ROLE OF COLLOIDAL CHEMISTRY IN SYNTHESIS AND PROCESSING OF ALPHA-ALUMINA

A Thesis in
Materials Science and Engineering

by

Rajneesh Kumar

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The thesis of Rajneesh Kumar was reviewed and approved* by the following:

James H. Adair  
Professor of Materials Science and Engineering  
Thesis Advisor  
Chair of Committee

Gary L. Messing  
Distinguished Professor of Ceramic Science and Engineering

Kwadwo Osseo-Asare  
Professor of Metals Science

Serguei Lvov  
Professor of Energy & Geo-Environmental Engineering

James P. Runt  
Professor of Polymer Science  
Associate Head for Graduate Studies  
Department of Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The role of colloidal chemistry in solution synthesis and processing of alpha-alumina (α-Al₂O₃, corundum) was investigated. Experiments were designed to investigate the role of water, produced by degradation of 1,4-butanediol, on equilibrium morphology of α-Al₂O₃ particles synthesized under glycothermal conditions. Development of platelet like morphology was promoted by low water concentrations in the solvent, and development of polyhedron morphology was promoted by high water concentrations in the solvent. A theoretical model predicting morphology for particles produced under solution conditions is proposed, with the possibility of extension of the model to any particle produced under solution conditions. A comparison was made between theoretically predicted and experimentally observed morphologies of α-Al₂O₃.

Glycothermal synthesis process for preparing sub 100 nm phase pure α-Al₂O₃ nanoparticles with platelet morphology has been developed. The role of treatment temperature, seed concentration, stirring speed and solvent water content was investigated in controlling particle size and shape. Phase pure α-Al₂O₃ nanoparticles were synthesized with specific surface area (SSA) as high as 40 m²/gm and temperatures as low as 235 °C.

An attempt has been made towards understanding the aggregation mechanism in alumina nanoparticles. The modeling of hydration and aggregation of alumina clusters was done using PM5 semi-empirical parameters as implemented in CAChe Worksystem. Prolonged aging of hydrated nanoparticles, even under ambient conditions, can cause bridging among the particles that can lead to neck formation resulting in aggregation of
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Chapter 1

Introduction

Advances in technology are dependent on new and innovative materials and processes that open avenues for improved applications as better, faster and cheaper consumer products. Ceramic materials are one such class of materials that have received considerable interest in materials science due to their potential applications in electronic, optics, catalytic, automotive and biomaterial industries [1]. Recently, the solutions to innovative applications and higher performance from ceramic materials require synthesis and processing of ceramic nanoparticles. The ability to synthesize ceramic nanoparticles with controlled shapes and sizes opens new avenues in existing technologies, producing new and improved processes and products with superior properties. High surface area nanoparticles can serve as more efficient adsorbates in the refining industry and also serve to improve the efficiency of catalytic converters. Ceramic armor and windows made of nano-grain ceramic materials have been projected to improve the mechanical and optical properties of these materials giving better protection and durability in extreme environments. The drive towards miniaturization of electronic components is one of the most critical challenges to improve the volume efficiency of electronic components. A true realization of these promises of nanoceramics begins with the synthesis and processing of aggregate free nanophase materials.

The ability to synthesize nanoparticles with controlled size and morphology results in the ability to control the surface area and packing density of the particles. The high
packing density facilitates porosity reduction in sintered ceramic bodies and reduces temperature and time for sintering [1, 2]. Platelet shaped particles can be used as substrates for templated nucleation and growth of highly oriented ceramic films and bulk materials [3]. Thin ceramic coatings thus produced can provide an array of interesting and useful anisotropic mechanical, optical, and rheological properties [4]. Highly anisotropic particles can be applied as composite reinforcement as platelets or needles. The effect of particle shape on its abrasive nature can be exploited in chemical mechanical planarization (CMP) processes for efficient surface finishing and tolerance control [5].

Bulk quantities of aggregate free nanoparticles are required for fabrication of materials and devices in commercial volumes. Typical problems in handling nanoparticles in bulk quantities are clogging of pipelines, loss of rheological properties, flocculation and gelation. Consolidation of aggregated materials compromises the packing density of green bodies and the final microstructure of the bulk materials [2, 6], thus compromising the advantages of “nano-properties” from fabricated materials and devices.

Solution synthesis and processing of ceramic nanoparticles have the potential to satisfy the emerging demands by achieving better control over particle size, shape and form. The key advantages of solution synthesis are the production of high purity, monodispersed powders with controlled morphology [7-9]. Solution methods have developed wide spread interest in the ceramic community due to their potential to synthesize otherwise high temperature (>1000 °C) materials, produced by solid-state reactions such as calcination, sol-gel, plasma arc or chemical vapor deposition techniques.
at relatively low temperatures (< 500 °C). The ability to control the behavior of particles by controlling solvent type, pH, ionic strength, temperature, surfactants and specific adsorbents, can give control over size, shape, dispersability, rheological properties of slurries and suspensions, and packing behavior of particles [12].

The dispersion of particles (dimensions of the order of 10⁻⁶ m or less) in a dispersing medium is termed as a colloidal [13]. Thus, controlling the colloidal chemistry provides control over the synthesis and processing of ceramic nanoparticles. The interactions at the surface of the particle with the surrounding medium dictate the surface behavior of the particles. The dissolution of materials from the surface, development of surface charge, changes in surface energies, and surface adsorption, are some of the surface behavior controlled in turn by particle-particle and particle-solvent interactions. These interactions are controlled by the arrangement of atoms/molecules and chemistry at the interface. Thus, an approach to understanding and implementation of the role of colloidal chemistry in synthesis and processing of ceramic nanoparticles is an important step in meeting the emerging demands towards achieving better control over morphology, size and dispersability of nanoparticles.

Considering the existing state of ceramic powder synthesis and processing routes and the demands of the current and future technologies, the research goals set for the current work focused on addressing three critical issues in advancing ceramics powder processing to applications in nanotechnology:

i. Control of particle morphology

ii. Synthesis of nanoparticles

iii. Production of high concentration slurries of nanoparticles
Alpha-alumina ($\alpha$-Al$_2$O$_3$) is one of the most important ceramic materials with properties and applications having been thoroughly explored [14, 15]. Alumina finds extensive applications in all walks of life: household potteries, ceramic tiles, high temperature refractory, catalytic substrates, precious gems as ruby and sapphire, lasing material, hard abrasive, tough ceramic armors, translucent ceramic arc tubes, substrates for microelectronic packaging, artificial bio-implants and nontoxic drug delivery medium. Apart from its traditional applications, $\alpha$-Al$_2$O$_3$ is finding new and advanced applications as a nanophase material in nanotechnology [16]. The ability to synthesize $\alpha$-Al$_2$O$_3$ nanoparticles (1-100 nm) with controlled size and shape makes it one of the most technologically viable materials for future technologies. Due to its technological importance and widespread demand in ceramic industry, synthesis and processing of $\alpha$-Al$_2$O$_3$ nanoparticles was studied in the present work. This can also serve as a model for understanding solution-based synthesis and processing of ceramic/inorganic particles in general.

The role of colloidal chemistry in controlling morphology, size and de-aggregation/dispersion behavior of nanophase alumina is addressed in the current work. Based on the above-mentioned research goals, the present dissertation is divided into five major sections.

Chapter 2 and Chapter 3 are focused towards achieving better morphological control of ceramic particles in general and $\alpha$-Al$_2$O$_3$ particles, in particular, and emphasize the role of solvent in controlling particle morphology. Chapter 2 outlines the experimental observations on changing morphology and explores the role of changing
solvent composition in controlling the morphology of $\alpha$-Al$_2$O$_3$ particles synthesized under glycothermal conditions. Chapter 3 theoretically calculates the surface charge and isoelectric point (IEP) for various equilibrium shapes of $\alpha$-Al$_2$O$_3$ particles and correlates them to experimentally measured zeta potential. A theoretical model is also proposed for predicting equilibrium shape of particles grown from solution. The model presented has the ability to consider changes in colloidal chemistry due to changes in solvent pH, ionic strength, temperature and composition, in predicting equilibrium morphology of particles grown from solution.

Chapter 4 focuses on synthesizing $\alpha$-Al$_2$O$_3$ nanoparticles with platelet morphology in sizes less than 100 nm, under glycothermal conditions. Increase in nuclei density was achieved through controlled seeding in the experiments. The role of (i) treatment temperature, (ii) seed concentration, (iii) stirring rate and (iv) solvent water content on the size and aspect ratio of synthesized $\alpha$-Al$_2$O$_3$ nanoparticles was investigated.

Chapter 5 focuses on understanding the aggregation behavior of alumina nanoparticles. The state of surface hydration and aggregation were experimentally determined for different nanophase aluminas. A series of semi-emperical calculations were used to study the interactions of water molecules with cluster models of alumina. Theoretical infrared (IR) spectra were generated for different $\alpha$-Al$_2$O$_3$ cluster sizes with and without surface hydration. Theoretical IR was compared to the experimental IR spectra to show the existence of oxygen bridges between alumina nanoparticles with excess surface hydration.
Chapter 6 reports the use of design of experiment (DOE) to identify the main effects that dominate the de-aggregation process in chemically aided attrition milling (CAAM) as a function of time. Optimum milling conditions will be proposed from the DOE analysis for obtaining efficient milling of nanophase alumina powder from about 11 µm in size, to near primary particle dimensions of 20-50 nm. The parameters studied by DOE were media size, agitator shaft speed and powder addition rate.

Chapter 7 outlines the conclusions and suggests future work drawn from the developments of the current work.

1.1 References


Chapter 2

Equilibrium Morphology of Crystals Grown from Solution-1: Role of Solvent in Glycothermal Synthesis of Alpha-Alumina

2.1 Introduction

Advances in technology are dependent on new and innovative materials and processes that open avenues for improved applications as better, faster and cheaper products. Ceramic materials are a class of materials that have received considerable interest in materials science due to their potential applications in electronic, optical, catalytic, automotive and biomaterial industries [1]. The ability to synthesize ceramic particles with controlled shapes and sizes contribute to existing technologies with new and improved processes and products with superior properties. Sub-micron particles with polyhedral morphology can pack up to 70% of theoretical density in the green state. The high packing density facilitates porosity reduction in sintered ceramic bodies and reduces temperature and time for sintering [1, 2]. Platelet shaped particles can be used as substrates for templated nucleation and growth of highly oriented ceramic films and bulk materials [3]. Thin ceramic coatings produced with platelets can provide an array of interesting and useful anisotropic mechanical, optical and rheological properties [4]. Particles with platelet morphology can also form self-assembled structures for potential applications as photonic materials [5-7]. Highly anisotropic particles can be applied to composites as the reinforcement in platelet or needlemorphologies. The effect of particle
shape on abrasive behavior can be exploited in chemical mechanical planarization (CMP) processes for efficient surface finishing and tolerance control [8].

Alpha-alumina (α-Al₂O₃) is one of the most important ceramic material with properties and applications thoroughly explored [9, 10]. Alumina finds extensive applications in all walks of life: household pottery, ceramic tile, high temperature refractory, heterogeneous catalytic substrates, precious gems as rubies and sapphires, lasing material, hard abrasives, tough ceramic armor, translucent ceramic arc tubes, substrates for microelectronic packaging, artificial bio-implants and as a nontoxic drug delivery medium. Due to its technological importance and widespread demand in the ceramic industry, morphological control of α-Al₂O₃ particles was studied under glycothermal conditions using 1,4-butanediol as the solvent. This undertaking also serves as a model to understand morphological control of ceramic/inorganic metal oxide particles precipitated from solution.

Solution synthesis and processing of ceramic particles have the potential to satisfy emerging demands by achieving better control over particle size, shape and form. The key advantages of solution synthesis are the production of high purity, often narrowly distributed, unagglomerated powders with controlled morphology [11-13]. Solvothermal synthesis methods are non-aqueous solution synthetic approaches with precipitation of the desired metal or ceramic materials brought about at elevated temperatures (50 - 550 °C) and under autogenous pressure of the solvent phase. The usual solvents used are water, aqueous alkaline or acidic solutions, inorganic liquids such as ammonia, or organic solvents such as alcohols, glycols, and the organic diols [14-17]. These methods have
generated wide spread interest in the ceramic community due to their potential to synthesize otherwise high temperature (>1000 °C) materials usually produced by solid-state reactions such as sol-gel with calcination, plasma arc or chemical vapor deposition techniques [18, 19]. The relatively low temperatures and better control over particle size and shape [14]. In addition, cost reduction can result from eliminating high temperature (>1000 °C) processing and materials handling. The ability to easily manipulate solvent composition, solution pH and specific adsorbates gives better control over the final size and morphology of the particles. Certain disadvantages of solvothermal methods are use and handling of high-pressure vessels and relatively low yield of products, compared to competitive sol-gel, plasma arc and some other solid-state methods. Solvothermal methods also offer advantages over hydrothermal synthetic schemes by the direct, low temperature formation of the desired phase such as $\alpha$-Al$_2$O$_3$. For example, hydrothermal synthesis of $\alpha$-Al$_2$O$_3$ requires at least 400°C at pressures in the range of 20,000 psi (138 MPa). In contrast, formation of $\alpha$-Al$_2$O$_3$ in 1.4-butanedrol only requires ~250-350°C and less than 8 MPa pressure. Thus, solvothermal approaches are useful to particulate material synthesis if the desired phase, not to mention, size and shape control are desirable for a particular phase and the material is not available to these features using water as a solvent.

