

## Chapter II

### Theoretical Part.

#### 2.1 Introduction

Ball milling consists of placing the particles to be ground [the "charge"] in a close cylindrical container with ball grinding media, and rotating the cylinder horizontally on its axis so that the media cascade. The ceramic particles move between the much larger media, and between the media and the wall of the mill and are effectively broken into successively smaller particles. Compressive shear forces produced by crushers occur many times per second in an operating ball mill, causing the materials fractured. The liners must have remarkable resistance to both sliding and impact abrasion, the two most important properties are hardness and toughness. These are often interdependent in that one increases as the other decreases, and it is a combination of the two properties that determines the suitability of an abrasive for a particular application.

Hardness has been defined as the resistance of the surface layer of the body to penetration under the effect of external mechanical forces concentrated in a restricted area of the body. The different surface-indentation tests [Vickers, Knoop, Rockwell] are based on the relation between hardness and load required to produce a definite indentation. The methods differ in the shape of the diamond indenter usually of a pyramidal diamond shape, on a polished section of the material, and in the loading.

Toughness , or the ability to resist fracture, is a difficult property to measure; it may be done by ball milling or by shooting the abrasive grains against a barrier but no single method has proved entirely satisfactory and an assessment is often made on the basis of practical operating experience. Additionally, the way in which a material fractures is an important consideration. Fracture may generate a sharp edge that is useful where a deep cutting action is required, or it may generate a smooth surface useful in polishing or buffing operations.

Ball mill liners are classified as wear resistant component which composed of more than 85 %  $Al_2O_3$  content, depends on forming method. From which the major part of the liners' composition is alumina, it is necessary to study the details of this material.

## 2.2 General Background on Raw Materials.

### 2.2.1 Calcined Alumina

The native aluminous minerals, corundum, emery and the clays, have been associated with ceramic operations from antiquity. Exclusive of these raw materials, bauxite is the principle source of alumina for ceramic purposes.

In bauxite, gibbsite is the most stable form at normal temperatures and pressures found in the tropics. As it is likely that temperatures above  $100^{\circ}C$ . were involved in the genesis of bauxite, the formation of diaspore and boehmite probably resulted from high pressure.

Bauxite is used directly in adsorbents, abrasives and refractories, aside from its use in preparing metal. For these applications, specific grades must be sized, dried, and calcined.

Bauxite is the impure hydroxides, that are the source of industrial grade aluminas derived by the Bayer Process.

#### The Different Forms of Alumina.

In 1930, The Aluminum Company of America introduced the use of Greek letters in the naming of different forms of alumina with the alpha designation always being given to the form occurring most abundantly in nature.

Thus; 1. Alpha-alumina trihydrate ; more correctly called alpha-alumina trihydroxide or gibbsite , the principle constituent of tropical bauxites; it is a direct product of the refining of bauxite by the Bayer Process and consists of almost spherical grains measuring 50 to 100 microns through individual tabular and prismatic crystals, either monoclinic or triclinic, may be much smaller. It is a non-abrasive powder with Moh hardness of 2.5 to 3.5 and a specific gravity of 2.42 which is manufactured in a wide range of grades and particle sizes.

2. Beta-alumina trihydrate ; or beta-alumina trihydroxide, occurs in nature in small quantities as the mineral bayerite, it is already synthesised and consists of monoclinic crystal of about 1 micron in aggregates of diameter up to 100 microns.

3. New beta-alumina trihydrate ; or nordstrandite, a triclinic crystalline form, does not occur in nature.

4. Alpha-alumina monohydrate ; or boehmite, is a major constituent of Mediterranean type bauxites; the crystal structure is orthorhombic.

5. Beta-alumina monohydrate : or diaspore, is a constituent of some high alumina clays and of bauxite; the crystal structure is orthorhombic.

6. Alumina gels are amorphous forms of alumina hydroxides or hydroxyoxides.

7. Anhydrous alumina is prepared from the hydroxides or hydroxyoxides by heating. This results in water molecules being eliminated and, depending on the starting material and conditions, different types of alumina are formed; this include,

7.1 Activated alumina in the form of porous white powders with a pore diameter of 20°A to 100°A, a pore volume of 0.2 cc./gm. to 0.9 cc./gm. and specific surface area between 50 m<sup>2</sup>/gm. and 400 m<sup>2</sup>/gm.

7.2 Calcined alumina or alpha-alumina is the densest and most stable, belong to the trigonal system, refractive index 1.765. It is insoluble in water and only slowly soluble in alkalis and strong mineral acids, but is attacked by hydrofluoric acid and potassium bisulfate. The alpha form of alumina melts at 2040°c., with creeping and sintering of the pure mineral beginning at about 1750°c. In sintering, this permits the discrete crystallites to react with each other to form the large crystals making up the sintered mass. The applications of abrasiveness and wear resistance of alumina involve alumina both in particulate form and in massive shapes. Minerallizers and fluxes permit sintering at lower temperatures. The sintered bodies take on the properties of the basic materials. In 100 % Al<sub>2</sub>O<sub>3</sub> bodies, mechanical failure will occur through the alumina grains as readily as grain boundaries.

Calcined aluminas are available in various grades based on the degree of heat treatment received, crystal size [1 micron to 20 microns median] and  $\text{Na}_2\text{O}$  content [0.01 to nominally 0.5 %]. Varying amounts of transitional alumina phases which enhance measured surface area can remain in the alumina because of incomplete thermal conversion to the alpha phase. The calcined aluminas are nominally 100-325 mesh grain size, but finer grades also are produced by ball milling. Tabular grades have higher alpha content than the regular calcined alumina.

Water - based ground calcined alumina slips can be deflocculated with hydrochloric acid or nitric acid or with aluminum chloride in the region of pH 3.5-4.5. The surface charge under these conditions is positive with the anions acting as counterions. Acid having polyvalent anions [e.g. sulfuric acid] are not satisfactory deflocculants for alumina owing to the close approach of the multiple-charged anions to the positively charged surface. As the pH of alumina slips is increased, the surface charge diminishes until, at pH 8-9, there is no charge and the slip is strongly flocculated. However, if the pH is raised to 11-12 with additives of alkali-hydroxide or hydrolyzable alkali-salt the particle becomes negatively charged with alkali cations as counterions, and the slip is again deflocculated.

