# CHAPTER II

THEORY AND LITERATURE REVIEWS

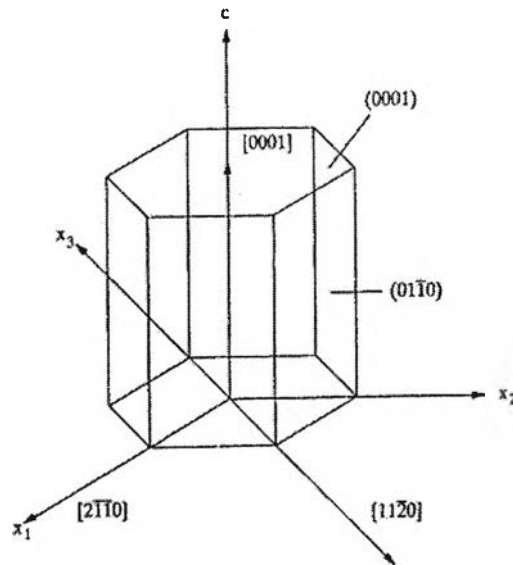## 2.1 CRYSTAL STRUCTURE OF ALUMINA

2.1.1 Alpha-alumina

Alpha-alumina (α-Al_2O_3) is a thermodynamically-stable phase of alumina. It has a hexagonal close packed structure with aluminum ions at the octahedral interstitial sites. Each aluminum ion is surrounded by six equidistant oxygen ions. Figure 2.1 shows the hexagonal close packed structure of α-alumina. The A and B layers contain oxygen ions while the C layers contain aluminum ions and vacant sites. It should be noted that two-third of sites in the layers indicated as C1 and C2 are occupied by aluminum ions while one-third are vacancies. Figure 2.2 shows common basal and prismatic planes in a hexagonal structure of α-alumina. For alumina, at temperature below 1000°C, slip can occur on these two slip planes.
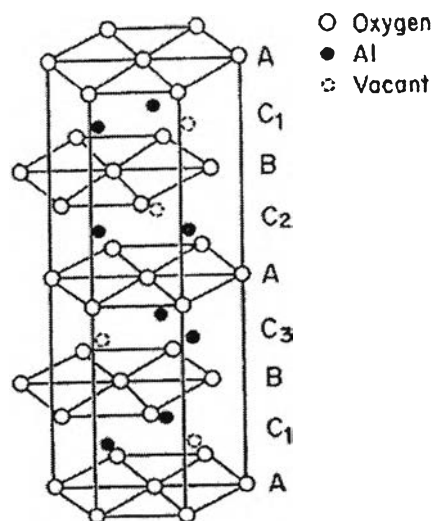
Figure 2.1 The hexagonal close-packed structure of α-alumina [Chawla 1998].

Figure 2.2 Basal (0001) and prismatic (01 10) phases in a hexagonal structure of α-alumina [Chawla 1998].

2.1.2 Boehmite

Boehmite is the major constituent of many bauxite minerals. It can also be synthesized in the laboratory, for instance, by neutralizing aluminum salts at temperature over $80^{\circ}C$ by treating activated aluminum with hydrothermal reaction. The boehmite crystal structure consists of the cubic packed oxygen ions with the aluminum cations sandwiched between adjacent layers. The distribution of hydrogen atom results in an orthorhombic unite cell that has been described by the *Cmcm* space group. The lattice parameters of boehmite are a = 2.861 Å, and c = 12.233 Å [Corbalo et al. 1985].

In addition to the stoichiometric crystal structure described above, the name of boehmite has been used to describe the product of aging aluminum hydroxide gel, better referred as pseudoboehmite or gelatinous boehmite [Wefers and Misra 1987]. A pseudoboehmite typically contains 15% excess water comparing to the stoichiometric composition AlOOH. Controversy continues concerning the exact location of the excess water in this structure. In boehmite, Al atoms are surrounded by a distorted octahedral group of O atoms, which are linked together to form a complex layer structure. Van Oosterhout [Oosterhout 1960] reported an easy method to describe the structure for the aluminum compounds as well.