Use of solvent at elevated temperatures (50 - 550 °C) and pressures increases the solvation effect of the solvent, promoting dissolution-precipitation of inorganic/ceramic materials at relatively lower temperatures. The liquid phase can act simultaneously as a solvent, reducing agent, crystal growth medium and sometimes as complexing agent for
ionic species [15, 20, 21]. The use of water has been most widely investigated, specifically because of the role of hydrothermal processes in geological phenomena occurring in the Earth’s crust. A number of fundamental properties of water are greatly affected by pressure and temperature [20, 21]. For example, the viscosity of water decreases with increasing temperature, and at 500 °C and 10 bar, viscosity is only 10% of its magnitude under ambient conditions. Even under more mild conditions the viscosity is still lowered, making the mobility of dissolved ions and molecules higher under hydrothermal conditions than at ambient pressure and temperature. Similarly, the dielectric constant of water is affected by temperature and pressure. The dielectric constant decreases with rising temperature and increases with rising pressure, and is considerably reduced above the critical point. This has major implications on the solubility of solid reagents under reaction conditions. Thus, the use of the hydrothermal conditions assist in achieving controlled chemical transport for dissolution-precipitation of the desired chemical species.

Glycothermal synthesis is a solvothermal synthesis method in which organic glycols or diols are used as solvent. Various inorganic, metal and ceramic materials have been produced by glycothermal synthesis methods [22-39]. Synthesis of $\alpha$-Al$_2$O$_3$ by glycothermal synthesis method was first reported by Inoue et al. in 1989 [22]. Various workers have since reported synthesis of $\alpha$-Al$_2$O$_3$ particles using glycols such as 1, 5-pentanediol, 1,4-butanediol and ethylene glycol as the solvent [25, 27, 30, 40, 41]. Use of glycols crystallizes $\alpha$-Al$_2$O$_3$ particles at temperatures and pressures much lower (200-350 °C, less than 8 MPa) [22, 27] than that by water or hydrothermal techniques (400-550
°C, greater than 100 MPa) [16, 42]. The reaction mechanisms and effect of starting materials and solvents on the synthesis of $\alpha$-Al$_2$O$_3$ has been discussed by Inoue et al. [39, 43-45].

Morphological control of $\alpha$-Al$_2$O$_3$ particles synthesized using 1,4-butanediol as the solvent, was first reported by Cho et al. [27, 46]. Cho et al. reported that shear rate controlled the morphology of synthesized particles by changing the local growth environment of the particles. Experimentally, high shear rates develop platelet morphology and low shear rates develop a polyhedral morphology in $\alpha$-Al$_2$O$_3$. It was proposed that the control of morphology is a combination of two effects. First, a kinetic effect where transport of chemical species along the diffused layer adjacent to the growing interface controls the growth rate of various crystallographic planes. Second, an interfacial effect where adsorption or desorption of chemical species inhibited the growth rate of certain crystallographic planes. Cho et al. also studied the effect of the base reagents including KOH, NaOH, and NH$_4$OH, to precipitate aluminum hydrous oxide precursors from aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O), on the subsequent synthesis of $\alpha$-Al$_2$O$_3$ particles using the precursors under glycothermal conditions. It was reported that phase pure $\alpha$-Al$_2$O$_3$ could be produced only with aluminum hydrous oxide precursors precipitated from aluminum the nitrate/KOH system in the pH range from pH 10 to 10.5. Highly alkaline conditions promoted the formation of a mixture of $\alpha$-alumina and boehmite or $\gamma$-alumina phases.

Bell et al. reported that various organic and inorganic additives such as tetrahydrofuran (THF), methanol, 2-butanol, acetic acid, pyridine, tetraethylammonium
hydroxide (TEAOH), nitric acid and ammonium hydroxide act as specific adsorbates for particular crystallographic planes inhibiting specific habit plane growth rates and thus can be used to control the morphology of the particles [41]. However, Bell et al. were unable to resolve the effect of solvent degradation products and water upon the morphological development of \( \alpha \)-Al\(_2\)O\(_3\) particles under glycothermal conditions. The use of kinetic or chemical approaches, either individually or in combination, has the possibility to change the chemical composition and physical properties of the solvent during synthesis [41, 47-52]. There is ample evidence in the literature that the final morphology of a crystal is sensitive to both chemical and kinetic parameters including solution pH, synthesis temperature, agitation rate, reactant concentrations, additives and impurities [11, 12, 53]. But a systematic understanding of these parameters on morphology is neither well understood nor documented. However, the discrepancies between theoretically predicted and experimentally observed morphologies have often been attributed to the decrease in surface energy obtained by adsorption of solvent molecules and other solution species to specific facets of the crystals [54-57]. This raises a question whether the morphological variations are truly caused by kinetic effects from changing shear rates or specific adsorbate effects, or these are just means to change solvent conditions that have a primary effect on controlling particle morphology. It is apparent that a study was required to explore the role of solvent in controlling the morphology of particles/crystals synthesized from solution in the \( \alpha \)-Al\(_2\)O\(_3\) – 1,4-butanediol system.

The present research was focused towards achieving better experimental and theoretical understanding over the morphological development of ceramic particles in
general and $\alpha$-Al$_2$O$_3$ particles, in particular. Improved understanding of the experimental aspects and integration of theoretical modeling will aid in development of improved synthetic routes achieve morphological control of particles grown from solvents. The research outcomes are divided into Chapter 2 and Chapter 3. Chapter 2 is focused towards reporting experimental observations on the changing morphology of $\alpha$-Al$_2$O$_3$ particles and exploring the role of changing solvent composition in controlling the morphology of the $\alpha$-Al$_2$O$_3$ particles synthesized under glycothermal conditions. In Chapter 3 a theoretical calculation of surface charge and isoelectric point (IEP) for various equilibrium shapes of $\alpha$-Al$_2$O$_3$ particles that gives a correlation to experimentally measured zeta potential is developed. Chapter 3 also proposes a theoretical model to predict equilibrium shape of particles grown from solvent and compares theoretically predicted and experimentally observed morphologies of $\alpha$-Al$_2$O$_3$.

2.2 Materials and Methods

2.2.1 General Synthesis Method

The general synthesis method is summarized in a flow sheet shown in Figure 2.1. Glycothermal synthesis of $\alpha$-Al$_2$O$_3$ was performed in a 1-liter hydrothermal bomb$^1$ using a precursor solid loading of 10 gm/250 ml of commercial gibbsite$^2$/1,4-butanediol$^3$. The

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$^1$ Parr Instrument Company, Moline, Illinois
$^2$ Spacerite S11, ALCOA, Pittsburgh, PA
$^3$ Sigma Aldrich, St. Louis, MO
chemical analysis via x-ray fluorescence\(^4\) of the as-received gibbsite is summarized in Table 2.1. The precursor materials is nominally 99.47 percent pure with chief impurities ZrO\(_2\) (520 ppm), CaO (490 ppm), and Na\(_2\)O (3840 ppm). Gibbsite (aluminum hydroxide, Al(OH)\(_3\)) was dispersed in methanol by rapid stirring for 2 hr followed by ultrasonication for 90 second to obtain narrow particle size distribution of precursor phase with average particle size \(~\) 0.7 \(\mu\)m. To the methanol suspension, 200 ml of 1,4-butanediol was added and maintained at 60 \(^\circ\)C under rapid stirring and nitrogen atmosphere for about 12 hr to evaporate the methanol. The resulting suspension was transferred to the pressure vessel along with an additional 50 ml of 1,4-butanediol, used to wash the vessel. The trapped air inside the solvent and the interior of the vessel was removed by applying a vacuum (~30 in. Hg) for 60 min., followed by a 5 min. purge with nitrogen gas. The vessel was filled with nitrogen gas to an over pressure of 0.1 MPa (15 psi). Replacing the trapped air by nitrogen reduces solvent degradation by oxidative air and water [41]. An Omega temperature controller was used to control the reaction vessel temperature and a digital pressure gauge monitored the autogenous pressure. Synthesis was performed by heating the reaction vessel to 275 \(^\circ\)C or 300 \(^\circ\)C for 1 to 72 hr, while stirring the contents in the vessel via a magnetic stirrer. For selected experiments, the reaction vessel was heated to 200 \(^\circ\)C or 250 \(^\circ\)C, and maintained for 0-16 hr, followed by heating to the final reaction temperature of 275 \(^\circ\)C or 300 \(^\circ\)C. Suspensions from selected experiments were measured for water content by Karl Fisher (KF) titration.\(^5\) Extraction of samples at temperature was obtained through a sample port and pressure fitting for rapid disconnect into a Teflon

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\(^4\) W. R. Grace & Co.-Conn., Columbia, Maryland

\(^5\) Denver Instrument Company, Arvada, Colorado
lined stainless steel tube for approximately 5 ml samples. All samples were washed and collected by centrifugation/re-dispersion, four times each with methanol and pH 3 HNO₃ aqueous solutions. The sample powders were characterized for phase by Scintag X-ray diffractometer⁶ (XRD), particle size by light scattering (Malvern Mastersizer⁷) and morphological features by Hitachi S-3500N scanning electron microscopy⁸ (SEM). A quantitative trace element analysis of selected, synthesized α-Al₂O₃ particle of different morphologies was performed using X-ray fluorescence spectrometry (XRF, performed at W. R. Grace & Co.-Conn., Columbia, Maryland). For comparison purposes, a sample of high purity α-Al₂O₃ (AESAR, certified at 99.99w/o (w/o-weight percent), Ward Hill, MA) was also analyzed by XRF. The XRF analyses are provided in Table 2.1.

### 2.2.2 Effect of Autogenous Pressure

Observations were made on the maximum autogenous pressure developed in the reaction vessel and the final α-Al₂O₃ particle morphology obtained after synthesis, for experiments summarized in Table 2.2. Experiments P-2, P-7 and P-9 had solids loading of 20 gm/250 ml and were treated for 72 hr. The remaining experiments had solids loading of 10 gm/250 ml and were treated for 48 hours. Selected experiments were soaked at 200 ºC or 250 ºC for varying time before being heated to the final reaction

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⁶ Scintag, USA, Cu Kα λ = 1.54 Å  
⁷ Malvern Instruments Ltd. Malvern, UK  
⁸ Hitachi Instruments Inc., Japan
temperature of 275 °C. Equilibrium suspension pH remained constant from pH 9 to 10pH. Suspension pH was increased to pH 11 for experiment P-4 and decreased to pH 1.8 for experiment P-9 by adding 10 µl of 1 M KOH and 5 gm of oxalic acid, respectively. Reaction contents for all the experiments, summarized in Table 2.2, were stirred at the same stirring speed of 480 rpm and treated to a reaction temperature of 275 °C.

2.2.3 Effect of Water on Autogenous Pressure

The role of water on autogenous pressure during glycothermal treatment of 1,4-butanediol was monitored by heating 250 ml of 1,4-butanediol to 300 °C with varying water content. Solvent composition with 0 ml (0v/o) (v/o-volume percent), 2.4 ml (1v/o) and 4.8 ml (2v/o) water was used for the experiments. No precursor (gibbsite) was added to these experiments in order to unambiguously evaluate the effect of water on 1,4-butanediol.

2.2.4 Effect of Stirring Speed

Table 2.3 summarizes the synthesis conditions for experiments performed to observe the effect of stirring speed on α-Al₂O₃ particle morphology and autogenous pressure developed under glycothermal conditions. Reaction contents for experiments S-1, S-2, S-3 and S-4 were stirred at 0, 240, 480, 720 rpm, respectively. Precursor solid loading of 10 gm/250 ml, and identical treatment of heating the reaction contents at 200
°C and soaking for 6 hr, followed by 48 hr treatment at 275 °C, was performed for all experiments.