At pH 7-9 alkali polyelectrolytes can be used to deflocculate alumina slips. Increasing the concentration of polyanions causes formation of hemimicelles on adsorption sites and the particle surface charge reverses from positive to strongly negative, with alkali cations and counterions.

Alumina slips prepared from narrow distributions tend to be dilatant. However, when several different narrow distributions of alumina are blended to form

extended distributions, slip properties resembling those of clay slips may be obtained.

7.3 Tabular alumina is nearly 100 % alpha phase, the conversion being effected by heating the material above 1870° c. The typically analyze above 99.5 % Al<sub>2</sub>O<sub>3</sub> and the Na<sub>2</sub>O content can be made less than 0.02 %. Tabular alumina are recrystallized, sintered alpha-alumina products made by using calcined alumina which is produced by the Bayer Process. The large, hexagonal, elongated tablet-shaped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals [40 to 200 microns median] characterized and give rise to the name "tabular alumina".

7.4 Fused alumina is produced by melting calcined alumina above 2040° c. in an electric furnace. Lower grades of fused alumina use bauxite as feed to the electric furnace. Some TiO<sub>2</sub> may be added to increase grain toughness. Tabular and fused aluminas are available in grain size from 0.5 in. to -325 mesh.

7.5 Synthetic boehmite alumina is commercially produced in large volume for applications in the catalyst industry as well as in sol-gel ceramics. Its properties differ significantly from those of the "trihydrate". Boehmite or psuedoboehmite alumina can be made by at least two routes. First, and leading to the most pure alumina, is via aluminum alkoxide hydrolysis. The alumina produced can be dispersed to the sol state by the addition of an aqueous acid or, in some cases, water. Seeding with various other inorganics is known to give "ceramic" aluminas. The formular is Al<sub>2</sub>O<sub>3</sub> .x H<sub>2</sub>O, where x varies depending on alumina crystallite size. Boehmite alumina also can be synthetically prepared by the hydrothermal treatment sodium aluminate from the Bayer Process. The alumina is produced by crystallization in the presence of an appropriate seed material.

### Methods of Alumina Production

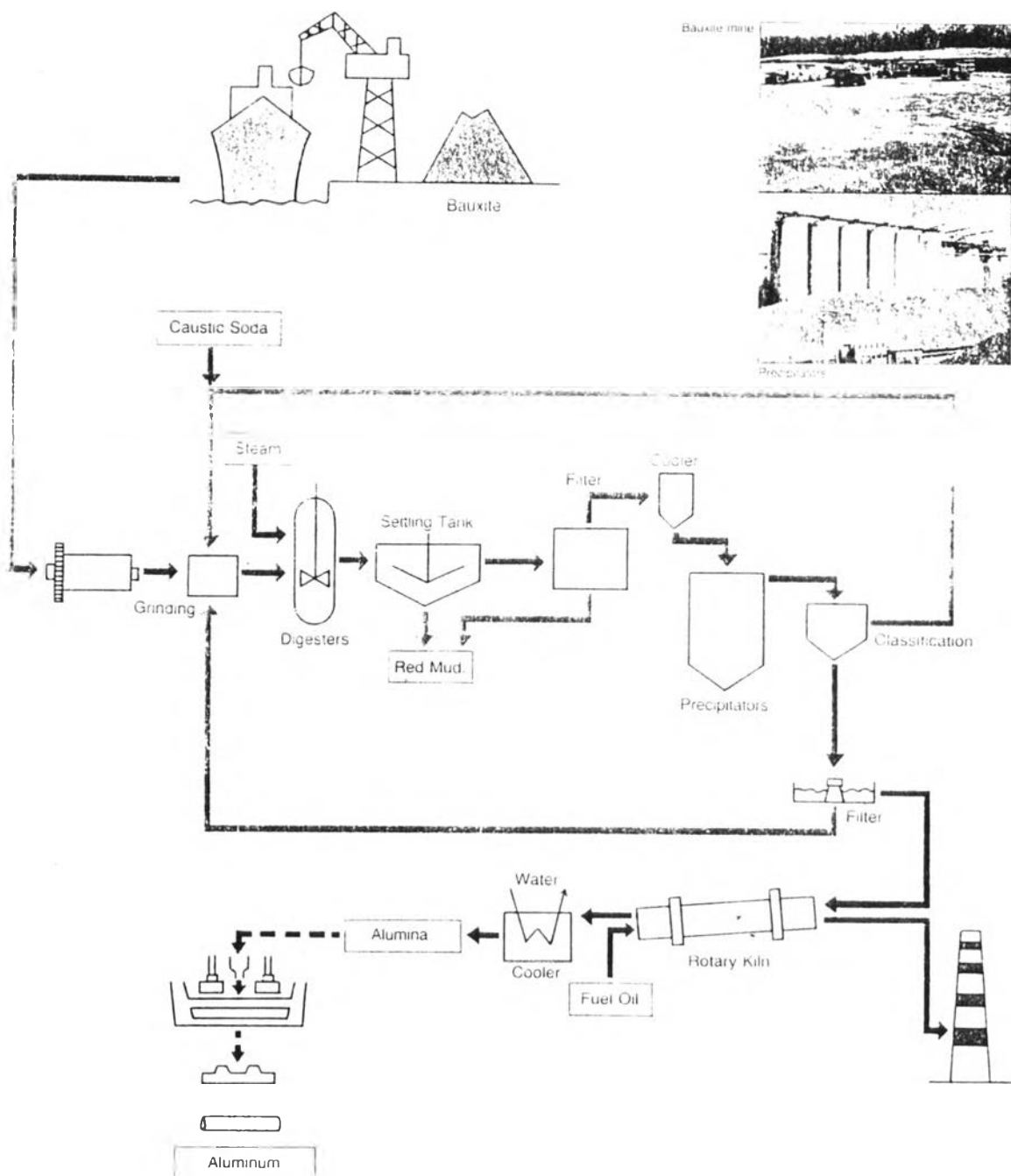
The Bayer Process, the wet alkaline process, is the most economical of modern methods, and it is most suitable for low silica bauxites containing gibbsite and boehmite. The dried, ground bauxite is digested in an autoclave with a solution of sodium hydroxide and sodium carbonate, containing a flocculant [starch] and lime added to causticize the soda and to act as a filter aid.

