

Chapter 2

Literature review

2.1 Alumina

Alumina (Al_2O_3) has molecular weight of 101.94, specific gravity of 3.4-4.0. A material appears in several crystalline forms such as alpha, beta,..., of which alpha-alumina is the densest and the most stable⁽³⁾. Minerals containing alumina represent 15% of the earth's crust. It is therefore an abundant material and virtually inexhaustible, unlike raw materials for many alloys which are developed for special applications.

The structure of alumina oxide consists of close packed planes of the large oxygen ions stacked in the sequence A-B-A-B, thus forming a hexagonal close packed array of anions⁽²⁾. The cations are placed on the octahedral sites of this basic array and form another type of close packed plane, which are inserted between the oxygen layers. To maintain charge neutrality, however, only two thirds of the octahedral sites available are filled with cations.

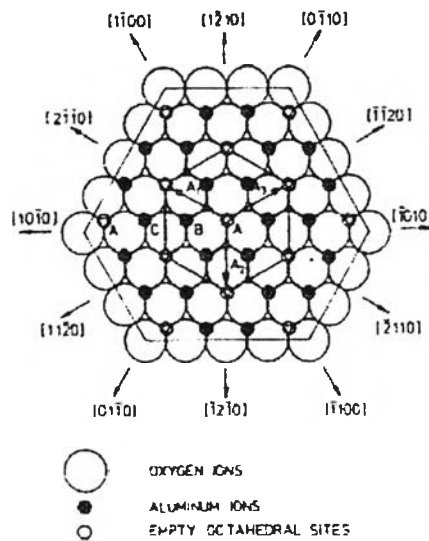


Fig.2.1 Packing of Al and O ions in the basal plane. The upper layer of O ions is not shown.

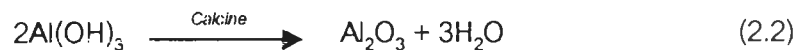
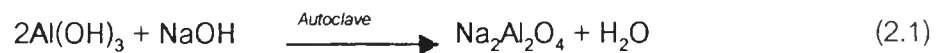
Fig 2.1 illustrates the packing of Al and O in the basal plane. Since the vacant octahedral sites also form a regular hexagonal array, three different types of cation layers can be defined, depending on the position of the vacant cation site within the layer, which may be named a, b, and c, and which are stacked in the sequence a-b-c-a-b-c. This gives the complete stacking sequence of anion and cation layers of the form A-a-B-b-A-c-B-a-A-b-B-c-A. It is only reproduced after the sixth oxygen layer, or after the sequence a-b-c is repeated twice. The unit cell defined in this way is called the crystallographic, or structural unit cell.

Many investigators have determined the several properties of alumina, both on single crystal and polycrystalline ceramics. The several properties of alumina is shown in Table 2.1⁽⁵⁾.

Table 2.1 Typical properties of alumina.

Properties	Value	
	Single crystal	Polycrystalline
Molecular weight (Al ₂ O ₃)	101.94	
Crystal structure	Rhombohedral $\frac{2}{3}$	
Melting point (°C)	2051.0 ± 9.7	
Boiling point (°C)	3530	
Electrical resistivity (ohm-cm)	1.0 × 10 ¹⁵	
Dielectric constant	12.3	
Dielectric strength (volt/mm)	27,500	
Thermal expansion, Linear (× 10 ⁻⁶ /°C)	5.51	6.03
Thermal conductivity (W/m K)	42	-
- dense	-	36.1
- 23.4 % porosity	-	23.1
- 48.7 % porosity	-	16.7
Bending strength : Modulus of Rupture (psi)	102,000	35,000-67,000
Compressive strength (psi)	443,000	560,000
Tensile strength (psi)	71,000	37,600
Hardness : Knoop (kg/mm ²)	3,000	
Poisson's Ratio (μ)	-	0.257

Alumina is one of the most widely used inorganic chemical for ceramics and is produced worldwide for the aluminum and ceramic industries using Bayer process. The Bayer process, in particular the wet alkaline process, is the principal production method in use today which is the most suitable for low silica bauxite. The dried, ground bauxite is digested in an autoclave with a solution of sodium hydroxide and sodium carbonate, contains starch as a flocculant and lime added to causticize the soda and to act as a filter aid. The solution is required a stable supersaturated against auto precipitation at temperature 105°C. After digestion, the suspension is cooled and the waste solids (red mud) are separated by sedimentation and filtration. The clarified solution is cooled to about 55 °C and a portion of dissolved alumina is precipitated by introducing fine seed alumina trihydrate. The precipitated trihydrate is separated from the solution, washed and calcined to form the alumina powder. The reactions are



The combination of high thermal conductivity, and high compressive strength leads to good thermal shock resistance, so alumina is suited for furnace use as crucibles, tubes and thermocouple sheaths. High purity alumina has high refractoriness and can be used up to 1700°C. Alumina also shows good electrical insulation property at high temperatures, good wear resistance and hardness, making it suitable for components such as ball valves, piston pumps and deep drawing tools. There are several applications of alumina shown in Appendix 1⁽⁴⁾.