2.1.3 Phase transformation

Alumina can exist in many metastable phases before transforming to the stable α-alumina (corundum form). There are six principal metastable phases of alumina designated by the Greek letters chi (χ), kappa (κ), eta (η), theta (θ), delta (δ), and gamma (γ), respectively. Although the range of temperature in which each transition phase is thermodynamically stable has been reported by many researchers, it depends upon various factors such as degree of crystallinity of sample, amount of impurities in the starting materials, and thermal history of sample. Most of the studies on phase transformation of alumina were conducted by calcinations of alumina precursor. It was found that difference in the phase transformation sequence is resulted from the difference in the precursor structure [Lippens and Boer 1964; Wilson 1979]. Moreover, the transformation sequence is irreversible. The nature of the product obtained by calcination depends on the starting hydroxide and on the calcination condition.
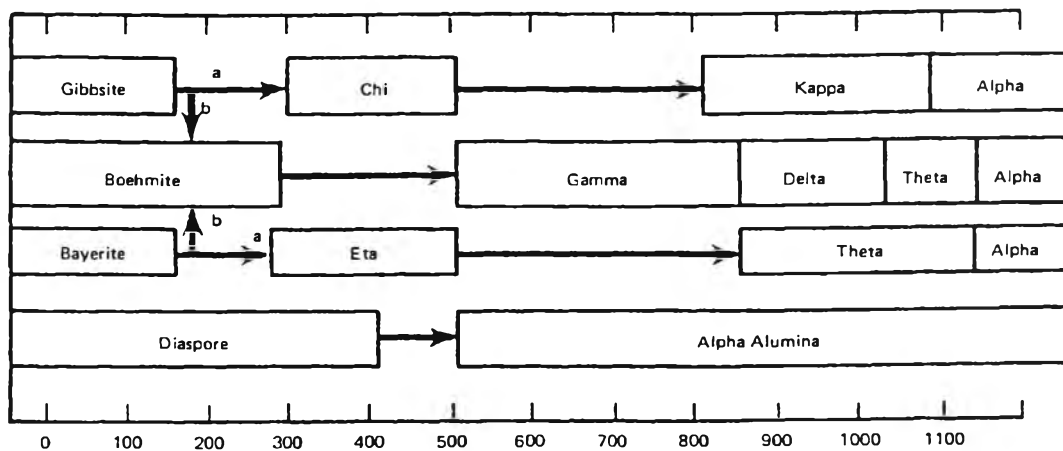
Figure 2.3 Transformation sequence of aluminum hydroxides [Gitzen 1970].

The phase transformation sequence normally starts with aluminum hydroxide ($Al(OH)_3$ and $AlOOH$) transforming to low-temperature phase of alumina (η and χ) at temperature around 150-500°C, and subsequently to high temperature phase (δ, θ, κ) at temperature around 650-1000°C. Finally, the thermodynamically stable phase, α-alumina, is formed at temperature around 1100-1200°C. It is generally believed that α-phase transformation takes place through the nucleation and growth mechanism.

Normally, transition alumina start to lose their surface area even at temperature below 800°C due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000°C when the crystallization to the thermodynamically stable α-alumina occurs [Dynys and Halloran 1982].

Several studies have been carried out on the direct phase transformation of alumina. The mechanism of direct phase transformation and the direct phase transformation from γ-alumina to α-alumina involving the conversion of the cubic close packing of oxygen ions into a stable hexagonal close packing which have been examined [Simpson et al. 1998; Levin and Brandon 1998]. Morinaga et al. studied the phase transformation that occurred during the thermal decomposition of ammonium aluminum carbonate hydroxide into α-alumina. Amorphous, γ-, θ-alumina were identified as intermediate products [Morinaga et al. 2000]. They have found that the atmosphere affects the grain size distribution of the final α-alumina particles

2.2 SOL-GEL PROCESS

2.2.1 Fundamental of sol-gel processing

Colloid is a system of two-phase suspension, in which the dispersed phase is so small that gravitational force is negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges. The inertia of the dispersed phase is small enough that it exhibits Brownian motion, a random walk driven by momentum imparted by collision with molecules of the suspending medium. Sol is the colloidal suspension of solid particles in the liquid. In sol-gel process, precursors (starting compounds) for preparation of the colloid consist of a metal or metalloid element surrounded by various ligands (appendages not including another metal or metalloid atom). For example, common precursors for sol-gel synthesis of alumina include inorganic salts such as $Al(NO_3)_3$ and organic compounds such as $Al(OC_4H_9)_3$. The latter is an example of alkoxides, a class of precursors most widely used in sol-gel research [Brinker and Scherer 1990].