After digestion, the slurry is cooled by flash heat interchange to near boiling at atmospheric pressure and the waste solids [red mud] are separated by sedimentation and filtration. The red mud comprises mainly iron oxides, titania, carbonated lime, and desilication product. The lime represents make up causticization of soda lost in previous cycles and in some cases, filter aid. The desilication product represents mainly soda and alumina lost by combination with reactive silica to form zeolitic compounds resembling sodalite. The clarified [green or pregnant] liquor is cooled by heat exchange with spent liquor to about 55° c., and a portion of the dissolved alumina is precipitated by introducing fine seed alumina trihydrate, the other phases are possible at different temperatures and with different seeding phases present, as long as the solution is supersaturated with respect to these phases. The precipitated trihydrate is separated from the spent liquor, washed and is calcined for ceramic applications. The spent liquor plus washings is evaporated and returned to process. Complete separation of the hydrate from the green liquor can be realized by gassing with carbon dioxide.

The conditions of seeding, temperature, agitation and time during precipitation are controlled to obtain the most economic separation of the Bayer trihydrate, and the most advantageous particle size distribution for subsequent

operations. Factors which affect the purity and texture of the precipitated trihydrate also influence the quality of the calcined alumina, even though the product has passed through several transitions.

Fig. 2 Alumina Production Process.





### 2.2.2 Bentonite.

A natural clay-like substance, a hydrous silicate of alumina derived from volcanic ash with the clay mineral montmorillonite  $[\text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2 \cdot 7 \text{H}_2\text{O}]$  as the chief constituent. Montmorillonite is a trilayered clay, or smectite material. For practical purposes it is necessary to subdivide bentonite into two parts ;

1. those that swell enormously when wetted, and
2. those that swell no more than other plastic clay.

Type 1. bentonite is used as a plasticizer. A 2.5% bentonite addition improve plasticity more than a comparable 10% ball clay addition, and also lower the PEC. of whiteware mixtures although it increases drying and firing shrinkage somewhat.

Type 2. bentonite is widely used as a clarifying clay, a carrier and sticking agent for insecticides, and for workability in non-color critical ware such as sewer pipe and other structural clay products.

White bentonite are of interest where color effect on electrical properties must be considered.

Treated or refined products having greater plasticizing properties also are available at high prices. One type consists chiefly of organophillic [solvent dispersive] clays. During refinement their ions are exchanged for amines, which makes them inert in water-base system. Another refined product is an air classified, high-purity montmorillonite with a 20 microns average dry particle size. It is widely used as a glaze suspension agent and plasticizer.

Bentonite is available in its outward appearance and superficial properties. Crude bentonite can be pale buff, green and blue-green, but gray dull blue and pink also are found. The usual commercial product is cream color, firing to a buff or light red, and may discolor whiteware if more than 2-2.5% is used.

As stated above, the dominant clay - mineral component of bentonite is smectite, the composition of the smectite itself varies greatly in different bentonites. The variation may be within the smectite lattice itself or in the nature of the exchangeable cations. With regard to exchangeable cations, most bentonites carry  $\text{Ca}^{+2}$  as the most abundant ion. Only a few are known which carry  $\text{Na}^{+}$  as a dominant ion. Also only a few bentonites that carry  $\text{H}^{+}$  or  $\text{K}^{+}$  as a dominant ion.  $\text{Mg}^{+2}$  is frequently present as an exchangeable ion in relatively small amounts, and this is particularly the case when  $\text{Ca}^{+2}$  is the dominant ion.

Smectite clays carrying either  $\text{Na}^{+}$  or  $\text{Ca}^{+2}$  are suitable for foundry molding-sand use, but they have quite different properties in such sands. Thus a sodium smectite provides relatively high dry strength and lower green strength, whereas calcium smectite gives high green strength and lower dry strength.

The different thermal analysis curve for bentonite is characterized by its large endothermic peak in the low temperature region and two small endothermic peaks at approximately  $680^{\circ}\text{C}$ . and  $880^{\circ}\text{C}$ . There is complete absence of any exothermic peak in the  $1000^{\circ}\text{C}$ . region.

### 2.2.3 Ball Clay.

This classification of clays originally applied to sedimentary lignite-bearing aluminum silicates that are plastic, fine-grained, easily slake in water and would fire to a clean, cream to white color. The term "ball" was derived from the original method of mining the plastic clay in England, where it was cut from the bank in the form of balls weighing about 33 lbs. each. Later, the expression ball clay was adopted for a wide range of clays that could not be categorized as kaolin or fire clays.

Because of the slow movement of the streams, only the finest sediments could be carried, which accounts for the very fine grained nature of some ball clays. And upon reaching the lagoons, the blackish water and acids from decaying vegetation would have a pronounced flocculating effect on the fire-clay particles, causing them to settle in a dense plastic mass.

The refractoriness [PCE.] of ball clays normally ranges from cone 28-34. The clays fire more or less white to cream and approach vitrification in the range of cone 10-12. These clays slake down readily in water and, when completely dispersed with appropriate electrolytes, will exhibit a particle size from 80% less than 0.5 micron down to 20%.

The principle clay mineral in ball clay is kaolinite, but there can be minor amounts of montmorillonite, halloysite or illite. Mica, quartz, and/or organic material such as lignite also may be present. It is the colloidal fraction of the clay minerals and the organic colloid that promote plasticity. Plasticity, one of the most important contributions made by certain ball clay, is most difficult to predict by laboratory tests. However, it can be recognized and determined qualitatively in commercial plants through comparative production trial.

The presence of soft colloidal lignite, as opposed to hard massive lignite, appears to promote a type of plasticity frequently referred to as waxy plasticity. The presence of fine-grain clay colloids [-0.5 micron fraction] will improve plasticity, yielding a sticky plasticity. The presence of montmorillonite is known to increase the plasticity of the clay, and some authorities believe that minor amount of illite and /or mica make worthwhile contributions.

Another characteristic of ball clay is its ability to be flocculated through the adsorption of ions from electrolytes. This phenomenon permits a wide range of viscosities in ball clay slurries or slips and serve as the basis for casting in plaster of Paris molds. Ball clay is an important raw material in ceramic for plasticity, bonding strength and refractoriness. It also is useful as an auxiliary flux.

The differential thermal analysis curve for ball clay is characterized by;

1. a small endothermic peak in the 100° c. to 200° c. region, this is due to the heat required to remove water that has been adsorbed on the surfaces of the clay particles ,
2. the gradual exothermic effect in the 300° c. to 500° c. temperature range, this is due to the oxidation of organic matter present in most ball clay.