2.2.5 Effect of Soak Time at 200 °C

Experiments were also designed to observe the effect of heating the reaction contents to 200 °C and soaking for various times before heating to the final treatment temperature of 300 °C. The hypothesis for the soak time experiments was that pressure changes observed in preliminary experiments were consistent with water evolved from the Gibbsite (Al₂O₃ ⋅ 3 H₂O) precursor. Preliminary soak experiments gave lower pressures than those without a soak at 200°C possibly because of water trapped in the liquid phase. As summarized in Table 2.3, reaction contents for experiments H-1, H-2, H-3, H-4 and H-5 were heated to 200 °C and soaked for 0, 0.33, 1.0, 3.0 and 6 hour, respectively, before heating to 300 °C for 36 hr. A constant stirring speed of 240 rpm and precursor solid loading of 10 gm/250 ml was used for the experiments. Small samples (~5 ml) were extracted as soon as the reaction temperature reached 300 °C to identify the intermediate phase for experiments H-1 and H-3. Extracted samples were washed with methanol to remove excess 1,4-butanediol and dried overnight at 70 °C before being examined for crystalline phase(s) by X-ray diffraction.
2.3 Results and Discussions

2.3.1 Chemical Purity of Glycothermally Synthesized $\alpha$-Al$_2$O$_3$

A quantitative trace element analysis of selected samples is summarized in Table 2.1. The results indicate that the glycothermally synthesized $\alpha$-Al$_2$O$_3$ had an average purity of 99.90±0.03 w/o. Cho et al. also reported purity levels of 99.84 w/o for glycothermally synthesized $\alpha$-Al$_2$O$_3$. The main impurities detected are listed in Table 2.1. The cesium, barium and phosphorous impurities detected in the synthesized powders are cross contamination from the XRF instrumentation, since these were also detected in the standard certified at (99.99w/o) $\alpha$-Al$_2$O$_3$ from AESAR. The gallium, zirconium and praseodymium impurities were carried over from the precursor gibbsite (Spacerite S11, ALCOA, Pittsburg, PA) used for synthesis. Sodium and calcium present in the precursor were not detected in the glycothermally synthesized $\alpha$-Al$_2$O$_3$ powders, indicating that the synthesized powders were higher in purity than the precursor. Trace amounts of chromium (90 ppm (sample X5), 20 ppm (sample X6)) present in the synthesized powders is probability from the alloying elements present in the 316L stainless steel reaction vessel used for synthesis. The remaining impurities detected were 30 ppm of titanium (sample X3) and 40 ppm of zinc (sample X5).

Analyzing the impurities present after eliminating the cross contamination from the XRF instrumentation and the stainless steel reaction vessel, there is no preferential impurity present in any particular morphological form of glycothermally synthesized $\alpha$-Al$_2$O$_3$ particles. Gallium and zirconium were present in all the samples, irrespective of
the morphological form, were carried over from the precursor gibbsite. Titanium (30 ppm) present in sample X3 having platelet morphology was not present in sample X4 having platelet morphology. Similarly, chromium present in sample X6 having polyhedron morphology was not present in sample X7 having polyhedron morphology.

The impurity analysis on samples with different morphologies eliminates the possibility of morphological forms being dominant due to presence of particular impurities. The elimination of impurities in controlling the morphology of glycothermally synthesized \(\alpha\)-\(\text{Al}_2\text{O}_3\) particles substantiate the experimentally determined finding that relative amounts of water and 1,4-butanediol in the solvent control the stability of various crystallographic facets, and hence the final morphology of the synthesized \(\alpha\)-\(\text{Al}_2\text{O}_3\) particles.

### 2.3.2 Effect of Autogenous Pressure

Alpha-alumina particle morphologies synthesized under experimental conditions summarized in Table 2.2, were observed under SEM and the corresponding crystal morphologies reproduced using the SHAPE\textsuperscript{©9} software. Central distances for various crystallographic planes/facets, evaluated from SEM images of the particles, were used to reconstruct the various morphologies. The results indicate that facets or planes (these two terms will be used interchangeably throughout) belonging to \{0001\} basal, \{\(\bar{1}0\)12\} rhombohedral and \{10\(\bar{1}\)0\} prism forms (form is defined as collection of crystal facets

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\textsuperscript{9} Shape Software, 521 Hidden Valley Road, Kingsport, TN
equivalent by the crystal symmetry) were the three major crystallographic forms dictating the morphology of the glycothermally synthesized \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles. It is well documented that the final morphology of a crystal is dictated by a “combination of forms” \([60]\) that have the lowest relative surface energy. Low surface energy facets have greater stability for the growth environment and slower growth rates, and thus dominate the morphology of the crystal \([58\text{-}60]\).

Central distances for the three major equilibrium forms of \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles were plotted against the autogenous pressure developed during glycothermal synthesis and are shown in Figure 2.2. The apparent results indicate that the central distances for \{0001\} facets increases from 0.1-0.75 \( \mu \)m with pressure, throughout the measured range of 1.5-6 MPa, indicating that the surface energy of the basal plane increases with pressure. The \{\( \overline{1} 012\)\} facets do not stabilized below 2.3 MPa, but above 2.3 MPa the central distance for \{\( \overline{1} 012\)\} facets remain fairly constant at about 0.4 \( \mu \)m with pressure up to the measured pressure of 6 MPa. This indicates that the surface energy for the rhombohedral plane is greater than the basal and prism planes at pressures below 2.3 MPa, and remains relatively constant above 3 MPa. Central distance for \{10\,\( \overline{1}\)0\} facets decreases from 0.9-0.3 \( \mu \)m when pressure increases from 1.5-3 MPa, but above 3 MPa \{10\,\( \overline{1}\)0\} facets are not stabilized. This indicates that the surface energy for prism planes are intermediate to that of basal and rhombohedral plane below 3 MPa, but are higher than basal and rhombodehral plane above 3 MPa.

Through the experimental observations it became apparent that the morphology of \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles correlate to the pressure developed inside the vessel or some change in
the reacting system that is indicated as changes in pressure. However, pressure to
directly affect the surface energies of the crystal facets and alter the equilibrium
morphology of the particles, pressure differences on the order of tens to hundreds of MPa
are required [61]. Thus, changes in pressure were hypothesized to be a secondary effect
to some chemical reaction that gave volatile species under the reaction conditions. The
specific adsorption of any of the reaction products could be affecting the surface energy
of the crystal facets [41].

There is evidence in literature that 1,4-butanediol can lose a water molecule and
undergo dehydration to tetrahydrofuran (THF) under acidic or basic conditions [47, 49,
50]. The presence of water at high temperatures can also cause this dehydration reaction
without any acid or base catalyst due to the relatively high ion-product $K_w$ of water at
elevated temperatures ($pK_w (25 \, ^\circ C) = 14.0; \, pK_w (100 \, ^\circ C)) = 12.3; \, pK_w (300 \, ^\circ C)) = 11.4$)
[47, 62]. Increased concentrations of water in 1,4-butanediol can further catalyze the
dehydration reaction to produce even higher concentrations of water and THF. Since
both THF and water can be present in gaseous form under glycothermal synthesis
conditions, degradation of 1,4-butanediol by dehydration to THF can increase the
autogenous pressure developed in the pressure reactor. Inoue et al. have also reported
gradual increase in the pressure on treatment of gibbsite under alcohothermal conditions
due to formation of water during the course of reaction [43].
2.3.3 Effect of Water on Solvent Degradation

Experiments were designed to evaluate the hypothesis that 1,4-butanediol degrades in presence of water in solution. Solvent mixtures of 250 ml of 1,4-butanediol with 0 ml (0%), 2.4 ml (1%) and 4.8 ml (2%) water were heated to 300 ºC, without precursor present. Changes in autogenous pressure associated with various concentrations of water in 1,4-butanediol were monitored and plotted in Figure 2.3. Though the pressure developed was not as high as observed during the glycothermal synthesis of \( \alpha \)-Al\(_2\)O\(_3\), the data indicated that increased water increases the autogenous pressure developed inside the reaction vessel. Higher pressures developed during conversion of gibbsite to \( \alpha \)-Al\(_2\)O\(_3\) can be explained by the presence of the higher concentration of water resulting from dehydration of Al(OH)\(_3\). Each mole of \( \alpha \)-Al\(_2\)O\(_3\) stoichiometrically flows from three moles of water removed from gibbsite. In addition, the presence of acidic or basic reactive sites on alumina has been reported to catalyze the dehydration of 1,4-butanediol to THF [50]. Thus, it became evident that a pressure change under various synthetic conditions indicates changes in solvent composition caused by the degradation of 1,4-butanediol to THF and water. Bell and Adair reported the presence of THF and water, verified by gas chromatography (GC), in solvent recovered after glycothermal synthesis of \( \alpha \)-Al\(_2\)O\(_3\) using 1,4-butanediol as the solvent. Vacuum distillation of the as–received solvent, to remove entrained water, reduces the extent of degradation of 1,4-butanediol to THF and water [41].
2.3.4 Effect of Stirring Speed

Synthesis parameters and the maximum autogenous pressure developed for experiments designed to investigate the role of stirring speed on morphology are summarized in Table 2.3. Selected SEM micrographs of synthesized \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles are shown in Figure 2.4. Alpha-alumina morphology changed from polyhedral to columnar to plate-like particles while the total autogenous pressure decreased, with increasing stirring speed. No stirring of the reaction content (experiment S-1) produced \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles with a polyhedral morphology with equilibrium facets belonging to \{0001\} and \{1\overline{0}12\} forms, and had developed up to about 5.3 MPa of pressure during the reaction. Stirring the reaction contents at 240 rpm and 480 rpm, as in experiment S-2 and S-3, produced \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles with columnar morphology having aspect ratios of 2 and 2.5 respectively, equilibrium facets belonging to \{0001\} and \{10\overline{1}0\} forms, and developed about 2.3 MPa and 1.9 MPa of pressure, respectively. Maximum stirring speed of 720 rpm (experiment S-4) produced \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles with platelet morphology having an aspect ratio of 4, equilibrium facets belonging to \{0001\} and \{10\overline{1}0\} forms, and had developed about 1.9 MPa of pressure.

It was hypothesized that water released from the dehydration of gibbsite becomes entrained in the precursor suspension solvent and the intermediate phase of intercalated pseudoboehmite/boehmite particles [27]. The entrained water accelerates the degradation of 1,4-butanediol to THF and additional water. On stirring the reaction contents, water trapped inside the solvent and the intercalated pseudoboehmite particles, escapes to the empty headspace of the reactor at an early stage of the reaction, reducing
the interaction of water with 1,4-butanediol. Reduction in water/1,4-butenediol interactions in stirred experiments, reduces the extent of degradation of the solvent. The reduced pressure is consistent with decreased entrained water and less solvent degradation. Thus, the hypothesis is supported that the extent of degradation of the solvent 1,4-butanediol controls the composition of the solvent, which in turn influences the resulting morphology of the synthesized $\alpha$-Al$_2$O$_3$ particles.

### 2.3.5 Effect of Soak Time at 200 °C

Experimental observations reported above indicated that solvent degradation controlled the equilibrium morphology of $\alpha$-Al$_2$O$_3$ particles synthesized under glycothermal conditions. Experiments, summarized in Table 2.3, were designed to achieve *in situ* control over solvent degradation to THF and water. Thus, control over the final morphology of the synthesized $\alpha$-Al$_2$O$_3$ particles is obtained. Reaction contents were heated to 200 °C and soaked for different times before heating to the final treatment temperature of 300 °C. It was anticipated that soaking at a lower temperature of 200 °C permits the release of water from the dehydration of gibbsite to the intermediate phase of boehmite or pseudoboehmite [27, 39] to escape into the headspace of the reaction vessel. The escape of water should reduce the extent of degradation at the higher treatment temperature of 300 °C.

Effect of soak time at 200 °C on morphology of $\alpha$-Al$_2$O$_3$ particle is shown by selected SEM micrographs in Figure 2.5. The effect on maximum autogenous pressure
and residual water content as a function of time are shown in Figure 2.6. Variations in $\alpha$-Al$_2$O$_3$ particle morphology follow a similar trend to the polyhedral-columnar-platelet trend, reported for decreasing autogenous pressure. Experiment H-1, which was not given a soak at 200 °C, generated the maximum autogenous pressure of 5.9 MPa, maximum amount of residual water ~ 12 vol. % and produced particles with a polyhedral morphology and equilibrium facets belonging to $\{0001\}$ and $\{\overline{1}012\}$ forms. Experiment H-2, which was soaked for 0.33 hr at 200 °C, generated an autogenous pressure of 4.6 MPa, residual water ~ 8 vol. % and produced particles with morphology intermediate to the polyhedral and columnar morphologies having 20 faceted crystals with $\{0001\}$, $\{10\overline{1}0\}$ and $\{\overline{1}012\}$ forms. Experiments H-3, H-4 and H-5, which were soaked for 1.0, 3.0 and 6.0 hr at 200 °C, generated autogenous pressures of 3.5, 3.3 and 3.8 MPa, respectively, with residual water content of approximately 7 vol. % and produced particles with a platelet morphology with facets belonging to $\{0001\}$ and $\{10\overline{1}0\}$ forms. The aspect ratio for platelets decreased after soaking for over 3 hr. This may be caused by over-holding the reaction contents at 200 °C which may not be beneficial in reducing the degradation of 1,4-butanediol. The residual water content did not vary much from the 1 hr soak to the 6 hr soak, although the difference may not be detectable by the Karl Fisher method due to error in sampling or changes in moisture content of the environment. Through the above experiment, simply soaking the reaction contents at a lower temperature provides control over the extent of degradation of 1,4-butanediol to water and THF, providing control over the equilibrium morphology of the synthesized $\alpha$-Al$_2$O$_3$ particles.
To understand how the changing solvent composition or increasing water concentration affects the equilibrium morphology for glycothermally synthesized $\alpha$-Al$_2$O$_3$ particles, small amounts of sample (~5 ml) from experiments H-1 and H-3 were extracted, as soon as the reaction temperature reached 300 °C. The powders recovered were analyzed by XRD to identify the intermediate transformation phases between the gibbsite precursor and $\alpha$-Al$_2$O$_3$. The XRD patterns for the extracted samples are shown in Figure 2.7. The intermediate phase formed from experiment H-1, with no soak at 200 °C and high water content, showed a low-angle diffraction peaks at $2\theta \sim 14.5^\circ$, corresponding to the (020) boehmite XRD peak. In contrast, the intermediate phase formed from experiment H-3, after a 1 hr soak at 200 °C and low water content, gave a low-angle diffraction peak at $2\theta \sim 7.9^\circ$, corresponding to the (020) pseudoboehmite XRD peak.