2.2 Sintering of alumina

The fundamental characteristics of sintering phenomena of materials were classified into 3 stages that are initial, intermediate and final stage respectively.

The classification of sintering into three stages is generally accepted today. Sintering phenomena in material consists of the dominant mechanism by which matter transport occurs⁽⁶⁾. The sintering phenomena of Al_2O_3 is solid state sintering. The driving force of sintering in the solid state has early been recognized to be the surface tension. The kinetics of the process, however; may be controlled during the initial stage of sintering by diffusion processes, which defines different paths for matter transport.

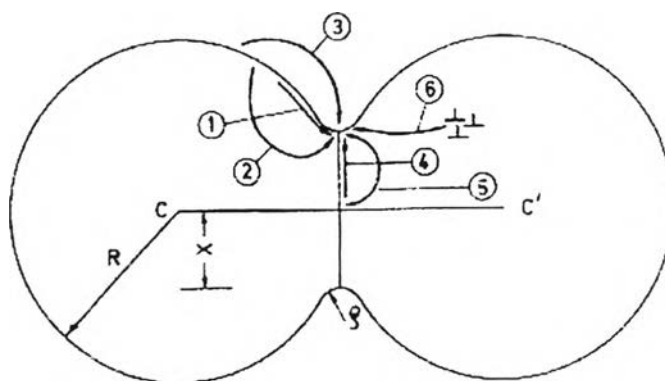


Fig.2.2 Schematic of the geometry of sintering of two spheres, showing six alternate paths for matter transport⁽⁷⁾.

Fig 2.2 shows the typical sintering geometry between two powder particles according to Kingery and Berg⁽⁷⁾. According to Ashby⁽⁸⁾, there are six paths for matter transport as following

- (1) surface diffusion,
- (2) lattice diffusion from the surface region,
- (3) vapor transport,
- (4) boundary diffusion,
- (5) lattice diffusion from boundary region, and
- (6) lattice diffusion from dislocations or other internal sources to the neck surface.

The growth of the neck on the initial sintering of alumina is formed between a sphere and a plate as a function of time and sphere radius. The shrinkage of powder compacts is a function of time at various temperatures⁽⁹⁾. The initial stage is characterized by the neck growth between the original powder particles and a slight increase in density of about 10%. The kinetics and size dependence of the sintering of alumina follow the sintering model⁽⁷⁾. This model is based on the assumptions that the driving force for solid state sintering is the surface tension, the dominant transport mechanism is lattice diffusion, and the grain boundaries operate as vacancy sinks. The later stages of sintering are decisive for the final density of the product. The beginning of the immediate stage coincides with the beginning of grain growth. During this stage, particles grow to a grain-like structure, the pore phase forming an array of interconnected cylindrical channels lying on three-grain edges. The final stage starts at about 95% porosity, when cylindrical pores are transformed into spherical voids by a pinch-off process. The pore phase is now present as discontinuous pores lying at four-grain corners⁽¹⁰⁾.

During sintering of intermediate and final-stage sintering kinetics in alumina, the porosity decreased linearly with the logarithm of time. The necessary condition to achieve theoretical density in solid stage sintering consists of eliminating or suppressing the occurrence of discontinuous grain growth⁽⁶⁾. Grain boundaries will remain attached to the pores and the normal grain growth will be sufficiently slow that the pores can move off the grain boundaries and do not become trapped inside the grains. Since the pore phase remains intersected by the boundaries, the diffusion path is short and facilitates the complete removal of porosity.

2.3 Influence of additives

Alumina can be sintered to theoretical density⁽¹¹⁾, it has been known that additives may have a beneficial influence on the sintering kinetic of alumina.

2.3.1 Effect of MgO

Magnesium oxide is the most widely used additive in the sintering of alumina. Adding small amount of MgO will prevent discontinuous grain growth and allow the material to be sintered to theoretical or nearly theoretical density⁽¹¹⁾. Discontinuous grain growth means that grain boundaries break away from the pores, thereby including the pores inside the new large grains^(11,12).

Several experimental studies demonstrate that alumina may be sintered to theoretical density using MgO additions even below the solubility limit.