The reactions occurring in kaolinite when heated;

100° - 200° c. Endothermic peak.

free water adsorbed on the surface of particles were driven off.



#### 2.2.4 Wallastonite [CaSiO<sub>3</sub>]

A naturally occurring calcium silicate, wallastonite imparts low moisture expansion, reduced drying and firing shrinkage, higher fired strength, improved heat shock, faster firing, easy pressing, better bonding, and superior electrical properties to bodies, glazes, porcelain enamels and frits. Wallastonite applications in the ceramic industry can be classified into two general groups ;

1. replacement of flint and limestone,
2. a material for producing bodies and glazes for superior properties.

Among the many other ceramic applications in which wallastonite can be used are ; glaze porous ceramics of nearly every kind, dinnerware, ovenware, artware, structural clay products, terra cotta, sanitaryware, chemical stoneware, ceramic bonded abrasives, refractories, high alumina bodies, spark plugs, electrical porcelains, frits and investment coatings.

Theoretically, wallastonite is composed of CaSiO<sub>3</sub> with 48.25 % of CaO and 51.75 % of SiO<sub>2</sub>, its melting point being at 1540 °C. The natural as well as synthetic wallastonite are never completely pure, as Ca<sup>+2</sup> is partly substituted by Mg<sup>+2</sup>, Fe<sup>+2</sup>, or Mn<sup>+2</sup>.

There are three different modifications of CaSiO<sub>3</sub> ;

$\alpha$  - CaSiO<sub>3</sub> = pseudowallastonite is the triclinic-pseudo hexagonal modification, resistant above 1125±10 °C.

$\beta$  - CaSiO<sub>3</sub> = the actual wallastonite which is triclinic

$\beta'$  - CaSiO<sub>3</sub> = parawallastonite is another seldomly occurring deep-temperature modification.

Wallastonite can be produced synthetically by a solid phase reaction, a sintering process or by thermal dehydration of xonotlite,  $\text{Ca}_2\text{Si}_6\text{O}_{17}[\text{OH}]_2$ , of this three processes, only the first one has proven to be economic. But even this one can only be carried out without problems when the following requirements are met ;

1. Finest, if possible iron-free and therefore costly grinding of the basic materials quartz  $[\text{SiO}_2]$  and limestone powder  $[\text{CaCO}_3]$  or quick lime or whitewash lime  $[\text{CaO}]$  or calcium hydrate  $[\text{Ca}(\text{OH})_2]$ .

2. Careful addition of a mineralizing agent [e.g. lithium - carbonate]

3. Sufficient time of reaction [approx. 2 hrs.]

4. Thorough control of the temperature around  $1450^\circ \text{C}$ . when  $\alpha - \text{CaSiO}_3$  is formed.

5. Controlled cooling for transformation into  $\beta - \text{CaSiO}_3$ .

Comparing the homogeneity, purity, low and regular heat expansion, low gas expulsion and even the whiteness of the synthetic wallastonite, it is equal to the nature one and even superior in some cases.

#### 2.2.5 Talc. $[\text{3 MgO} \cdot \text{4 SiO}_2 \cdot \text{H}_2\text{O}]$ .

Melting points above  $1400^\circ \text{C}$ ., a hydrous magnesium silicate considered as having the formula  $3 \text{MgO} \cdot \text{4 SiO}_2 \cdot \text{H}_2\text{O}$ , although some talcs analyze almost  $4 \text{MgO} \cdot \text{5 SiO}_2 \cdot \text{H}_2\text{O}$ . It is very soft, and is used as the standard for a Moh. hardness of 1. Mineral masses of the composition are known as talc, the impured varieties as soapstone. Relatively pure massive varieties are known as steatite. The mineral is white, greenish-white, or light green and has a specific gravity 2.6-2.8.

The advantages of talc in ceramic bodies are ;

1. It is a cheap source of MgO which acts as flux.
2. It imparts high thermal shock and high electrical resistance at elevated temperatures, low dielectric loss and low power factor. The thermal shock resistance is due to the development of cordierite and mullite which have low thermal expansion.
3. It has a high specific heat and high resistance to acid attack.
4. In low temperature bodies it increases thermal expansion.
5. In both high temperature and low temperature bodies, it decreases expansion.

It should be noted that all talcs are different and the result obtained with one cannot be directly translated to another talc. The lime content of various talc is sometime taken as a basis of comparative classification.

#### Reaction occurring in talc on heating.

Talc undergoes decomposition followed by several transitions on heating. The temperature at which the changes occur vary not only with the nature and amounts of impurities but also on the fineness of grinding and hence cannot be given exactly.

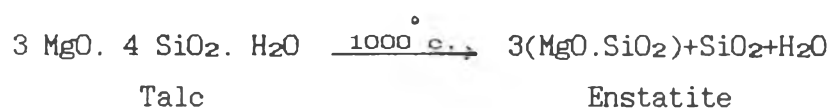
On heating a talc, which has a composition varying between the limits :

3 MgO.	4 SiO <sub>2</sub> .	H <sub>2</sub> O	and	4 MgO.	5 SiO <sub>2</sub> .	H <sub>2</sub> O
31.8 %	63.5 %	4.7 %		33.5 %	62.7 %	3.8%

associated with impurities introducing alumina , iron , lime , alkalis and more water, the total ignition loss of 5.5 % (slightly above average) water is lost in three stages,

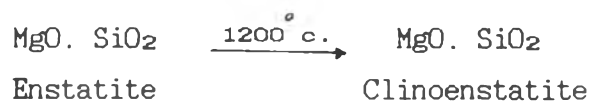


some 0.4 % which is held as H<sub>2</sub>O molecules comes off in the range from 120° to 200° C. and 350° to 500° C. and the remaining 5.1 % is present as chemically bound hydroxyl groups and comes off at 600° to 1050° C. At the same time free silica splits off, leaving magnesium metasilicate



At about 1200° C., there is a faster recrystallization, the enstatite gradually changing to clinoenstatite (called proto enstatite) and the amorphous silica to cristobalite around 1300° C. They found two endothermic heat effects, a small one at 530° to 572° C. and a larger one at 860° to 953° C.

Talc does not split into free magnesium and silicon dioxide.



Magnesium silicate readily reacts either by solution, formation of eutectics etc; or chemically, with alumina, iron oxides, lime, etc. The results obtained by introducing varying amounts of talc with different impurities into different ceramic bodies are therefore very varied. A large range of effects can be achieved by using talc, but often only within carefully defined limits of composition and firing temperature.