Pseudoboehmite has been reported as a alcohol or glycol derivative of boehmite, with a shift in the (020) XRD peak created by expansion of the crystal lattice in the $b$ direction [39, 45]. The incorporation of glycol molecules between the boehmite layers, composed of chains formed by double molecules of AlOOH [10], expands the crystal structure through the formation of Al-O-C type covalent bonds. The expansion of the lattice in the $b$-direction was verified by constructing the boehmite crystal structure and modifying the lattice parameter b and the atom positions, using ATOMS© software, and comparing the theoretical diffraction pattern to the experimental XRD pattern. The lattice parameters, atom positions and unit cell structure, for boehmite and
pseudoboehmite, are summarized in Table 2.4. Pseudoboehmite formed in sample H-3 has lattice parameters $a = 3.7 \, \AA$ and $c = 2.87 \, \AA$, identical to boehmite. But, the lattice parameter $b$ changed from $12.23 \, \AA$ to $22.5 \, \AA$ due to expansion caused by incorporation of 1,4-butanediol molecules. The equivalent crystal structure for pseudoboehmite with 1,4-butanediol incorporated is shown in Figure 2.8. The –OH ions of one double layer located between the –OH ions of the adjacent layer in a boehmite crystal structure, are replaced by the –O-R-OH group in pseudoboehmite, expanding the lattice structure in the $b$-direction, where -R represents the carbon chain in glycol. Increasing the amount of glycol or the number of carbon atoms in glycol shifts the low-angle diffraction peak to even lower angles by increasing the distance between layers of boehmite [27, 39, 43].

From the identified intermediate phases, the transformation of gibbsite to $\alpha$-$\text{Al}_2\text{O}_3$ takes place through an intermediate phase of boehmite and/or pseudoboehmite. Under glycothermal conditions, the relative amount of the two intermediate phases depends on the water content in the solvent. High water content produces boehmite and high glycol content produces pseudoboehmite. Inoue et al. [43, 45] have reported that the relative amounts of boehmite and pseudoboehmite also depend on the number of carbon atoms in the glycol, particle size of precursor gibbsite and treatment temperature.

The dehydration reactions for conversion of gibbsite to $\alpha$-$\text{Al}_2\text{O}_3$ through the intermediate phase of boehmite can be written as follows:

Step 1: \[2\text{Al(OH)}_3 \leftrightarrow 2\text{AlOOH} + 2\text{H}_2\text{O}\] [2.1 (a)]

Step 2: \[2\text{AlOOH} \leftrightarrow \alpha-\text{Al}_2\text{O}_3 + \text{H}_2\text{O}\] [2.1 (b)]
For dehydration of gibbsite to $\alpha$-Al$_2$O$_3$, through the intermediate phases of pseudoboehmite, the corresponding two step reactions are given by:

Step 1: \[ 2 \text{Al(OH)}_3 + 2 \text{HO-(CH}_2\text{)}_4\text{-OH} \leftrightarrow 2 \text{AlO(O-(CH}_2\text{)}_4\text{-OH)} + 4 \text{H}_2\text{O} \quad [2.2 \text{ (a)}] \]

Step 2: \[ 2 \text{AlO(O-(CH}_2\text{)}_4\text{-OH)} + \text{H}_2\text{O} \leftrightarrow \alpha\text{-Al}_2\text{O}_3 + 2 \text{HO-(CH}_2\text{)}_4\text{-OH} \quad [2.2 \text{ (b)}] \]

The reactions above suggest that under high water concentrations and dehydration through boehmite, the equilibrium morphology will be dictated by crystallographic facets stabilized by relative adsorption/reactivity of water to the surface. But, at low water concentrations and dehydration through pseudoboehmite, the equilibrium morphology is dictated by crystallographic facets stabilized by relative adsorption/reactivity of 1,4-butanediol at the growing surfaces-$\alpha$-Al$_2$O$_3$. Since, low water concentrations in 1,4-butanediol stabilizes facets belonging to the $\{0001\}$ basal form and high water concentration stabilizes facets belonging to the $\{\overline{1}012\}$ rhombohedral form, this suggest that at low water concentrations, the basal plane is stabilized by specific adsorption of 1,4-butanediol, and at high water concentration, the rhombohedral plane is stabilized by water. Inoue et al. [39] have also reported the formation of $\alpha$-Al$_2$O$_3$ particles with platelet morphology through an intermediate phase of pseudoboehmite, under glycothermal conditions.

2.3.7 Effect of Solvent on Crystallographic Facets & Equilibrium Morphology

There have been no experimental reports on the competitive adsorption of glycols, alcohol and water on different crystallographic planes of sapphire or $\alpha$-Al$_2$O$_3$. A
molecular dynamics study has shown that water molecules are attracted to the unhydroxylated \{0001\} plane of $\alpha$-Al$_2$O$_3$ and can easily penetrate through most of the adsorbed alkane films [63]. The kinetic barrier to penetration is proportional to the alkane film thickness and alkane chain length, but inversely proportional to the temperature. Increased water content in the solvent is expected to displace adsorbed 1,4-butandiol molecules from the surface of $\alpha$-Al$_2$O$_3$. Water adsorption reduces the stability of the basal plane, promoted by specific adsorption of glycol or glycolic species. This causes the basal plane to grow faster at high water concentrations. To better understand the effect of solvent on morphology of glycothermally synthesized $\alpha$-Al$_2$O$_3$ particles, a qualitative comparison was made between the surface reactivity and surface site densities for the three experimentally observed crystallographic planes of $\alpha$-Al$_2$O$_3$, in 1,4-butandiol and water.

Many have speculated about the surface sites of $\alpha$-Al$_2$O$_3$ [10, 51, 64-66]. The simplest models for the \{0001\} basal, \{10\overline{1}0\} prism and \{\overline{1}012\} rhombohedral facets, shown in Table 2.5, were used for the current work. The model assumes all surface sites have exposed aluminum and oxygen atoms, with no hydroxyl groups on the surface. The surface terminations were chosen so that the overall charge remains neutral on each crystallographic plane. Any surface relaxation of the atoms and their effect on the local charge unsaturation, as proposed by many workers, has been neglected to maintain the simplicity of the model [51, 64-67]. Charge on each ion on the surface was calculated based on coordination of cations and anions in the bulk solid. For bulk $\alpha$-Al$_2$O$_3$, Al$^{3+}$ cations are coordinated to 6 O$^{2-}$ nearest neighbor anions, and O$^{2-}$ anions are coordinated
to 4 Al\textsuperscript{3+} cations. Charge per bond in the bulk for Al cation and O anion can be calculated as \(\frac{+3}{6} = +0.5\) and \(-\frac{2}{4} = -0.5\), respectively. Atoms on the surface of the solid will be bonded to neighboring atoms towards the bulk, but will have dangling or unsatisfied bonds on the surface contributing to local charge unsaturation. The magnitude for local unsaturated charge can be calculated from the number of missing coordination atoms or dangling bonds above the surface of the ion.

### 2.3.8 Model for of \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} Crystallographic Facets

Alpha-alumina facets were drawn using the slice option in ATOMS© software by defining space group as \(R\bar{3}c\), lattice parameters \(a = b = 4.759\ \text{Å}, c = 12.992\ \text{Å}, \alpha = \beta = 90^\circ, \gamma = 120^\circ\), and atom positions for Al as \(x/a = 0.00, y/b = 0.00, z/c = 0.34\), and O as \(x/a = 0.33, y/b = 0.00, z/c = 0.25\). The surface termination for the three \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} crystallographic facets, their site densities, number of dangling bonds/atom, charge/atom and net surface charge, are summarized in Table 2.5. The \(\{0001\}\) plane is terminated such that it has an Al site density of \(6.25 \times 10^{18}\ \text{atoms/m}^2\) and O site density of \(18.75 \times 10^{18}\ \text{atoms/m}^2\). Each surface Al\textsuperscript{3+} cation is coordinated to 3 neighboring O\textsuperscript{2-} anions and each O\textsuperscript{2-} anion is coordinated to 3 neighboring Al\textsuperscript{3+} cations (1 top & 2 bottom), leaving the (+3) Al cation with \((+3) - 3 \times (+0.5) = +1.5\) unsaturated surface charge per atom, and O anion with \((-2) - 3 \times (-0.5) = -0.5\) unsaturated surface charge per atom. The \(\{10\bar{1}0\}\) plane is terminated such that it has an Al site density of \(7.50 \times 10^{18}\ \text{atoms/m}^2\) and O site density of \(11.25 \times 10^{18}\ \text{atoms/m}^2\). Each surface Al\textsuperscript{3+} is coordinated to 4 neighboring O\textsuperscript{2-} anions (2 bottom & 2 in plane) leaving the (+3) Al with \((+3) - 4 x\)
(+0.5) = +1.0 unsaturated surface charge per atom. Two-thirds of the O\(^{2-}\) anions are coordinated to 3 neighboring Al\(^{3+}\) cations (2 top & 1 bottom), leaving this 2/3\(^{rd}\) O anions with (-2) – 3 x (-0.5) = -0.5 unsaturated surface charge per atom. The remaining 1/3\(^{rd}\) O anions are coordinated to 2 neighboring Al\(^{3+}\) cations (1 top & 1 bottom), leaving these 1/3\(^{rd}\) O anions with (-2) – 2 x (-0.5) = -1.0 unsaturated surface charge per atom. The \{\bar{1}012\} plane is terminated such that it has Al site density of 15.0 x 10\(^{18}\) atoms/m\(^2\) and O site density of 15.0 x 10\(^{18}\) atoms/m\(^2\). Each surface Al\(^{3+}\) cation is coordinated to 5 neighboring O\(^{2-}\) anions, and each O\(^{2-}\) anion is coordinated to 3 neighboring Al\(^{3+}\) cations (1 bottom & 2 approx. in plane), leaving Al cation with (+3) – 5 x (+0.5) = +0.5 unsaturated surface charge per atom, and O anion with (-2) – 3 x (-0.5) = -0.5 unsaturated surface charge per atom. By taking the summation of site density for each atom multiplied by its unsaturated charge, the net charge on each crystallographic facet sum to zero, to maintain charge neutrality over the surface.

### 2.3.9 Equilibrium Morphology Under Low Water Concentrations

Specific adsorption of 1,4-butanediol onto the basal plane can be explained through a higher affinity of the glycol molecules for the basal plane over the prismatic or the rhombohedral plane. Adsorption of long chain organic surfactants on the \{0001\} plane or \{\bar{1}012\} plane of sapphire indicates the surfactant has a higher affinity for the basal plane [68, 69]. Various workers have studied the adsorption and reaction mechanisms of straight chain and secondary alcohols on alumina by infrared techniques [70-75]. Since, 1,4-butanediol is similar to an alcohol, except for bifunctional hydroxyl
(–OH) groups on either end of the carbon chain, similar mechanisms were adopted to explain the affinity of 1,4-butanediol to various crystallographic facets of α-Al₂O₃.

