyltoluene sulfonamides
Glycerine (Glycerol)
Tri-n-butyl phosphate
Butyl stearate
Methyl abietate
Tricresyl phosphate
Propylene carbonate
Water*

* Humidity acts as a plasticizer for water soluble polymers.

2.4.2.2 Tape casting process

A) Slip preparation

Ceramic powder, solvent and additives will be fully mixed following the designed formula to achieve the desired properties of tape.

1. Dispersion milling

The first step in the preparation of tape casting slip is dispersion milling by mixing the powder with solvent and dispersant or defloculant to eliminate the agglomerates, disperse the particles and enhance the efficiency of dispersant in the slip. The important factor to identify the efficiency of mixing is %solid loading following (2.3)

$$\% \text{ Solids} = \text{Powder weight}/(\text{Powder weight} + \text{Solvent weight}) \tag{2.3}$$

It depends on the density of powder, particle size and dispersant effectiveness. Normally, it should be in the range of 70 - 80% for the excellent dispersion. The mixing time should be in the range of 4 – 24 hours.

2. Plasticizer and binder mixing

After the dispersion milling process is complete, the plasticizer and binder are added and mixed to make homogeneous in tape casting slip.

3. Slip de-airing

The next step is to de-air the slip to remove any air that may have been entrained during the milling and mixing process. Air bubbles cause defects in the tape casting product. Pinholes (small hole left by air bubbles) are the most common defect, and these can lead to crows, foot cracking (crack radiate from the pinhole) upon drying.

Other defects attributable to air bubbles, especially in thin tape, are elongated streaks or thin spots in the tape in the casting direction.

The most common technique for de-airing a slip for tape casting is to use a partial vacuum accompanied by gentle stirring or agitation. Agitation tends to lower the viscosity in a pseudoplastic slip and therefore it makes the air removal easier.

B) Tape Casting

The tape casting slip will be transferred to casting head. The pressure is applied to the slip for viscosity control and it is cast under the control of thickness and flatness by doctor blade on the moving carrier or moving blade as shown in Fig.2.12
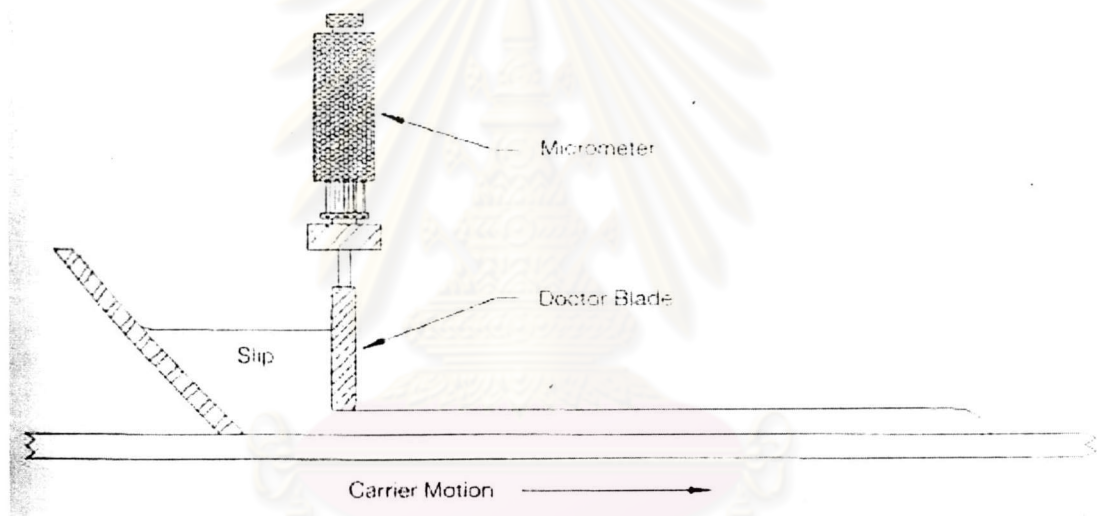

Fig.2.12 Schematic diagram of tape casting process [16]

The further process is to dry the green tape for removal the liquid solvents while maintaining a homogeneous and crack free in drying chamber or provide several ventilation zone [17] of drying for continuous process.