### 2.2.6 Dispex

Dispex dispersants are low molecular weight, anionic, water soluble polymers. The presence of Dispex in water permits a high loading of mineral particle resulting in very fluid slurry

#### Properties:

Dispex N40 = sodium salt of polycarboxylic acid, pH = 7.5

Dispex A40 = ammonium salt of polycarboxylic acid, pH = 8.0

These polymers are non-foaming dispersant with a narrow molecular weight distribution results in consistent products with maximum effectiveness. The Dispex action produces a stabilizing and dispersing effect by the process that involves the ionization in water to produce either a sodium or ammonium cation together with a polyanion. This polyanion absorbs irreversibly on to the mineral surface causing the particle to become negatively charged. Cations then surround each mineral particle and adjacent particles repel one another to maintain a state of dispersion.

#### Dispex stability:

Dispex N40 is stable over a wide range of pH and temperature, the effective pH range is 5-14 and up to the temperature of 100° c without any deterioration in dispersing efficiency. Dispex A40 is also very stable to varying conditions of pH and temperature although being an ammonium salt that will be loss of the volatile base at high temperature.

#### Dispex used in ceramic:

Dispex can be used to fluidise and stabilise ceramic casting slip and also helps to reduce "casting spot".

### Raw Material Selection

Considering of the starting raw materials, these can be purchased from a vendor and received at a manufacturing site and can vary widely in nominal chemical and mineral compositions, purity, physical and chemical structure, particle size and price. These include ;

1. refined industrial minerals that have been beneficiated to remove mineral impurities to significantly increase the mineral purity and physical consistency. These are ball clay, bentonite, talc and wallastonite ;

2. high-tonnage industrial inorganic chemicals that have undergone significant chemical processing and refinement to significantly upgrade the chemical purity and improve the physical characteristics. This raw material is calcined alumina [Bayer Process].

The choice of a raw material for a particular product will depend on material cost, market factor, vendor services, technical processing considerations, and the ultimate performance requirements and market price of the finished product.

The selection for ceramic starting powders are dependent on the properties required in the finished component. Purity, particle size distribution, reactivity, and polymorphic form can all affect the final properties and thus must be considered from the outset.

1. Purity :- strongly influences high-temperature properties such as strength. The effect of the impurity is dependent on the chemistry of both the matrix material and the impurity. Impurities present as inclusions do not appreciably affect properties such as creep or oxidation, but do act as flaws that can concentrate stress and decrease component tensile strength. The effect on strength is dependent on the size of the

inclusion compared to the grain size of the ceramic and on the relative thermal expansion and elastic properties of the matrix and inclusion.

2. Particle size and reactivity :- Particle size distribution is important, depending on which consolidating or shaping technique is to be used. The objective of the consolidation step is to achieve maximum particle packing and uniformity, so that maximum shrinkage and retained porosity will result densification. A single particle size does not produce good packing. Optimum packing for particles all the same size result in over 30% void space. Adding particles of a size equivalent to the largest voids reduces the void content to 20%. Adding a third, still smaller particle size can reduce the pore volume to 23%. Therefore, to achieve a maximum particle packing, a range of particle sizes is required.

A controlled optimum particle size distribution is required to achieve maximum reproducible strength. The strength is controlled by flaws in the materials. A single particle which is significantly larger than the other particles in the distribution can become the critical flaw that limits the strength of the final component. Similarly, a large void resulting from a nonhomogeneous particle size distribution or from particle too close to the same size may not be eliminated during sintering and may become the strength-limiting flaw. Small particle size is important if high strength is the primary objective.

Another important aspect of starting powder is reactivity. The primary driving force for densification of a compacted powder at high temperature is the change in surface free energy. Very small particles have high surface free energy and thus have a strong thermodynamic drive to bond together. Very small particles can be compacted into a porous shape and sintered at high temperature to near theoretical density.

Particle size distribution and reactivity are also important in determining the temperature and the time at the temperature necessary to achieve sintering. Typically, the finer the powder and the greater its surface area, the lower are the temperature and time at temperature for densification. This can have an important effect on strength. Long times at temperature, result in increase grain growth and lower strength. To optimize strength, a powder that can be densified quickly with minimal grain growth is desired.

3. Polymorphic Form :- Many ceramics occur in different polymorphic forms. For most applications one polymorph is preferred. Before selecting a material for an application, it is necessary to verify that the material does not have an unacceptable transformation. A good first step is to check the phase equilibrium diagram for the composition. Even if more than one polymorph is present within the intended temperature range of the application, the material may be acceptable. The important criterion is that no abrupt volume changes occur. This can be determined by looking at the thermal expansion curve for the material.

### 2.3 Production Process of Ball Mill Liners :

Ceramic products are used in applications where the performance and reliability of the product must be predictable and assured that the product must be fabricated successfully in a productive manner. The manufacture of ball mill liners from a complex batch containing ceramic materials and processing additives into a finished product involves many operations. All of the materials and operations must be carefully controlled. Principles of science should be used in addition to empirical tests for understanding, improving, and controlling these liners' processing.

Alumina liners are made from alumina powders and in general the higher the purity of the powders, the finer the particle size and the smaller the particle size distribution, then the better the end product. There are however problems increase as particle size decreases. Agglomeration into clusters must be avoided , as this is likely to result in pores in the final structure that can totally destroy its strength. This is achieved with plasticizers and deflocculants that effectively make the powder into a viscous fluid. Other additives may include binders to improve green strength and sintering aids to help densification.

Because the shapes finally produced are hard and thus difficult and expensive to machine, it is important that the green ceramic is shaped so that the final part , after sintering , requires little or no machine. The main technique for consolidating alumina powders and forming shape is extrusion.

Sintering is the next stage of the fabrication process and its control is critical in that densification , recrystallization , and grain growth all occur in this. Grain growth inhibitors are used to produced a fully densified sintered

body with fine grain microstructure. As sintering progresses the density of the body increases linearly until it reaches saturation (zero water absorption). Densification during sintering results in linear shrinkage of about 20 %. While this can usually be taken into account in designing the green shape final machining by way of grinding or polishing is often necessary.

### 2.3.1 Ball Milling - Powder Sizing.

According to the fact that the particle size distribution is important in achieving the optimum properties in the final component. Raw materials are not usually available with the optimum particle size distribution. The further fabrication process for raw materials must be provided.