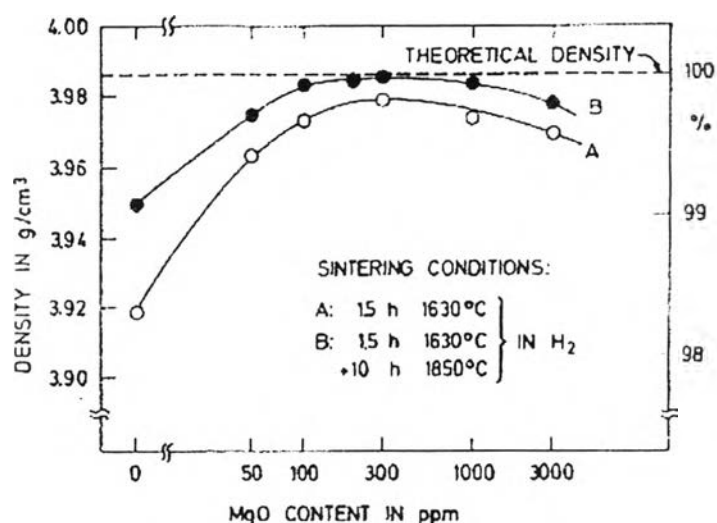


Fig.2.3 Effect of MgO content on the density of sintered alumina.

Fig 2.3 show the density results from the work of Peelen⁽¹³⁾, who sintered specimens containing between 0 and 3000 ppm MgO. A maximum density was found at 300 ppm MgO, which is just the solubility limit reported⁽¹⁴⁾ at the sintering temperature of 1630 °C. This result is evidence that the densification rate in the absence of discontinuous grain growth is controlled by the solute concentration.

The beneficial effect of the MgO additive is due to the increase of the densification rate (pore removal rate) with respect to the grain growth rate. In the other words, the ratio of the pore mobility to the grain boundary mobility, M_p/M_b , must exceed a certain value. An increase in the pore mobility will favor the increase of the mobility ratio^(15,16).

In the case of pore movement due to surface diffusion, the pore mobility is given by the expression⁽¹⁷⁾.

$$M_p = KD_s/r^4 \quad (2.3)$$

Where D_s is the surface diffusion coefficient,

r is the pore radius, and

K is a constant.

The sintered product of MgO-doped alumina sample will have a smaller pore size compared to a sample made of pure alumina because the presence of the dopant increases the rate of pore removal. Therefore, the doped material will also be characterized by a greater pore mobility which is simply due to the size effect given by equation (2.3), and hence will show a decrease or retard tendency for discontinuous grain growth⁽¹⁶⁾.

2.3.2 Effect of ZrO₂

Grain growth inhibition is desirable 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. Second-phase inclusions can inhibit grain growth. Theory that treats the inhibition of grain growth by inclusion has generally been on refinements of Zener's original concept⁽³⁴⁾, 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. Ashby and Centamore⁽³⁴⁾ showed that the inclusion could move with the junction if the inclusion exhibits sufficient self-diffusion. Theory suggests that the velocity of the moving inclusion will depend on its radius r as either r^3 or r^4 , for interfacial diffusion or volume diffusion, respectively.

Lange and Hirlinger⁽³⁴⁾ reported that the materials containing ≤ 2.5 vol% ZrO₂ were strongly bimodal at temperature ≥ 1600 °C, whereas grain growth control (normal grain growth) was achieved for ZrO₂ contents ≥ 5 vol%. Microstructure of composites exhibited controlled grain growth (≥ 5 vol% ZrO₂). Fracture surface observations showed that the ZrO₂ grains were primarily located at 4-grain junctions.

Abnormal grain growth occurred when the inclusion distribution was not sufficiently uniform to hinder the growth of all Al₂O₃ grains. This condition was observed for compositions containing ≤ 2.5 vol% ZrO₂, 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 ZrO₂ inclusion, viz., for compositions containing ≥ 5 vol% ZrO₂. For this condition, the grain size was inversely proportional to the volume fraction of the inclusions.

2.3.3 Effect of SiO₂, SiO₂-CaO etc.

Commercial Al₂O₃ ceramics shown in Appendix 2 usually contain SiO₂ or SiO₂-CaO or SiO₂-CaO-MgO plus small amount of alkaline oxides to lower the sintering temperature. In the SiO₂ doped materials, an aluminosilicate glassy phase is formed at triple junctions and at almost all of the grain boundaries.