Three different surface species, shown in Figure 2.9, are proposed for adsorption of 1,4-butanediol to the alumina surface sites, depending on the coordinative unsaturation of the alumina surface sites- Species I has physically adsorbed structure, Species II has glycoxide-like chemisorbed structure, and Species III have carboxylate-like chemisorbed structure. Species I is formed by lateral hydrogen bonding interactions between the –OH group of 1,4-butanediol and the coordinatively unsaturated aluminum ions (Lewis acid sites) and the neighboring oxygen ions (Lewis base sites). Depending on the degree of unsaturation of aluminum ion and temperature of reaction, specie I can be held loosely or can go further reactions to form, Species II and/or Species III. Loosely bound 1,4-butanediol can lead to reversible adsorption and can be easily replaced by highly polarized molecules like water. On the other hand a surface site with a relatively high degree of unsaturation can cause dissociative chemisorption on acid-base pair sites, forming Species II with glycoxide-like structure. High binding energy of the dissociatively chemisorbed glycoxide species makes 1,4-butanediol irreversibly adsorbed on to the alumina surface. Greenler et al. [70] and Kagel et al. [71] have reported that heat treatment of surface alkoxide species above 150 °C produced carboxylate-like species on the surface of alumina by release of hydrogen. Similar species can be expected to form by adsorption of 1,4-butanediol to alumina and will be held to the alumina surface by two covalent bonds forming Species III, as shown in Figure 2.9. Species III will be irreversibly adsorbed on the alumina surface by the relatively higher binding energy and will be difficult to remove or replace without a chemical reaction.
The coordination of the aluminum atoms on the surface of the $\alpha$-Al$_2$O$_3$ facets determines the binding mechanism of the adsorbed 1,4-butanediol molecules, thus determining the relative specificity of 1, 4-butarediol to the various crystallographic facets. Since, Al cations on the {0001} plane have the highest degree of coordinative charge unsaturation of $+1.5$, it is most likely that 1,4-butanediol chemically adsorbes on the {0001} facets by forming irreversible carbon-like (Species III) and glycoxide-like (Species II) structures. Chemisorption of irreversible species makes it difficult for the growth species, in the solvent, to precipitate on {0001} facets, slowing down growth rates. Thus, at low water concentrations, Species II and Species III stabilize the {0001} facets. Additional 1,4-butanediol molecules can also hydrogen bond to the attached Species II and III [74] to increase the adsorption density of 1,4-butanediol on the basal plane.

The Al cations on the {$\bar{1}012$} plane have the lowest charge at $+0.5$, compared to {0001} and {10\bar{1}0} planes. The low degree of charge is expected to only physisorb 1, 4-butanediol molecules over {$\bar{1}012$} facets by forming reversible loosely bound hydrogen bonded structures, as in Species I. Relative ease to replace the physisorbed 1,4-butanediol by new growth species from the solvent can make {$\bar{1}012$} facets grow much faster than the {0001} or {10\bar{1}0} facets, causing {$\bar{1}012$} facets to grow themselves out of existence. Therefore, {$\bar{1}012$} facets are not observed stabilizing under low water concentrations.

The Al cations on the {10\bar{1}0} plane have an intermediate degree of charge unsaturation at $+1.0$, compared to {0001} and {$\bar{1}012$} planes. Adsorption of 1,4-
butenediol on \{10\overline{1}0\} facets can form structures with species I and/or II that can be easily replaced relative to Species II and/or III formed on \{0001\} facets, but cannot be replaced as easily as Species I formed on \{\overline{1}012\} facets. Thus, the growth rate for the prismatic plane is relatively faster compared to the basal plane but has slower growth than the rhombohedral plane at low water concentrations.

\(\alpha\)-Al\(_2\)O\(_3\) particle morphology, observed at low water concentrations, corresponds to the relative stability of the three \(\alpha\)-Al\(_2\)O\(_3\) facets. Platelet morphology, equilibrated at low water concentrations forms due to the high stability of time \{0001\} plane and moderate stability of \{10\overline{1}0\} plane. The \{\overline{1}012\} plane has the least relative stability and rapidly grows out of existence.

### 2.3.10 Equilibrium Morphology at High Water Concentrations

As the concentration of water increases in the solvent, the conversion of gibbsite to \(\alpha\)-Al\(_2\)O\(_3\) goes through the intermediate phase of boehmite as shown in Equations [2.2 (a) & (b)]. The relative adsorption/reactivity of the water generated by the dehydration reaction to the crystallographic facets of the Al\(_2\)O\(_3\) dictates the morphology of the synthesized particles. Water can molecularly adsorb (physisorb) or dissociatively adsorb (chemisorb) to alumina surfaces at either Al or O sites [76]. Oxygen on water molecules can hydrogen bond to surface Al acting as a Lewis acid site, or surface O acting as Lewis base site. Molecular adsorption serves as a prerequisite for dissociative adsorption, on which water molecules dissociate to form two hydroxyl groups, one on Al site and other
on O site, as shown in Figure 2.10. Adsorption of water can also take place by
dissociation catalyzed by other water molecules close to the oxide surface. Calculations
of molecular and dissociative adsorption of water on alumina clusters show roughly the
same exothermic energies of adsorption [77]. The desorption of H$_2$O from a
hydroxylated alumina surface, studied using laser-induced thermal desorption (LITD) and
temperature-programmed desorption (TPD) techniques, have shown a variety of hydroxyl
surface sites with different binding energies [78]. The studies revealed that dissociative
adsorption of H$_2$O randomly filled the adsorption sites independent of their adsorption
energy. Due to negligible diffusion of the hydroxyl groups among the various surface
sites, the hydroxyl groups did not diffuse to minimum energy sites, but filled the sites at
random. Thus, it is reasonable to assume that the adsorption of water on various
crystallographic facets of $\alpha$-Al$_2$O$_3$ is not very sensitive to the surface site type but will be
strongly dependent on the total number of surface sites (i.e., the sum of Lewis acid
(cationic or Al site) and Lewis base (anionic or O site)). Facets with high surface site
density will adsorb higher concentration and/or show maximum reactivity to water, and
give the highest stability in an aqueous environment.

Based on the total number of surface sites for the three $\alpha$-Al$_2$O$_3$ facets, shown in
Table 2.5, the facets can be arranged in decreasing order of surface sites as \{1012\} ($30.0$
\(\times\) \(10^{18}\) atoms/m$^2$) > \{0001\} ($25.0\ x\ 10^{18}\ \text{atoms/m}^2$) > \{10 \(\overline{1}\) 0\} ($18.75\ x\ 10^{18}\ \text{atoms/m}^2$). The \{1012\} plane will have the highest stability to water, followed by the \{0001\} plane
and \{10 \(\overline{1}\) 0\} plane. Other workers have also reported high reactivity of water to the
\{1012\} plane over the \{0001\} plane [79]. The $\alpha$-Al$_2$O$_3$ particle morphology, observed
at high water concentration, corresponds to the relative stability of the three facets in water. Polyhedron morphology equilibrated under high water concentration stabilizes the \{\bar{1}012\} plane and the \{0001\}, the relative area of \{\bar{1}012\} facets being greater than the \{0001\} facets. The\{10\bar{1}0\} plane has the least stability among the three planes and rapidly grows out of existence. At an intermediate concentration of water in the solvent, particles with 20 sided polyhedron are observed, with stabilizing facets that express all three forms.

Based on the experimental observations and arguments of specific adsorption/reactivity of 1,4-butanediol and water to the \{0001\}, \{10\bar{1}0\} and \{\bar{1}012\} planes, a qualitative trend is predicted for the change in central distances or surface energies for the three $\alpha$-Al$_2$O$_3$ facets, with increasing water content in 1,4-butanediol, as shown in Figure 2.11. Under low water concentrations the \{0001\} plane will be stabilized to the greatest extent having the smallest central distance or surface energy (for equilibrium morphology, central distance $\propto$ surface energy) [80], followed by the \{10\bar{1}0\} plane and the \{\bar{1}012\} plane. But at high water concentrations, the \{\bar{1}012\} plane will be stabilized the most having the smallest central distance or surface energy, followed by the \{0001\} and the \{10\bar{1}0\} planes.

In future work there is a need to verify the proposed behavior of the crystal facets by a combination of experimental and computational techniques. Also, the relaxation of surface atoms in the local solvent environment should be accommodated, before studying the interaction of various solution species with specific crystallographic surfaces.
2.4 Conclusions

The role of solvent degradation and water on morphological control of $\alpha$-Al$_2$O$_3$ particle synthesized under glycothermal conditions has been resolved. Specific adsorption/reactivity of solvent on certain crystallographic facets can significantly lower the surface energy of particular facets dictating the morphology of the crystals. The impurity analysis on samples with different morphologies eliminated the possibility of morphological forms being dominant due to the presence of specific growth directing impurities. The formation of a platelet morphology can be explained through specific adsorption of 1,4-butanediol molecules on the $\{0001\}$ basal plane. On the other hand, formation of polyhedron morphology can be explained by the stabilization of the $\{\bar{1}012\}$ rhombohedral plane by the relatively high reactivity of water molecules on the surface. There is a need to investigate the mechanisms proposed for the effect of solvent on controlling morphology through a combination of experimental and computational techniques. Integration of techniques such as infrared spectroscopy, contact angle measurements, atomic force microscopy, and calculation of dissociation constants of surface groups and interaction energies of solvent molecules with crystal surfaces using molecular dynamics or ab Initio simulation techniques, can help accurately evaluate the behavior of crystal surfaces in solvent.

The next chapter proposes a theoretical model that can calculate the isoelectric point (IEP) and surface charge for various morphologies of $\alpha$-Al$_2$O$_3$ particles, and account for the various solid/solvent interactions, solution pH and ionic strength on
various crystallographic facets, and assist in accurate prediction of equilibrium morphology for single crystals grown from solution.

2.5 References


J. George and N. V. Sastry, "Densities, Dynamic Viscosities, Speed of Sound, and Relative Permittivities for Water + Alkanediols (Propane-1,2- and -1,3-diol and Butane-1,2-, -1,3-, -1,4-, and -2,3-Diol) at Different Temperatures," *Journal of Chemical Engineering Data*, vol. 48, pp. 1529-1539, 2003.


[68] C. Messerschmidt and D. K. Schwartz, "Growth Mechanisms of Octadecylphosphonic Acid Self-Assembled Monolayers on Sapphire (Corundum)"


A quantitative trace element analysis by XRF. The results indicate that the glycothermally synthesized $\alpha$-Al$_2$O$_3$ had an average purity of 99.90±0.03 w/o (w/o-weight percent).

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$^*$ Impurity from XRF instrumentation
$^*$ Impurity from precursor gibbsite
$^*$ Impurity from steel reaction vessel
Table 2.2. Summary of experimental parameters, maximum autogenous pressure developed, central distance of \{0001\} basal, \{\overline{1}012\} rhombohedral and \{10\overline{1}0\} prismatic forms (form→ all crystal facets equivalent by crystal symmetry) and equilibrium morphology of \(\alpha\)-Al\(_2\)O\(_3\) particles synthesized using 1,4-butanediol (1, 4-BDO) as the solvent. Reaction contents for all the experiments were stirred at the same stirring speed of 480 RPM and treated to a reaction temperature of 275 °C.

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<th>Time (hrs)</th>
<th>Max. Pressure (MPa)</th>
<th>Crystal Form</th>
<th>Central Distance (µm)</th>
<th>Morphology</th>
<th>SEM Micrograph</th>
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<td>20/500</td>
<td>----</td>
<td>9.8</td>
<td>250</td>
<td>16</td>
<td>72</td>
<td>[0001]</td>
<td>0.1</td>
<td>----</td>
<td>1.4 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-3</td>
<td>10/250</td>
<td>----</td>
<td>10</td>
<td>200</td>
<td>6</td>
<td>48</td>
<td>[0001]</td>
<td>0.21</td>
<td>----</td>
<td>1.6 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-4</td>
<td>10/250</td>
<td>1 M KOH (10µl)</td>
<td>11.0</td>
<td>200</td>
<td>6</td>
<td>48</td>
<td>[0001]</td>
<td>0.26</td>
<td>----</td>
<td>1.2 µm</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-5</td>
<td>10/250</td>
<td>----</td>
<td>10</td>
<td>200</td>
<td>12</td>
<td>48</td>
<td>[0001]</td>
<td>0.27</td>
<td>----</td>
<td>0.8 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-6</td>
<td>10/250</td>
<td>----</td>
<td>8.5</td>
<td>250</td>
<td>3</td>
<td>48</td>
<td>[0001]</td>
<td>0.42</td>
<td>----</td>
<td>1.2 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-7</td>
<td>20/500</td>
<td>----</td>
<td>9.2</td>
<td>-----</td>
<td>72</td>
<td>2.90</td>
<td>[0001]</td>
<td>0.43</td>
<td>0.8 µm</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-8</td>
<td>10/250</td>
<td>----</td>
<td>10</td>
<td>250</td>
<td>3</td>
<td>48</td>
<td>[0001]</td>
<td>0.63</td>
<td>1.3 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-9</td>
<td>20/500</td>
<td>Oxalic Acid (5 gm)</td>
<td>1.8</td>
<td>-----</td>
<td>72</td>
<td>5.48</td>
<td>[0001]</td>
<td>0.75</td>
<td>1.5 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[\overline{1}012]</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Pressure release at 200 °C.
Table 2.3. Summary of synthesis conditions for experiments performed to study the effect of stirring speed and soak time at 200 °C, on morphological development of \( \alpha \)-Al\(_2\)O\(_3\) particles under glycothermal conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Soak Time @ 200°C (hrs)</th>
<th>Treatment Temp. (°C)</th>
<th>Treatment Time (hrs)</th>
<th>Solid Loading (gm/250 ml)</th>
<th>Stirring Speed (rpm)</th>
<th>Maximum Autogenous Pressure (psi)</th>
<th>Residual Water (% vol)</th>
<th>Morphology (Aspect Ratio)</th>
<th>Particle Size (Mode, ( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>6</td>
<td>275</td>
<td>48</td>
<td>10</td>
<td>0</td>
<td>5.3</td>
<td>--</td>
<td>Polyhedron (1)</td>
<td>2.3</td>
</tr>
<tr>
<td>S-2</td>
<td>6</td>
<td>275</td>
<td>48</td>
<td>10</td>
<td>240</td>
<td>2.3</td>
<td>--</td>
<td>Columnar (2)</td>
<td>1.7</td>
</tr>
<tr>
<td>S-3</td>
<td>6</td>
<td>275</td>
<td>48</td>
<td>10</td>
<td>480</td>
<td>1.9</td>
<td>--</td>
<td>Columnar (2)</td>
<td>2.0</td>
</tr>
<tr>
<td>S-4</td>
<td>6</td>
<td>275</td>
<td>48</td>
<td>10</td>
<td>720</td>
<td>1.9</td>
<td>--</td>
<td>Platelet (4)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Effect of Stirring Speed