High mechanical strength in sintered alumina requires fine grain size of the heat-matured body. Since some grain growth occurs during sintering, the raw alumina must be still finer. Fine grain size, achieved by grinding massive particles to size, requires the expenditure of much energy.

The use of different types of grinding equipment alters the properties of the ground alumina.

Several different types of grinding equipment have become available during the last two decades for preparing ceramic materials in the finer sizes for forming operations. These include, among others, various types of fluid energy mills, vibrating ball mills (Sweco), and the Attritor. Improvements in conventional ball milling have also been realized with the development of high-alumina mill liners and grinding balls, rubber liners, air-swept mills, hydrocyclone classifiers, and other classifying means for removing the ground product from the sphere of action efficiently. The Stag mill is a ball mill

provided with peripheral slots to allow removal of the completely ground material from the mill. It should be advantageous in grinding massive alumina.

Each of these grinding devices has its advantages and disadvantages. The air classification systems are limited in their ability to separate finer particle sizes. The fluid energy mills generally produce narrow, less particle size distributions, devoid of extreme fines, and have poor efficiency in breaking up massive alumina such as the fused and tabular grades. The ground products have markedly different surface properties than the usual ball-milled products, as indicated by standard oil titrations. The Attritor may accomplish in a few minutes the same extent of grinding that requires hours of ball milling, but wear and contamination from the equipment, and power consumption may be high. It is also necessary to operate in a liquid suspension.

The desired particle size distribution usually cannot be achieved simply by screening, classifying or elutriating the raw material. More typically, a particle size reduction [comminution] step is required. Ball milling is one of the most widely used, to change the particle size distribution and disperse agglomerates in materials, for high-capacity grinding and when a wide size distribution or mixing and dispersion of agglomerates with a minimum of damage to particle is preferred.

Ceramic-grade alumina is usually wet-ground in conventional ball mills in present commercial operations.

Surface active agents such as Darvan may be added during ball milling to reduce changes in the viscosity of the slurry, and to allow use of the minimum amount of water. Pickup of contamination from mill and ball wear in bench-scale tests were found to be about ten times higher in wet ball-milling than in the



equivalent dry ball-milling in grinding reactive alumina. Slightly higher reactivity, found for the wet-milled product, is attributed to the pickup of finely divided impurities.

Bayered-process alumina consists of solid agglomerates rather than individual primary particles. Breaking down the agglomerates by grinding results in many advantages, including denser compacts, lower firing shrinkage, lower firing temperatures, lower tendency for lamination and warpage, and, most important of all, better fired microstructures. Grinding does not breakdown the individual primary particles but instead fractures the agglomerates to form a combination of individual or several individual primary particles.

Milling can be conducted either dry or wet. Dry milling has the advantage that the resulting powder does not have to be separated from a liquid. The major concern in dry milling is that the powder does not pack in the corners of the mill and avoid milling. The powder must be kept free flowing. One method of accomplishing this is to use a dry lubricant such as stearate. In some cases, humidity or moisture in the powder causes packing. This has been resolved through the use of a heated mill.

Wet milling is usually very efficient if the correct ratio of fluid to powder to milling media is used. The ratio varies for different materials and usually has to be optimized experimentally.

Milling produces a broad particle size distribution rather than a narrow particle size range as achieved by screening. Milling can readily reduce the average particle size to 5  $\mu\text{m}$ . or less. Besides producing the required particle size distribution, ball milling can also produce a very active powder that is easier to densify in later process steps. In some cases, that is achieved by an active surface condition. In other cases it appears to be achieved by increased strain energy in the particle.

### 2.3.2 Filtration.

Filtration is used in ceramic processing to concentrate particles from a suspension or slurry. The plate and frame filter press is common filtering device and a common practice is filtration at a constant rate followed by constant pressure filtration to minimize the initial loss of fine particles and maintain a constant liquid content.

### 2.3.3 Extrusion.

After filter pressing, the particle filter cakes are taken to the extrusion system where paddles or augers mix the feed materials and force it through a shredder into a vacuum chamber shredded materials that is small in cross section a more uniformly de-aired without surface drying. De-aired material is consolidated, mixed and extruded continuously using an auger and an extrusion die.

The extrusion of alumina, cold extrusion, processes tax the ability of the "nonplastic" single oxides to acquire plastic properties sufficient to flow and assume a continuous formed shape. The addition of small amounts of various organic plasticizers or of the plastic clay materials to ground Bayer alumina in the proper consistency with water is sufficient to allow auger extrusion.

### 2.3.4 Drying.

Drying is an important process in producing ceramic raw materials and shaped products ready for firing. During drying, heat is transported to the liquid in the body, and evaporated liquid is transported into the surrounding atmosphere. The drying rate depends on the temperature of the liquid in the body and the temperature, humidity, and flow rate of the drying air.

After initial heating, the product dries at a constant rate during which shrinkage commonly occurs. Transition to a decreasing drying rate occurs when the external surface of the product is incompletely covered with liquid. When the drying rate is very fast, or nonuniform, the constant rate period is relative short, and the differential shrinkage can cause cracks. Warping is produced by nonuniform drying when the body is shrinking and can deform plastically. Dried products are commonly hygroscopic and may readsorb moisture in proportion to the relative humidity of the atmosphere. Products that have been dried, called "green products".

#### 2.3.5 Firing Process

The green products are heat-treated in a kiln or furnace to develop the desired microstructure and properties. This process called "firing", may be considered to proceed in three stages ;

1. reaction preliminary to sintering, which include the elimination of gaseous products of decomposition and oxidation,
2. sintering and,
3. cooling.

Sintering may be defined as the consolidation, densification, recrystallization and bonding obtained by heating agglomerated powders during or following compaction at temperatures below the melting point of the principle component.

Alumina has been prepared in massive form by the process of sintering. It may appear as a single-oxide component or in combination with various ceramic oxides or other refractory materials, including metals. The composition may be substantially crystalline or may contain vitreous phases.

Several theoretical models have been proposed for the sintering process of alumina, representing condition in which no vitreous phase is present as well as condition involve vitreous phase. Surface tension has generally been considered a driving force of sintering whether the sinter consists of pure crystalline phases or include a liquid phase.

Three stages of sintering are usually considered ;

1. an initial period of neck growth between adjacent particles,
2. a stage of material transport of densification,
3. a final stage of grain growth with elimination of isolated voids.