Sol-gel techniques have been long known for the preparation of metal oxides and have been described in several books and reviews. The process is typically used to prepare metal oxides via the hydrolysis of metal reactive precursors, usually alkoxides in an alcohol solution, resulting in the corresponding hydroxide. Condensation of the hydroxide molecules by giving off water leads to the formation of a network of metal hydroxide. When all hydroxide species are linked into network-like structure, gelation is achieved and a gel is obtained. The gel is a polymer of three-dimensional skeleton surrounding interconnected pores. Removal of the solvents and appropriate drying of the gel results in an ultrafine powder of the metal hydroxide. Further heat treatment of the hydroxide leads to the corresponding ultrafine powder of the metal oxide. Because the process starts with nanosized units and the reactions undergo in the nanometered scale, it results in nanometered materials.

The chemical and physical properties of the product from sol-gel process are primarily determined by the hydrolysis and drying steps. Hydrolysis of metal alkoxides ($M(OR)_z$) involves nucleophilic reaction with water as follows:

$$M(OR)_y + xH_2O \leftrightarrow M(OR)_{y-x}(OH) + xROH \qquad (2.1)$$
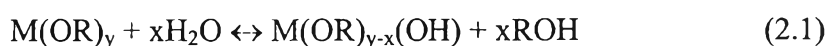
The mechanism of this reaction involves the addition of a negatively charged $HO^{\delta-}$ group to the positively charged metal center ($M^{\delta+}$). The positively charged proton is then transferred to an alkoxy group followed by the removal of ROH. Slow and controlled hydrolysis typically leads to small particles with unique properties. The hydrolysis and condensation rates depend on the electronegativity of the metal atom, the alkoxy group, solvent system, and the molecular structure of the metal alkoxides. Metals with higher electronegativities undergo hydrolysis more slowly than those with lower electronegativities. The sensitivity of metal alkoxides toward hydrolysis decreases as size of the OR group increases. Small OR groups lead to high reactivity of the corresponding alkoxide toward water. However, in some cases, high reactivity may result in uncontrolled precipitation of the hydroxide.

The rate of hydrolysis also becomes slower as the coordination number around the metal center in the alkoxide increases. Therefore, alkoxides that tend to form oligomers usually show slower rate of hydrolysis, and hence, are easier to control and handle. n-Butoxide is often preferred as a precursor for the synthesis of various oxides, including Al_2O_3, because it is the largest alkoxy group that does not prevent oligomerization.

Careful handling in dry atmospheres is required to avoid rapid hydrolysis and uncontrolled precipitation because most metal alkoxides are highly reactive toward water. For alkoxides with low rate of hydrolysis, acid or base catalysts can be used to enhance the process. The relatively negative alkoxides are protonated by acids creating a better leaving group and eliminating the need for proton transfer in the transition state. Alternatively, bases provide better nucleophiles (OH⁻) for hydrolysis. However, deprotonation of metal hydroxide groups enhances the condensation rate.

Developments in the area of solvent removal and drying facilitate the production of nanoscaled metal oxides with novel properties. When drying is achieved by evaporation under normal condition, the gel network shrinks as a result of capillary pressure inside the pores and the hydroxide product obtained is referred to as xerogel. However, if supercritical drying is applied, the shrinkage of the gel network is reduced, since there is neither capillary pressure nor liquid-vapor interface within the pores during drying. Consequently, the pore structure remains largely intact. The hydroxide product obtained in this manner is referred to as an aerogel.

Sol-gel processes have several advantages over other techniques for the synthesis of nanoscaled metal oxides. Because the process begins with a relatively homogenous mixture, the resulting product is a uniform ultrafine porous powder [Schwarz 2004].