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Soak Time @ 200°C (hrs)</th>
<th>Treatment Temp. (°C)</th>
<th>Treatment Time (hrs)</th>
<th>Solid Loading (gm/250 ml)</th>
<th>Stirring Speed (rpm)</th>
<th>Maximum Autogenous Pressure (psi)</th>
<th>Residual Water (% vol)</th>
<th>Morphology (Aspect Ratio)</th>
<th>Particle Size (Mode, ( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>0.0</td>
<td>300</td>
<td>36</td>
<td>10</td>
<td>240</td>
<td>5.9</td>
<td>11.9</td>
<td>Polyhedron (1)</td>
<td>1.5</td>
</tr>
<tr>
<td>H-2</td>
<td>0.33</td>
<td>300</td>
<td>36</td>
<td>10</td>
<td>240</td>
<td>4.6</td>
<td>6.8</td>
<td>20faced Polyhedron (3)</td>
<td>1.7</td>
</tr>
<tr>
<td>H-3</td>
<td>1.0</td>
<td>300</td>
<td>36</td>
<td>10</td>
<td>240</td>
<td>3.5</td>
<td>7.1</td>
<td>Platelet (4)</td>
<td>2.3</td>
</tr>
<tr>
<td>H-4</td>
<td>3.0</td>
<td>300</td>
<td>36</td>
<td>10</td>
<td>240</td>
<td>3.3</td>
<td>6.9</td>
<td>Platelet (6)</td>
<td>2.3</td>
</tr>
<tr>
<td>H-5</td>
<td>6.0</td>
<td>300</td>
<td>36</td>
<td>10</td>
<td>240</td>
<td>3.7</td>
<td>7.0</td>
<td>Platelet (3)</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Table 2.4. The lattice parameters, atom positions, unit cell structure and theoretical X-ray diffraction peaks for boehmite and pseudoboehmite as constructed using ATOMS©. The XRD for pseudoboehmite was obtained by expanding the boehmite lattice in b-direction, such as to match the experimental XRD pattern.

<table>
<thead>
<tr>
<th><strong>Boehmite, Space Group: Amam</strong></th>
<th><strong>Pseudoboehmite, Space Group: Amam</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice Parameters</strong></td>
<td><strong>Lattice Parameters</strong></td>
</tr>
<tr>
<td>$a = 3.7 \text{ Å}$</td>
<td>$a = 3.7 \text{ Å}$</td>
</tr>
<tr>
<td>$b = 12.23 \text{ Å}$</td>
<td>$b = 22.5 \text{ Å}$</td>
</tr>
<tr>
<td>$c = 2.87 \text{ Å}$</td>
<td>$c = 2.87 \text{ Å}$</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td><strong>Atom Positions</strong></td>
<td><strong>Atom Positions</strong></td>
</tr>
<tr>
<td>Atom</td>
<td>x/a</td>
</tr>
<tr>
<td>Al</td>
<td>0.250</td>
</tr>
<tr>
<td>O</td>
<td>0.250</td>
</tr>
<tr>
<td>OH</td>
<td>0.250</td>
</tr>
</tbody>
</table>

**Unit Cell**

**Theoretical X-Ray Diffraction Pattern**
Table 2.5. Model for \{0001\} basal, \{10\overline{1}0\} prism and \{\overline{1}012\} rhombohedral planes, the three equilibrium facets observed for α-Al₂O₃ particles synthesized under glycothermal conditions. The planes were constructed using “slice” option in ATOMS© with surface terminations such as to have charge neutrality over the surface.

<table>
<thead>
<tr>
<th>Crystal Facet</th>
<th>{0001} Basal Plane</th>
<th>{10\overline{1}0} Prism Plane</th>
<th>{\overline{1}012} Rhombohedral Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Model</td>
<td><img src="image1" alt="Basal Plane" /></td>
<td><img src="image2" alt="Prism Plane" /></td>
<td><img src="image3" alt="Rhombohedral Plane" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of Atoms on Surface (x10¹⁸ atoms/m²)</th>
<th>Al</th>
<th>O</th>
<th>Al</th>
<th>O</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.25</td>
<td>18.75</td>
<td>7.5</td>
<td>11.25</td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coordination of Atoms</th>
<th>Al</th>
<th>O</th>
<th>Al</th>
<th>2/3O</th>
<th>1/3O</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unsaturated Charge (per atom)</th>
<th>Al</th>
<th>O</th>
<th>Al</th>
<th>2/3O</th>
<th>1/3O</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.5</td>
<td>-0.5</td>
<td>+1.0</td>
<td>-0.5</td>
<td>-1.0</td>
<td>+0.5</td>
<td>-0.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Charge (per atom)</th>
<th>Al</th>
<th>O</th>
<th>Al</th>
<th>2/3O</th>
<th>1/3O</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>+9.375</td>
<td>-9.375</td>
<td>+7.5</td>
<td>-3.75</td>
<td>-3.75</td>
<td>+7.5</td>
<td>-7.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Net</th>
<th>Net</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 2.1. Flow sheet for glycothermal synthesis of $\alpha$-Al$_2$O$_3$ particles using 1,4-butanediol as the solvent.
Figure 2.2. Central distance vs. autogenous pressure for the three major forms, basal plane \{0001\}, rhombohedral plane \{\overline{1}012\}, and priom plane \{10\overline{1}0\} for glyothermally synthesized $\alpha$-Al$_2$O$_3$ particles. (The lines are used for guidance)
Figure 2.3. The water concentration increases autogenous pressure developed as shown for autogenous pressure vs. treatment time for 250 ml as-received 1,4 butanediol with 0ml (0 v/o), 2.4ml (1 v/o) and 4.8ml (2 v/o) of water at 300 °C (v/o – volume percent).
Figure 2.4. SEM micrograph for $\alpha$-Al$_2$O$_3$ particles glycothermally synthesized after soaking at 200 °C for 6 hrs, followed by 48 hrs treatment at 275 °C, precursor solids loading of 0.5M (10gm/250ml) and stirring speeds of; 0 rpm (S-1), 240 rpm (S-2), 480 rpm (S-3) and 720 rpm (S-4).
Figure 2.5. SEM micrograph for $\alpha$-Al$_2$O$_3$ glyothermally synthesized after soaking at 200 °C for 0 hr (H-1), 0.33 hr (H-2), 1.0 hr (H-3), 3.0 hr (H-4) and 6 hrs (H-5), followed by 36 hrs treatment at 300 °C. Reaction contents were stirred at 240 rpm and precursor solids loading was 0.5 M (10 gm/250ml).
Figure 2.6. Effect on maximum autogenous pressure and residual water content during glycothermal synthesis of $\alpha$-$\text{Al}_2\text{O}_3$ after soaking at 200 ºC for 0 hr (H-1), 0.33 hr (H-2), 1.0 hr (H-3), 3.0 hr (H-4) and 6 hrs (H-5), followed by 36 hrs treatment at 300 ºC. Reaction contents were stirred at 240 rpm and precursor solids loading was 0.5 M (10 gm/250ml).
Figure 2.7. X-ray diffraction (XRD) patterns for the samples extracted from experiments H-1 and H-3, as soon as the reaction temperature reached 300 °C. The intermediate phase formed with no soak at 200 °C and high water content, extracted from experiment H-1, showed a low-angle diffraction peaks at 2θ~14.5°, corresponding to (020) boehmite XRD peak. But the intermediate phase formed after 1 hr soak at 200 °C and low water content, extracted from experiment H-3, showed low-angle diffraction peak at 2θ~7.9°, corresponding to (020) pseudoboehmite XRD peak.
Figure 2.8. The equivalent crystal structure for pseudoboehmite with incorporated 1,4-butanediol.
Figure 2.9. Three different surface species proposed for adsorption of 1,4-butanediol (BDO) to the alumina surface sites, depending on the coordinative unsaturation of the alumina surface sites. *Species I* - physically adsorbed structure, *Species II* - glycoxide-like chemisorbed structure, and *Species III* - carboxylate-like chemisorbed surface structure.
Figure 2.10. Molecular adsorption of water serves as a prerequisite for dissociative adsorption by forming two hydroxyl groups, one on Al site and other on O site.
Figure 2.11. The expected relative change in central distances or surface energies (under equilibrium conditions, central distance $\propto$ surface energy) [80] for the three facets of $\alpha$-Al$_2$O$_3$ particles synthesized under glycothermal conditions, with increasing water content in the solvent. Under low water concentrations $\{0001\}$ facets will be stabilized.
Chapter 3

Equilibrium Morphology of Crystals Grown from Solution: Theoretical Considerations & Application to Alpha-Alumina

3.1 Introduction

The early work on precipitation of monosized particles was based on the concept of a short nucleation burst and diffusional growth proposed by LaMer and Dinegan in 1950 [1]. This seemed very simple and was universally accepted for years. But, with increasing research on synthesis of monodispersed particles it became evident that there are many other factors that can affect the growth of particles to the final size and shape. The mechanism of the formation of uniform colloids is more complex than originally thought and involves more than just a nucleation/diffusional growth process. Matijevic explained the morphological development of polycrystalline particles by aggregation of subunits into an irreversible capture of singlets [2]. But, morphological development of monodispersed single crystal particles under solution synthesis conditions still remains a mystery. The final morphology of a crystal is sensitive to a variety of experimental variables including solution pH, temperature, agitation, reactant concentrations, additives and impurities [3-5]. But a systematic understanding of these parameters on morphology is not well understood. The need to devise accurate theoretical models to better understand morphological control under solution conditions has long been a requirement in the powder community. The present work is an attempt to fill this need by developing
a theoretical model to predict equilibrium morphology of colloidal particles grown from solution based on a combination of experimentally and theoretically accessible variables applied within a consistent predictive framework.

The prediction of crystal morphology from structural data and its implications on crystal growing processes has been one of the persistent challenges in the field of crystal growth. The first analysis on morphological development of crystals was made in 1885 by Curie who postulated that for crystals grown in the vapor phase at constant temperature and pressure, the equilibrium shape of a single crystal is dictated by minimization of the total surface energy of the crystal [6]. The thermodynamic derivation for surface energy minimization was first performed by Gibbs [7] who stated that there exists a simple relationship between the pressure in each phase and the distance from the center of mass of the particles such that the condition for mechanical equilibrium is given by,

\[ P^c = P^v + 2 \frac{\gamma_j}{\lambda_j} \]  

\[ (j = 1, 2, ..., F) \]  

where; \( P^c \) and \( P^v \) are the pressure within the crystal and vapor phase respectively, \( \gamma_j \) is the surface energy, \( \lambda_j \) is the central distance for facet \( j \), and \( F \) is the total number of facets of the crystal. Wulff [8] incorporated Gibbs derivations in generalizing Curie’s analysis, and stated that for faceted particles, with a center of symmetry, the equilibrium shape or Wulff shape can be determined in terms of vectors normal to the facets. The magnitude of the vectors is proportional to the surface energy \( (\gamma) \) of the facets, such that the ratio of the surface energy to the central distance \( (\lambda_j) \) of the facet, from center of mass of the crystal is constant for all the facets with,
\[ \frac{\gamma_j}{\lambda_j} = \text{Constant} \quad (j = 1, 2, \ldots, F) \]  

The above relationship also results from Gibbs derivation if the pressure in the vapor phase and inside the crystal is identical for all the facets. Since the surface energy for individual faces are dependent on the crystallographic arrangement of atoms in the given plane or habit, the shape or morphology of the crystal will be such as to enclose a given volume of material with minimum energy surfaces.