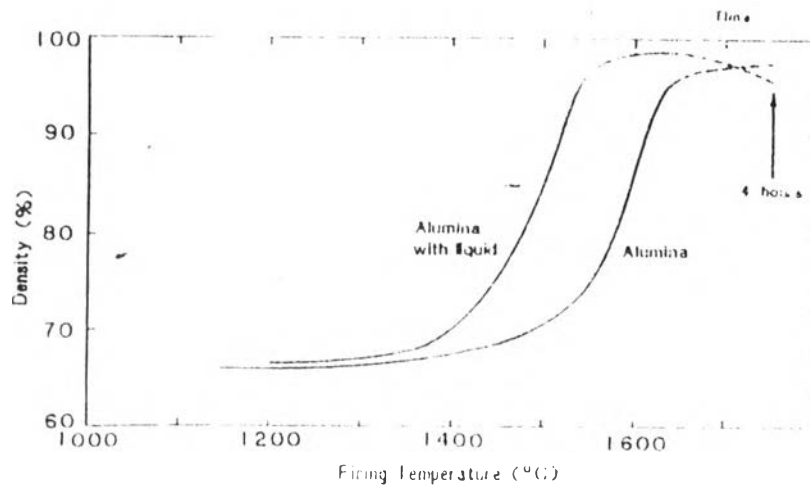
These are overlapping phenomena.

#### Sintering in the Presence of a Small Amount of a Liquid phase.

Liquid phase sintering initially requires that at least two solid powders are homogeneously mixed by dry or wet mixing techniques. The mixed powder is usually formed into a green compact of 50-65% relative density by various forming methods, for example, uniaxial dry pressing, cold isostatic pressing [CIP], slip casting, injection moulding. These green compact structures are best described as a random loose or dense packing. A liquid phase, typically 4 to 20% , is formed upon heating the mixed powder compact. While the mixture of solid particles and liquid sinters together, porosity of a powder compact gradually diminishes to form a dense ceramic part.

A drastic effect in sintering is the increase of grain-boundary diffusion and grain-boundary sliding by a liquid phase film coated each grains in the grain-boundaries. The small quantities of liquid phase can promote sintering, meaning high densities, see Fig. 3, in a short time at relative low temperatures with less of a tendency for exaggerated grain growth.

Fig.3 Comparative densification behavior of alumina powder with and without 5 wt.% of an alkaline earth aluminosilicate glass phase.

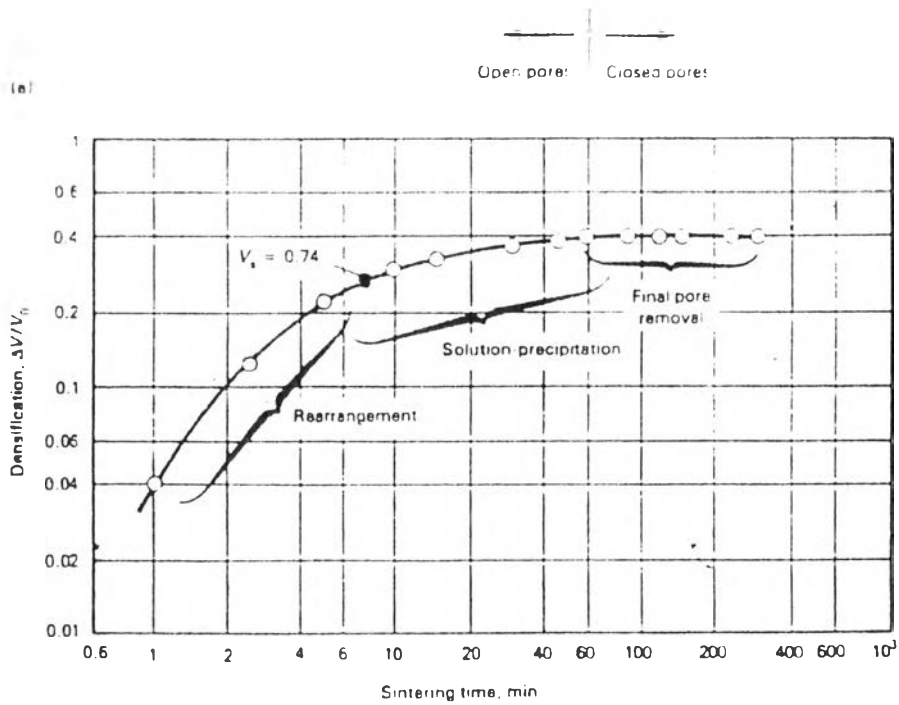
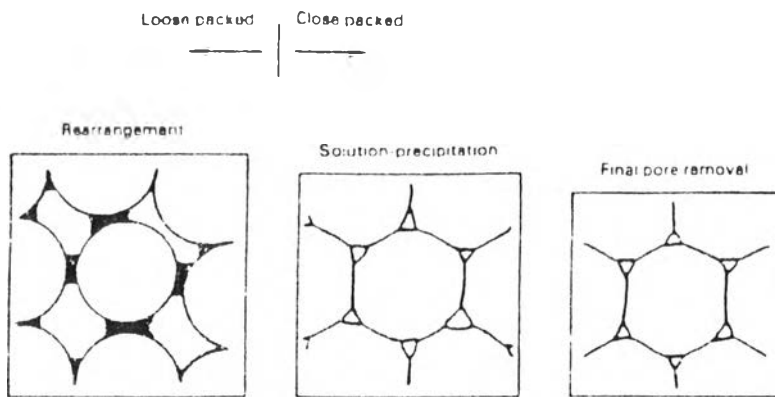


A liquid phase, especially when it wets the grain-boundaries, has also a large effect on the physical properties of the material. This high alumina liner, contains a calcium-magnesium-aluminosilicate glass phase. In sintering, the liquid draws the particles together, and angular particles may rotate, enabling sliding and rearrangement into a denser configuration. Pores surrounded by solid particles in contact. Liquid-phase-assisted sintering continues where there is some solubility of the solid, and a higher diffusivity in the liquid may increase the rate of mass transport and shrinkage. Sharp edges and small particles will preferentially dissolve, and diffusion through the liquid and crystallization in another region produce grain growth. A liquid phase that wets and dissolves the solid has been shown to rapidly penetrate between grains and disperse powder aggregates. This can reduce the tendency for exaggerated grain growth.