2.2.2 Alumina synthesis via sol-gel process

Alumina can be prepared by sol-gel method. Yoldas has proposed a method to prepare alumina sol by using aluminum alkoxides, $Al(OR)_3$, as precursors [Yoldas 1984]. The sol was later used in the process of making monolithic alumina, which

involved four basic steps: 1) Hydrolysis of aluminum alkoxides, 2) Peptization of the hydroxide to a clear sol, 3) Gel formation, 4) Pyrolysis to alumina [Yoldas 1984]. This process employs acid and it has been found that the acid used must meet two general requirements. First, it must have noncomplexing anion with aluminum. Second, it must have sufficient strength to produce the required charge effect at low concentration.

Kobayashi et. al. have reviewed on alumina films preparation by sol-gel method [Kobayashi et al. 2005]. In this review, they introduced various applications for coating of alumina film on substrate, e.g. gas separations, magnetism, catalysis, thin-film laser emission, hole-burning, nonlinear optics and high quality luminescence. Alumina films were prepared from alkoxide or inorganic salt. The synthesized films were amorphous and highly transparent in the range of visible light. The films also exhibited gas separation ability, good coating properties and possibility for hybridizing with organic polymer.

Suzuki and Onozato investigated a formation of poly(vinyl alcohol) (PVA)/alumina gel composite [Suzuki and Onozato 1990]. Alumina sol was prepared from aluminium isopropoxide. The alkoxide was hydrolyzed and the resultant hydrate was peptized to a clear sol with acetic acid. The effects of dispersed alumina on the sorption of water and mechanical properties of composite were examined. The results showed that alumina mixed homogenously with PVA. The residue obtained after calcination to remove PVA at 600°C remained in its original form and transparency.

Kolaczkowski and Kim produced new structure of alumina via sol-gel method [Kolaczkowski and Kim 2006]. A method has been devised such that alumina can be formed into layer of thin leaf-like structure. In this process, alumina was prepared from aluminium iso-propoxide via sol-gel technique. The obtained gel was freeze-dried and finally calcined. It was found that the product would readily act as a support, e.g., for a catalyst, or adsorbents, or act as a membrane filter.

2.3 ELECTROSPINNING

Electrospinning is a technique to fabricate well-defined nanofibers with diameter down to a few nanometers for many polymers [Huang et al. 2003]. Yet broad range of parameters seems to influence fiber formation and it is sometimes observed that electrospinning results in beaded fibers, i.e. fibers in combination with droplets, rather than uniform fibers. This technique is firstly developed to produce polymer nanofibers, but it has been later applied for various materials.

There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process, high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution in the jet evaporates or he melt solidifies, and they are collected as an interconnected web of small fibers. One electrode is placed into the spinning solution/melt and the other attached to the collector. In most cases, the collector is simply grounded. The electric field is subjected to the end of the capillary tube that contains the spinning fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension.

A characteristic feature of the electrospinning process is the rapid evaporation of the solvent in the case of solution spinning or the rapid temperature decrease in the case of electrospinning from the melt. Thus, structure of the fibers is formed within very short period of time. The nucleation of crystals within the fiber should therefore occur rapidly. The second important feature is the strong deformation taking place during the whipping mode, which should give rise to orientational process within the fibers [Schwarz 2004].

2.3.1 Parameters affecting fiber formation

In electrospinning, when high voltage is applied, the charge transport occurs mainly due to the flow of the polymer jet towards the collector. The increase or decrease in the current is attributed to the mass flow of the polymer from the nozzle tip. Deitzel et al. found that the change in the spinning current is correlated with the formation of bed defects in the fibers [Deitzel et al. 2001]. They experimentally showed that an increase in applied voltage causes a change in the shape of the jet initiating point, and hence the structure and morphology of fibers.

Structure and morphology of electrospun fibers is easily affected by the nozzle to collector distance because of their dependence on the deposition time, evaporation rate, and whipping or instability interval. Buchko et al. examined the morphological changes in Silk-Like Polymer with Fibronectin functionality (SLPF) and nylon electrospun fibers with variations in the distance between the nozzle and the collector screen. They showed that, regardless of the concentration of the solution, short nozzle-to-collector distance resulted in wet fibers and beaded structures. SLPF fiber morphology changed from round to flat shape with a decrease in the nozzle-to-collector distance from 2 cm to 0.5 cm [Buchkoa et al. 1999]. This result shows the effect of the nozzle-to-collector distance on fiber morphology. The work also showed that aqueous polymer solutions required greater distance for the formation of dry fiber formation than systems that used highly volatile organic solvents [Buchkoa et al. 1999].