In 1907, Bravais-Friedel proposed that the importance (frequency of occurrence and/or relative area) of a crystal form \{hkl\} decreases with its interplanar spacing \(d_{hkl}\) [9]. The inconsistencies in the law of Bravais-Friedel, due to constraints on growth rate imposed by halving, trisecting or quartering of the planes by dislocations and glide planes, were data accommodated by Donnay-Harker. Later, Donnay and Donnay extended morphological theory by introducing the concept of a pseudo unit cell to accommodate for the halving or trisecting of planes by pseudosymmetric features in the crystal structures extending in one, two or three directions [10]. In 1955, Hartman and Perdok quantitatively explained that a crystal is bounded by edges parallel to directions in which building blocks are added by forming uninterrupted periodic bond chains (PBC) [11]. In 1980, Hartman and Bennema extended Hartman–Perdok by proposing the concept of attachment energy as a habit controlling factor, defining attachment energy as the energy per molecule released on crystallizing one slice of thickness \(d_{hkl}\) on the face \(\{hkl\}\) [12]. Mackrodt et.al. incorporated the role of surface relaxation, in lowering the surface energy of crystal facets, towards controlling crystal morphology [13].
Despite the long history of models developed for morphological studies of crystals grown from vacuum or a vapor phase, there is little information on changes in surface energy and its effect on crystal morphology manifested by the solvent conditions in which the crystal is grown. The discrepancies in theoretically predicted and experimentally observed morphologies have often been attributed to decreases in surface energy by adsorption of solvent molecules and ionic species to specific facets of the crystals [14-17]. Morphological theories clearly require the incorporation of solvent effects in predicting the equilibrium morphology of crystals. Development of such a model has tremendous potential to improve our understanding and provide information that may aid in the design of better processes for improved morphological control of colloidal particles.

The initial derivation for the equilibrium shape of $\alpha$-Al$_2$O$_3$ particles under solvent conditions, that supports ionic species, was performed by Bell, et. al., assuming Gibb’s model of the interface [18, 19]. Through thermodynamic arguments it was shown that by replacing the vapor phase ($v$) with the liquid phase ($l$), the condition for mechanical equilibrium, originally proposed by Gibbs (Equations [3.1] and [3.2]), remains the same for crystals grown from solution. The extent of reaction at the solid surface accounts for the generation of surface charge, and electroneutrality is maintained by the exchange of reactive species across the solid/solvent interface [20]. But due to some inconsistencies in the proposed theory, the theoretical predictions did not entirely correlate to the experimentally observed morphology for $\alpha$-Al$_2$O$_3$ synthesized under glycothermal conditions. The current article expands the proposed theoretical model and explores the
possibility to adapt the model in predicting equilibrium morphologies for particles produced under solution conditions in general.

### 3.2 Theoretical Model for Predicting Morphology of Crystals Grown from Solution

The morphological model presented here adopts the condition for thermodynamic equilibrium developed by Bell et. al. for crystals grown in solution [19]. The equilibrium shapes are constructed using the Gibbs-Wulff theory by making the central distance for the various forms proportional to the surface energies of the facets of that form such that,

$$\lambda_1 \propto \gamma_1, \lambda_2 \propto \gamma_2, \ldots, \lambda_j \propto \gamma_j \quad [3.3]$$

Changes in surface energies are related to the charging of surfaces in solution by the Lippmann equation [21],

$$\frac{d\gamma}{d\psi} = -\sigma \quad [3.4]$$

where $\sigma$ is the charge and $\psi$ is the potential at the surface. Generation of surface charge and prediction of isoelectric point (IEP) were made using the multisite complexation (MUSIC) model first proposed by Hiemstra et. al. [22, 23]. The potential decay through the diffusion layer above the oxide interface was calculated using the Gouy-Chapman (GC) model [24-26].
3.2.1 Estimation of Surface Charge

Solid surfaces are terminated by surface reactive groups capable of undergoing physio-chemical reactions with species in the environment in order to lower surface energy. Under suitable conditions, adsorbed species on the surface of the solids undergo chemical reactions at reactive surface sites producing stable surface species. As a universal rule, all inorganic materials have some degree of surface hydration, either as absorbed moisture from atmosphere or residual water from synthesis and processing [27-31]. Under ambient conditions, water can dissociate over inorganic surfaces resulting in extensive hydroxylation with singly, doubly and/or triply coordinated or bridged surface hydroxyl M-OH groups [27, 28]. The two most important electrical phenomena arising from these reactions are the generation of charge at the solid surface and the nature of the distribution of potential or charged species in the diffused layer or the vicinity of the solid/liquid interface [26].

There are several surface chemical charging models that would be used to describe the solid-solution interface. The Healy and White ionizable surface group model proposed that the surface charge is generated by the dissociation of specific surface groups on the surface of solids that can have acid and/or base characteristics in a solvent [32]. The dissociation reactions depend on the concentration of the potential determining ions (i.e. pH, ionic strength, and the relative concentrations of various ionizable surface groups). Various models were proposed for surface charge generation on metal (hydr)oxides surfaces [32, 33]. The mono-protic acid group model or one-pK model assumes that the surface is mono-functional with surface groups that undergo only
one protonation step. The amphoteric surface group model or two-pK model assumes that the same surface is bi-functional and can undergo two steps, one protonation and one de-protonation forming both positively and negatively charged species, respectively, on the same surface group thus giving two pK values. The heterogeneous surface group model or multiple pK model assumes that there are different kinds of surface groups capable of undergoing one protonation or deprotonation reaction and their respective pK depends on the strength of the acidity or basicity of the group. The most comprehensive and successful model and the one used for the current work is the multisite complexation (MUSIC) model that considers different types of surface groups on the metal (hydr)oxides surface, each capable of undergoing multiple protonation/deprotonation reactions, thus giving multiple pK values.

The MUSIC model is based on the Pauling theory of bond valance and assumes the presence of several active surface oxygen groups on metal (hydr)oxides surfaces in solution. The surface charging behavior of the metal (hydr)oxides depends on the composition and the relative density of these active surface oxygen groups on various crystallographic planes (habits) present on the material surface [22, 34]. The surface oxygen groups can be singly (primary site), doubly (secondary site) or triply (tertiary site) coordinated with the cations (i.e., $c = 1, 2$ or $3$), capable of adsorbing zero, one, two or three protons or donating H-bonds (i.e., $m = 0, 1, 2$ or $3$). The general equation describing the protonation reactions can be expressed as follows,

$$M_c\text{-O(H)}_m^{(c.v + m - 2)} + H^+ = M_c\text{-O(H)}_{m+1}^{(c.v + m - 1)}$$

[3.5]
The proton association constant, $K_{c,m}$, for $c$-coordinated surface oxygen group with $m$ protons or donating H-bonds can be expressed by,

$$
K_{c,m} = \frac{[M_c - O(H)_{m+1}^{(c,v+m-1)}]}{[M_c - O(H)_{m}^{(c,v+m-2)}][H_s^{+}]} 
$$

where $[H_s^{+}]$ is the surface proton concentration; $v$ is the bond valance of the $M-O$ bond (i.e., the charge on the cation ($z$) divided by its coordination ($CN$) in the bulk (hydr)oxide, assuming all the bond distances are same for each $M-O(H)$ bond in the bulk) such that:

$$
v = \frac{z}{CN} \quad \text{[3.7]} 
$$

The surface proton concentration is related to the bulk proton concentration $[H^+]$ at some absolute temperature, $T$ (°K) by the Boltzmann factor, with $k$ as the Boltzmann constant:

$$
[H_s^{+}] = [H^+]\exp(-e\Psi_s/kT) \quad \text{[3.8]} 
$$

The fraction of $c$-coordinated oxygen sites having $m$ and $m + 1$ adsorbed protons (H-bonds), represented as $\alpha_{c,m}$ and $\alpha_{c,m+1}$, respectively can be expressed as:

$$
\alpha_{c,m} = \frac{1}{K_{c,m}[H_s^{+}] + 1} \quad \text{[3.9 (a)]} 
$$

$$
\alpha_{c,m+1} = \frac{K_{c,m}[H_s^{+}]}{K_{c,m}[H_s^{+}] + 1} \quad \text{[3.9 (b)]} 
$$

Values for $\alpha_{c,m}$ will range between zero and one depending on the pH of the solvent.

The proton association constants or $K_{c,m}$ values for the surface reactions are almost impossible to determine experimentally in certain pH ranges unless the surface
has only one type of surface reaction active in the measurable pH range of pH 1-14. Hiemstra et al. derived the expression to establish $K_{c,m}$ values for the protonation reactions in the MUSIC model. Differences in the local electrostatic and other unspecified contributions are considered to calculate Gibbs free energy of the reactions [22]. The MUSIC model was later revised by stating that the proton affinity of an oxygen atom originates from the undersaturated oxygen valence and that the neutralization of an oxygen by metal ion(s) should be calculated on the basis of the actual bond valence [23]. The revised MUSIC model shows that the proton affinity is not only determined by the number of donating H-bonds, but also by the number of accepting H-bonds. According to the revised MUSIC model, the proton association constant ($K_{c,m}$) can be estimated by:

$$\log K_{c,m} = -A(V + \sum v_{M-O} + m(S_H) + n(1 - S_H))$$  \[3.10\]

$$\Sigma v_{M-O} = c \cdot v$$  \[3.11\]

where $A$ is a constant (+19.8) obtained by regression analysis of various $\log K_{c,m}$ values for homogeneous aqueous protonation reactions at 298 °K versus the undersaturation of charge on the respective oxygen; $V$ is the valance of oxygen (-2), $\Sigma v_{M-O}$ is the sum of bond valance for all $M-O$ bonds, assuming all bond lengths are same in the bulk (Equation [3.11] can be extended to cations coordinated with multiple bond lengths [23], but to keep the model simple, these differences are ignored while calculating $log K_{c,m}$ values); $m$ is the number of donating H-bonds; $n$ is the number of accepting H bonds; and $S_H$ is the bond valance of an adsorbed proton (0.8). The proton bond valance $S_H$ was reduced from the usual value of 1 to 0.8 to compensate for the hydrogen bonding of the surface proton to the solvent molecules. Hiemstra et al. considered $m + n = 3$ for
solution monomers. However due to steric crowding, the surface groups will interact with no more than two donating or accepting H-bonds (i.e., \( m + n = 2 \)). Triply coordinated surface groups or *tertiary sites* have only one orbital for proton interaction \( (m + n = 1) \); doubly coordinated or *secondary sites* may have either one or two orbitals for proton interaction \( (m + n = 1 \text{ or } 2) \); and singly coordinated or *primary sites* have two orbitals for proton interactions \( (m + n = 2) \) [23].

The surface charge density for an individual crystallographic plane or habit \((p)\) can be calculated by taking the sum of the charges from each type of site. The expression for the net surface charge density for a particular habit \((p)\), \(\sigma_s(p)\), is given by,

\[
\sigma_s(p) = N_s(p) e C(p) \tag{3.12}
\]

\[
C(p) = \sum_{c=1}^{3} \left( F_c(p) \cdot \sum_{m=0}^{3} \left( s_{c,m} \alpha_{c,m} \right) \right) \tag{3.13}
\]

where \(N_s(p)\) is the total surface site density on a particular habit \(p\); \(e\) is the charge of an electron \((1.602 \times 10^{-19} \text{ Coulombs})\); \(C(p)\) is the sum of charge contributed from each type of surface site on habit \(p\); \(F_c(p)\) is the fraction of \(c\)-coordinated site on habit \(p\); \(s_{c,m}\) is the charge on a \(c\)-coordinated oxygen site with \(m\) adsorbed protons (H-bonds); and \(\alpha_{c,m}\) is the fraction (ranging between zero and one) of \(c\)-coordinated oxygen site having \(m\) adsorbed protons (H-bonds).

To maintain electroneutrality, the charge developed on the surface of a particular habit \((\sigma_s(p))\) is balanced by the charge on the solution side of the interface \((\sigma_d)\) such that,

\[
\sigma_s(p) + \sigma_d = 0 \tag{3.14}
\]
Assuming a simple Gouy-Chapman (GC) potential decay through the diffused layer extending from the oxide interface [32], charge density at the solvent side can be expressed by,

$$\sigma_d = -\frac{\varepsilon \varepsilon_0 \kappa kT}{2\pi e} \sinh\left(\frac{e\psi_s(p)}{2kT}\right)$$ \[3.15\]

with,

$$\kappa = \frac{8\pi N_A e^2}{\varepsilon \varepsilon_0 kT} \times 10^3$$ \[3.16\]

where $\psi_s(p)$ is the surface potential for habit $p$; $\varepsilon$ is the dielectric constant of the solvent; $\varepsilon_0$ is the permittivity of vacuum; $k$ is the Boltzman’s constant ($1.3085 \times 10^{-23}$ J/K); $T$ is temperature in °K; $1/\kappa$ is the Debye length in meters which relates to the ionic strength $I$ of the solvent expressed in molarity; and $N_A$ is Avogadro’s number ($6.023 \times 10^{23}$ atoms/mol).