Also viscous flow at boundaries may aid densification by progressive changing from

- a) rearrangement, to
- b) solution precipitation, to
- c) final pore removal stage , as shown in Fig.4

Fig.4 Role of densification as a function of rearrangement, solution-precipitation and final pore removal.



During liquid phase sintering, a relative stable packing arrangement of the solid particles is established in the early stages of sintering by rearrangement of the particles. Further lowering of the free energy of the array may then occur by redistribution of the liquid which depends on the uniformity and density of packing of the particles.

Densification during liquid phase sintering is driven by the thermodynamic driving force to minimize interfacial free energy of the system. In general, the change in free energy  $\Delta G$  going from one configuration to another (see Fig. 4a) in a solid-liquid-vapor system is given by ;

$$\Delta G = A_{sv} \gamma_{sv} + A_{ss} \gamma_{ss} + A_{sl} \gamma_{sl} + A_{lv} \gamma_{lv}$$

where  $A_{sv}$ ,  $A_{ss}$ ,  $A_{sl}$ , and  $A_{lv}$  are changes in the various interfacial areas and  $\gamma_{sv}$ ,  $\gamma_{ss}$ ,  $\gamma_{sl}$ ,  $\gamma_{lv}$  are their corresponding interface energies (subscripts s, l, and v represent solid, liquid, and vapor respectively). If good wetting of the solid by a liquid as assumed, the values  $A_{sv}$  and  $A_{ss}$  are unimportant. Also when there is no grain growth,  $A_{sl}$  is negligible. Therefore,  $A_{lv}$  is the primary and the most important variable in determining the driving force for liquid phase sintering.

### Rearrangement

In the initial liquid phase sintering stage, a number of consecutive and simultaneous processes may occur including melting, wetting spreading and liquid redistribution. Both solid and liquid are subjected to rearrangement because of unbalanced capillary forces around solid particles as dictated by particle contact and liquid meniscus geometries that results in shearing and rotational movements of particles. Liquid films between particles act as a lubricant. The rearrangement of

particles proceeds in the direction of reducing porosity. As density increases, particles increasing resistance to further rearrangement due to crowding by neighbouring particles to form a closed packing structure.

The driving force of rearrangement arises because of an imbalance in capillary pressure as a result of:

- particle size distribution
- irregular particle shape
- local density fluctuation in the powder compact
- anisotropic material properties

If the geometry of the particle contact is known, the driving force for rearrangement can be calculated for various particle shape and contact geometries. This model is based on the theory that the viscous flow of a liquid sandwiched between solid particles limits the rearrangement process.

Assuming the Newtonian liquid, the deformation rate is proportional to shearing stress, so the densification rate is given by

$$\frac{d(\rho/\rho_0)}{dt} = \frac{A(g) \times \gamma_{ts}}{\eta \cdot r_s}$$

where,  $\rho$  = relative density

t = time

A(g) = geometric constant

$\gamma_{ts}$  = surface tension

$\eta$  = viscosity of liquid

$r_s$  = radius of solid particle.

The value of A(g) decreases with increasing volume fraction of solid and relative density.

The volume fraction of liquid is an important factor in determining the extent of rearrangement. At approximately 30-35 vol.% liquid, full densification can be achieved by rearrangement alone. Sintering behavior of powder compact with



excessive amount of liquid is quite different from liquid phase sintering. In contrast, rearrangement in solid sintering state, can be limited by the absence of liquid capillary and lubricating films between particles.

#### Solution-Precipitation

When rearrangement becomes insignificant, additional densification can be achieved by dissolution of the solid at grain contact, this resulting in the center to center approach of particle. The solubility is proportional to the normal traction at grain contact arising from the capillary forces (Laplacian forces) that draw the solid particle together.

The mass transfer results in contact-point flattening and corresponding shrinkage in the powder compact. The dissolution rate of the solid decreases as the contact area increases. Accordingly, the densification (shrinkage) rate decreases as the density of the powder compact increases. At the later stage of solution precipitation, the interconnected pore structures pinch off to form isolated (closed) pores.

The rate limiting process for solution precipitation is controlled by diffusion rate and reaction controlled of material transport which are strongly depended on  $r_s$ .

#### Pore Removal

During intermediate stage sintering, interconnected pore channels pinch off to form closed pores, the final stage of liquid phase sintering starts after pore closure. The closed pores usually contain gaseous species from sintering atmosphere, vaporized liquid, and decomposed solid.

Several processes can occur simultaneously during this final stage. (including growth and coalescence of grains and pores, dissolution of liquid into solid, phase transformation, and formation of reaction products between liquid and solid.)

#### Sintering Additives.

Additives other than temporary binders have been used in ceramic alumina compositions for several purposes. Among these purposes might be cited ; crystal growth repression, crystal growth acceleration, acceleration of sintering or shrinkage rate, reduction in maturing temperature, alteration in porosity, changes in physical and chemical properties, and removal of impurities.

Crystal growth in sintered alumina was early recognized as an unfavorable factor affecting strength and thermal shock resistance. It was found that mere fineness of the starting alumina is not sufficient to avoid excessive crystal growth. Crystal growth was repressed by  $\text{SiO}_2$ , and particularly  $\text{MgO}$ , if the sintering temperature was held below the point at which eutectics form with alumina. Magnesia, was considered the ideal additive for sintering aluminum oxide because its eutectic point is at  $1925^\circ\text{C}$ ., well above the practical sintering point of pure alumina.  $\text{MgO}$  added to alumina causes spinel formation at  $700^\circ\text{C}$ ., The spinel is not soluble in alumina, but dissolves up to 50 % [mole]  $\text{Al}_2\text{O}_3$  in solid solution at  $1700^\circ\text{C}$ . Silica and silicates, particularly the native clays, have been common additives to sintered alumina. Reactions between  $\text{SiO}_2$  and kaolinite and  $\text{Al}_2\text{O}_3$  at about  $1600^\circ\text{C}$ . may involve a glassy phase formed by diffusion of alumina into a quartz zone surrounding cristobalite particles, and additionally, mullite crystals may form in the alumina. The addition of magnesia inhibits grain growth during the sintering of alumina by maintaining a high

diffusion flux of vacancies from the pores to the grain boundaries, causing a decrease in grain boundary mobility. The main purpose of a growth repressor is to allow substantially complete sintering, approaching theoretical density before secondary or discontinuous crystallization has reached excessive limits. If secondary recrystallization has occurred and pores become trapped, the theoretical density cannot be obtained within a reasonable sintering time and temperature.