Concentration of the spinning solution determines the limiting boundaries for the formation of electrospun fibers due to variations in the viscosity and surface tension. The solution with low concentration forms droplets due to the influence of surface tension, while higher concentration prohibits fiber formation due to higher viscosity. Previously published literatures have documented the difficulties in the electrospinning of polymers like poly(ethylene oxide) in certain concentration levels [Deitzel et al. 2001].

Fong et al. investigated the formation of the beaded nanofibers and reported that the cause for such morphology was the capillary breakup of the electrospinning

jets by surface tension, altered by the presence of electrical forces [Fong et al. 1999]. The surface tension and viscoelastic properties of the polymer solution were the key parameters in the process.

2.3.2 Applications of electrospun nanofibers

Electrospun nanofibers offer great potential for wide range of applications such as in the fields of specialty filters, tissue engineering, reinforcement, sensors, catalysis, and templating. Presently, most patents on electrospinning are focused on applications rather that on new materials or on new processes. Commercialized applications were accomplished by several companies worldwide in specialty filters with an increasing market in the coming years. Another unique application of electrospun nanofibers is their use as templates for the preparation of other nano-objects. Coating of electrospun nanofibers with various materials and subsequent removal of the core template fibers generates a whole set of nanotubes of different sizes and materials combinations, which has by far not been exploited [Schwarz 2004].

2.3.3 Alumina nanofibers via electrospinning

The idea of incorporating nanoscaled fillers into polymer solution to form electrospun composite nanofibers has been extended to prepare organic-inorganic composite materials via electrospinning. A number of research groups have tried to produce such nanofibers in recent years, for instance, polyurethane [Demir et al. 2002], poly(ethylene-co-vinyl alcohol) [Kenaw et al. 2003], poly(vinyl alcohol)/silica [Shao et al. 2003], and polyacronitrile/Ag [Yang et al. 2003].

Dai et al. have prepared alumina-borate/PVA composite fibers via sol-gel processing and the electrospinning technique [Dai et al. 2002]. The results indicated that $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$ formed during the calcination at 1000-1200°C and decomposed above 1400°C. The stable crystalline phase of α-Al_2O_3 formed at 1400°C. At the same time, the SEM micrograph showed that grain size of the fibers remained small upto 1000°C but increased drastically at 1200°C.

Azad produced transparent alumina nanofibers from a suitable inorganic-organic composite solution by spinning a solution of aluminum 2,4-pentanedionate in acetone under electric field [Azad 2006]. The resulting cermer composites were calcined at 1000-1500°C to investigate the pathway of phase evolution in the ultimate ceramic product. Analytical tools, such laser Raman spectroscopy, X-ray diffraction, scanning and high resolution transmission electron microscopy in conjunction with energy dispersive X-ray spectroscopy and selected area electron diffraction were employed to carry out systematic structural and microstructural characterization of alumina fibers as a function of heat-treatment given to the as-spun material. This investigation showed that transparent α-alumina nanofibers with uniform diameter and high aspect ratio could be produced by electrospinning technique.

The electrospinning of alumina nanofibers was studied by Panda and Ramakrishna [Panda and Ramakrishna 2007], using various precursors. The alumina nanofibers were successfully prepared by electrospinning technique using aluminium acetate and aluminium nitrate as alumina precursor combined with PVA or PEO as polymer precursor is spinning aid. It was possible to electrospun a solution containing up to 50% of alumina precursor.

Lindqvist has prepared alumina nanofibers by usingcommercial alumina sol mixed with polyethylene oxide (PEO). The results showed that the polymer content should be at least 27 vol% in the green fiber in order to avoid brittle fibers and the molecular weight of PEO should be at least 400,000 g/mol. The shear and elongation rheological properties of the suspensions were measured. A contraction flow method for measuring the elongational viscosity was evaluated and found to be suitable for highly shear thinning systems with high viscosity. The fiber diameters of calcined samples were in the range 400-700 nm. [Lindqvist et al. 2007]