As a result of the glassy phase in the grain boundary, thermal conductivity decreases with the increase of additives as shown in Fig.2.5. The SiO₂ doped material also exhibits an equiaxed microstructure but with a smaller average grain size⁽²⁸⁾. The sintered density generally increases as the SiO₂ content in the chemical composition decreases⁽²⁹⁾. SiO₂ strongly inhibits large grain growth and retards sintering slightly⁽³⁰⁾. In α -Al₂O₃ containing SiO₂-CaO, the presence of an amorphous phase at grain boundaries has been shown to cause faceting. When adding SiO₂-CaO, calcium aluminosilicate liquid phase favor discontinuous grain growth in alumina with some faceted interface.

In this experiment, our objective is to get alumina ceramics with better thermal conductivity using sintering aid. From above mentioned facts, we decided not to use SiO₂, CaO and other alkaline oxides as sintering additives.

2.4 Thermal conductivity of ceramic materials

2.4.1 Thermal Conduction Mechanism

The conduction of heat determines the heat flow through solids for a given temperature gradient, or determines the temperature gradient obtained when a fixed heat flow is employed⁽¹⁹⁾. The relationship between the heat flux and temperature gradient $\frac{\partial T}{\partial X}$ can be expressed by Equation (2.7).

$$\frac{\partial Q}{\partial t} = \kappa A \frac{\partial T}{\partial x} \quad (2.7)$$

where $\frac{\partial Q}{\partial t}$ is the heat transferred per unit time across a plane of area A normal to the flow of the thermal energy; and κ is a material property (equivalent to diffusivity) that describes the ability of a material to transport heat.

The thermal conduction mechanism is involved with physical phenomena. The thermal energy is transported by lattice vibration (phonons), free electrons and by radiation (photons). Unlike metal, the thermal conduction mechanism in ceramic is dominated by phonon mechanism due to the low concentration of free electrons. The heat does not simply enter one end of the sample and proceed directly in a straight path to the other end but diffuse through the sample, suffering random collisions and results in deflection or scattering. This explains why we used temperature gradient instead of the temperature difference between two ends regardless of the length of sample in Equation (2.7)⁽²¹⁾. When a small region of material is heated, atoms in that region will have large amplitudes of vibration. The vibrating energy will pass from one atom to another. Consequently, the atoms interaction caused by the application of heat propagates outward in a wavelike form. The scattering or deflection of this wave in a material is a result of defects, grain boundaries, pores or complexity of crystal structure.

The thermal conductivity can be expressed by equation (2.8), which is analogous to the electrical conductivity equation.

$$\kappa = (\text{Constant}) (N\lambda v) \quad (2.8)$$

where λ is the average distance that the disturbance travels before scattering or referred as the mean free path, N is the number of thermal energy carried, v is the average velocity.

The intrinsic thermal conductivity $\kappa_{\text{Intrinsic}}$ of nonmetallic solids in the temperature range $T \geq \theta_D$ can be described by Equation 2.9.

$$\kappa_{\text{Intrinsic}} = BM\delta\theta_D^3/(\gamma T^2) \quad (2.9)$$

where B is a constant, $\kappa_{\text{Intrinsic}}$ Intrinsic Thermal Conductivity, θ_D Debye Temperature, M Average mass, δ Average volume occupied by one atom, γ Gruneisen's Constant and T is the absolute temperature. Some of intrinsic thermal conductivity of nonmetallic materials are shown in Table 2.2.

Table 2.2 Value of intrinsic thermal conductivity of nonmetallic materials.⁽¹⁹⁾

Crystal	$\kappa_{\text{Intrinsic}}$ W/(m.K)	θ_D (K)	M (g)	δ (10^{-10} m)	γ	$M\delta\theta_D^3$ ($\text{gmK}^3 \times 10^4$)
Diamond	2000	2240	12.0	1.78	1.3	23.8
BN	760	1900	12.4	1.81		15.4
SiC	540	1080	20.1	2.18	0.76	5.5
BeO	370	1280	12.5	1.90		5.0
BP	360	985	20.9	2.27		4.5
AlN	320	950	20.5	2.18	0.77	3.8
Si ₃ N ₄	320	1100	20.0	2.18	0.72	5.8

Approximate values for thermal conductivities κ for a number of ceramics are collected in Table 2.3. The microstructure, atomic structure, second component and porosity have significant effect on the thermal conductivity. In order to have high thermal conductivity, the phonon scattering should be minimized. In the open, highly ordered structures made of atoms with similar size and mass has less phonon scattering, therefore lead to an increase in the thermal conductivity κ . For example diamond has one of the highest values of κ . Besides diamond, SiC, BeO and AlN also have high thermal conductivity.

Table 2.3 Approximate values for thermal conductivities of selected ceramic.

Material⁽²⁰⁾

Material	κ (W/m.K)	Material	κ (W/m.K)
Al ₂ O ₃	30.0-35.0	Si ₃ N ₄	25.0
AlN	200.0-280.0	Spinel (MgAl ₂ O ₄)	12.0
BeO	63.0-216.0	Soda-Lime-Silicate Glass	1.7
MgO	37.0	TiB ₂	40.0
PSZ	2.0	Ti ₃ SiC ₂	43.0
SiC	84.0-93.0	Cordierite (Mg-aluminosilicate)	4.0
SiAlON	21.0	Glasses	0.6-1.5
SiO ₂	1.4	Forsterite	3.0

As seen in Table 2.2 and 2.3, AlN, BeO and SiC have high values of thermal conductivity. AlN is chemically unstable, oxides even at room temperature. BeO and BP are toxic, SiC is not electrical insulator. TiB₂ and Ti₃SiC₂ are very expensive. Therefore, Si₃N₄ and Al₂O₃ rationally becomes potential candidate for Peltier element due to their moderate thermal conductivity, chemical stability, non-toxic. Si₃N₄ has higher cost than Al₂O₃. Finally Al₂O₃ becomes most potential candidate for Peltier element due to its properties and low cost.

2.4.2 Thermal Conductivity of Al_2O_3

Kingery (1954) investigated in the thermal conductivity of single crystal and polycrystalline samples. He found that the thermal conductivity was identical at temperatures below 1200°C . At higher temperatures, the thermal conductivity value of single crystal depart from the polycrystalline sample as shown in Figure 2.4⁽¹⁹⁾.

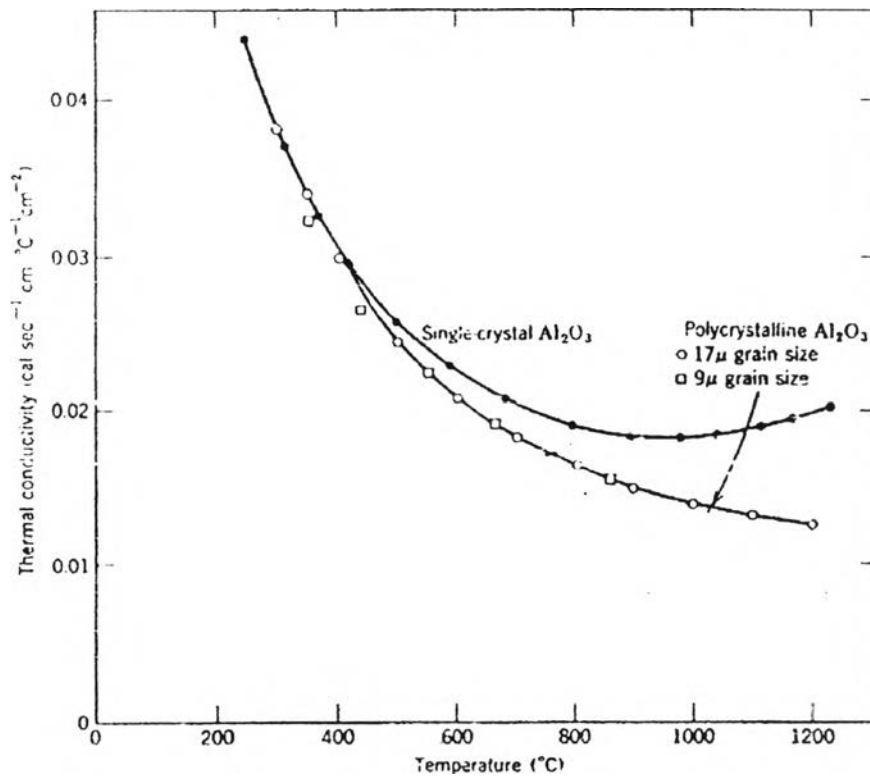


Fig. 2.4 Thermal conductivity of some ceramics as a function of temperature.

Selected data of thermal conductivity of the commercial alumina ceramics have been collected in Appendix 2, and Fig 2.5. As shown in Fig.2.5, Thermal conductivity of alumina ceramics is related to the content of Al_2O_3 . Thermal conductivity of alumina is higher at high purity. AISIN uses 96% purity alumina and that has thermal conductivity of $24 \text{ W/m}\cdot\text{K}$. While thermal conductivity of single crystal Al_2O_3 is about $40 \text{ W/m}\cdot\text{K}$. There is a possibility to improve thermal conductivity of Al_2O_3 substrate by very high purity using alumina powder.