The surface potential, using the MUSIC model for individual habits is given by solving the equality,

$$N_{s(p)} \cdot e \sum_{c=1}^{3} \left( F_{c(p)} \cdot \sum_{m=0}^{3} s_{c,m} \alpha_{c,m} \right) = \frac{\varepsilon \varepsilon_0 \kappa kT}{2\pi e} \sinh\left(\frac{e\psi_s}{2kT}\right)$$ \[3.17\]

Surface charge $\sigma_{s(p)}$ for a particular habit can be calculated from the surface potential $\psi_{s(p)}$, as a function of pH by using Equation [3.12]. The overall surface potential for a particle of particular morphology can be calculated as the weighted sum of the potential of the different habits present in the particle [34] is given by

$$\psi_s = \Sigma(f_{(p)} \cdot \psi_{s(p)})$$ \[3.18\]
where \( f(p) \) is the fractional area contributed by habit \( p \) to the total surface area of the particle. Likewise, the overall surface charge can be calculated by the sum of the product of the surface area and surface charge for all habits.

### 3.2.2 Estimation of Surface Energy

Surface energy has been related to the charge on colloidal particles through the electrocapillarity studies of Grahame and Whitney [20, 35]. Reduction in surface energy occurs as the electrical charge increases as solution pH moves away from the isoelectric point. The relationship between particle charge and surface energy is given by the Lippmann equation which states that the change in surface energy is equal to the negative of the surface charge density times the change in potential [21]:

\[
\frac{d\gamma(p)}{d\Psi_s(p)} = -\sigma_s(p)
\]  

[3.19]

An expression can be derived for surface energy of habit \( p \) as a function of \( pH \) by substituting surface potential \( \Psi_s(p) \) with the Nernst equation description of the oxide-solvent interface [32], given below:

\[
\Psi_s(p) = \frac{kT}{e} \ln \frac{a_{H^+_S}}{a_{H^+_S0}}
\]  

[3.20]

Approximating the activity of protons at the surface \( a_{H^+_S} \) and \( a_{H^+_S0} \) to concentration of protons at the surface \([H^+_S] \) and \([H^+_S0] \), and relating surface proton
concentration to the bulk proton concentration \([H^+]\) (Equation [8]), an expression can be derived for change in surface energy with respect to the change in solution \(pH\):

\[
\frac{d\gamma(p)}{d(pH)} = \frac{2.303kT}{2e} \sigma_s(p) \tag{3.21}
\]

The assumption that surface proton activity and concentration are equal is supported by the relatively low surface concentration associated with charged species [32]. By integrating the above expression in the required \(pH\) range, an expression can be derived for \(\gamma(p)\) as a function of \(pH\):

\[
\gamma(p) = \frac{2.303kT}{2e} \int_{pH_0(p)}^{pH} \sigma_s(p)d(pH) + \gamma_0(p) \tag{3.22}
\]

The resulting expression requires an integration constant \(\gamma_0(p)\), the surface energy at the isoelectric point \(pH_0(p)\) for habit \(p\) [26]. The expression for surface energy takes into account the changes in surface energy due to changing electrostatic interactions with \(pH\) and also accounts for the contributions from adsorption of solvent and/or impurity molecules, independent of \(pH\), in the integral constant term \(\gamma_0(p)\).

For considerations of the equilibrium shape, the Gibbs-Wulff construction depends on the value of \(\gamma_0(p)\), and change in surface energy with surface charge. At the IEP the concentration of negatively charged species are equal to the positively charged species, or \(\sigma_S = 0\), hence \(d(\gamma(p))/d(pH) = 0\), thus \(\gamma_{\text{max}} = \gamma_0(p)\). The surface site densities can be found by constructing slices of various low index surfaces for the crystal, using
Equilibrium morphology of the crystal can be constructed using SHAPE by considering surface energy for the various forms proportional to their central distances (Equation [3.3]) from the center of mass of the crystal.

3.3 Experimentation and Results

Alpha-alumina particles with platelet, columnar and polyhedral morphologies, shown in Figure 3.1, were synthesized by glycothermal synthesis method outlined previously [36]. Zeta potential was measured for the different morphologies of $\alpha$-Al$_2$O$_3$ using the ZetaPlus, zeta potential analyser via a phase amplitude light scattering technique. Samples were prepared for zeta potential measurements by washing through centrifugation and re-dispersion four times each in methanol, pH 3 HNO$_3$ aqueous wash solution and de-ionized water. After washing, the particles were re-dispersed in pH adjusted de-ionized water with $10^{-3}$ M KCl as background electrolyte. Drops of 1 M HNO$_3$ and 1 M KOH were used as acid and base to adjust the pH of deionized water. Particle suspensions were stored in 20 ml polyethylene vials and shaken overnight for equilibration. Any drift in suspension pH was readjusted to the targeted pH, if necessary, before making zeta potential measurements.

The experimental zeta potential measurements for platelet, columnar and polyhedral morphologies of $\alpha$-Al$_2$O$_3$ are shown in Figure 3.2. Thus, the current work has

\[ \text{Equation [3.3]} \]

---

10 Shape Software, 521 Hidden Valley Road, Kingsport, TN
11 Shape Software, 521 Hidden Valley Road, Kingsport, TN
12 Brookhaven Instruments Corporation, Brookhaven Corporate Park, Holtsville, New York 11742.
isolated the changes in IEP to changes in particle morphology. The different morphologies of $\alpha$-$\text{Al}_2\text{O}_3$ particles had different IEPs with platelet, columnar and polyhedral morphologies having IEP at pH 5.8, 7.0 and 9.2, respectively. Similar behavior has been observed by several workers [18, 37, 38]. IEPs for $\alpha$-$\text{Al}_2\text{O}_3$ have been reported in the range of pH 4 - 10. The variation in IEPs have been explained through varying charge development on different oxide surfaces due to variation in crystallographic planes (habits) dominant on the morphology, synthesis techniques, history of the powders and surface contamination. In the present work, it is unlikely that surface contamination plays a role because of the relatively high purity of the materials (Table 2.1). A common synthesis technique, precipitation from 1,4-butanediol was used in all cases.

3.4 Application of the Theoretical Model to $\alpha$-$\text{Al}_2\text{O}_3$

To predict equilibrium morphology of $\alpha$-$\text{Al}_2\text{O}_3$ particles by the proposed theoretical model, the surface site densities $N_s$ were determined by counting the theoretical number of Al atoms on the surface of the three experimentally observed facets [36]. Slices were made with different terminations for the (0001) basal plane, the ($\overline{1}012$) rhombohedral plane, and the (10$\overline{1}$0) prism plane, using ATOMS©. The MUSIC model assumes that the surface oxide groups are coordinated to surface cations and thus should provide sites for surface charging. Much speculation has been made regarding the surface sites of $\alpha$-$\text{Al}_2\text{O}_3$ [39-43]. For the current work, the simplest models for the {0001}, {10$\overline{1}$0} and {\$\overline{1}012\$} facets were adopted. The surface terminations were
chosen such that overall charge neutrality is maintained on each crystallographic facet [36]. Any surface relaxation of the atoms and their effect on the local charge unsaturation, as proposed by many workers, has been neglected to maintain simplicity of the model [28, 40-43]. The arrangement of atoms on a 20Å x 20Å surface is shown in Figure 3.3. The site density of Al ions is tabulated in Table 3.2. The basal plane is terminated with the least amount of surface sites \(6.25 \times 10^{18} \text{ sites/m}^2\), followed by the prism plane having \(7.5 \times 10^{18} \text{ sites/m}^2\) and the rhombohedral plane with \(15.0 \times 10^{18} \text{ sites/m}^2\).

The proton association constants \(K_{c,m}\) for the \(\text{Al}_c\text{-O(H)}^{(c.v + m - 2)}\) surface groups were calculated using Equation [3.10]. The \(\log K_{c,m}\) values for the various configurations of \(c\) and \(m\) are tabulated in Table 3.1. The surface group species with \(\log K_{c,m}\) lying within the normal pH range of pH 1 - 14 were considered to actively participate in the surface charging of the various alumina habits dominating the various morphologies. Even though it has been reported that triply coordinated sites can have only one available orbital for H-bonding \((n = 1 & m + n = 1)\), in this work, an \(\text{Al}_3\text{-O}\) surface group with \(n = 2\) and \(m + n = 2\) resulting in \(\log K'_{3,0} = 2.0\), was calculated. Similar values have been reported and used for triply coordinated surface oxygen sites by several workers [22, 44]. Thus, two independent \(\text{Al}_3\text{-O}^{0.5}\) surface group will be considered, one with \(n = 1\) and another with \(n = 2\), represented as \(\text{Al}_3\text{-O}^{0.5}\) and \(\text{Al}_3\text{-O}^{+0.5}\) having corresponding proton association constants \(K_{3,0}\) and \(K'_{3,0}\), respectively. The protonation reactions for the active surface groups are given below:

\[
\text{Al-OH}^{0.5} + \text{H}^+ = \text{Al-OH}_2^{+0.5} \quad \log K_{1,1} = 9.9 \quad [3.23 (a)]
\]

\[
\text{Al}_2\text{-O}^{1.0} + \text{H}^+ = \text{Al-OH}^{0.0} \quad \log K_{2,0} = 11.9 \quad [3.23 (b)]
\]
$$\text{Al}_3\text{-O}^{-0.5} + \text{H}_s^+ = \text{Al}_3\text{-O'}\text{H}^{+0.5} \quad \log K'_{3,0} = 2.0 \quad [3.23 \text{ (c)}]$$

$$\text{Al}_3\text{-O}^{-0.5} + \text{H}_s^+ = \text{Al}_3\text{-OH}^{+0.5} \quad \log K_{3,0} = 5.9 \quad [3.23 \text{ (d)}]$$

The expression for the fraction $\alpha_{c,m}$ of $c$-coordinated oxygen site having $m$ adsorbed protons (H-bonds) for the active sites is written as,

$$\alpha_{1,1} = \frac{1}{K_{1,1}[H_s^+]+1}, \quad \alpha_{1,2} = \frac{K_{1,1}[H_s^+]}{K_{1,1}[H_s^+]+1} \quad [3.24]$$

$$\alpha_{2,0} = \frac{1}{K_{2,0}[H_s^+]+1}, \quad \alpha_{2,1} = \frac{K_{2,0}[H_s^+]}{K_{2,0}[H_s^+]+1} \quad [3.25]$$

$$\alpha_{3,0} = \frac{1}{K_{3,0}[H_s^+]+1}, \quad \alpha_{3,0}' = \frac{K_{3,0}'[H_s^+]}{K_{3,0}'[H_s^+]+1} \quad [3.26]$$

$$\alpha_{3,0} = \frac{1}{K_{3,0}[H_s^+]+1}, \quad \alpha_{3,0} = \frac{K_{3,0}[H_s^+]}{K_{3,0}[H_s^+]+1} \quad [3.27]$$

The surface charge for each habit $\sigma_{s(p)}$ was calculated using the expression for $\alpha_{c,m}$ and the corresponding $s_{c,m}$, $F_{c(p)}$ and $N_{s(p)}$ values from Table 3.1 and Table 3.2. The surface potential $\Psi_{s(p)}$ for each habit was calculated by solving for the equality given in Equation [3.17] using Mathcad Version 11.\textsuperscript{13} The surface energies for each habit were calculated by integrating Equation [3.22] over the pH range from 1pH to pH14. Background ionic strength of $10^{-3}$ M of 1:1 electrolyte was assumed for all calculations.

The effective site density $N_{s(p)}$ (number of sites/m$^2$) available for surface charging, and fraction of $c$-coordinated sites on habit $p$ ($F_{c(p)}$) were used as adjustable parameters to fit the surface potential for various morphologies to their corresponding experimentally

\textsuperscript{13} Mathsoft Eng. & Education, Inc., Cambridge, MA
measured zeta potentials. To obtain a good fit of the model to experimental values, only 
1/300th of the surface sites were actively engaged in surface charging. This behavior can 
be explained through shielding of surface sites by physisorped water molecules at certain 
sites over the alumina surface [28, 45, 46]. The fractional area contributed by each plane 
$f(\rho)$, shown in Table 3.3, to the total surface area of the particle was estimated from 
geometrical calculations made by reproducing the morphologies using SHAPE®, shown 
beside the corresponding SEM micrographs in Figure 3.1. The surface potential for the 
platelet, columnar and polyhedron morphologies of $\alpha$-Al$_2$O$_3$ in water predicted from the 
model are plotted using the experimentally determined zeta potential in water shown in 
Figure 3.2. The goodness of fit, measured using the non-linear correlation coefficient, R-
squared value, of the surface potential curve calculated from the model to the 
experimental zeta potential was between 0.90 - 0.95. The IEP from the model for the 
platelet, columnar and polyhedral morphologies were calculated as pH 6.1, pH 6.8 and 
pH 9.8, respectively, which are consistent with the experimental values shown in Figure 
3.2.

The surface potential for the three individual planes calculated by the model are 
plotted in Figure 3.4 with the corresponding theoretical IEP values listed in Table 3.4. 
IEP for basal plane, prism plane and rhombohedral plane were calculated to be pH 6.0, 
pH 8.2 and pH 10.0, respectively. These IEP values were used to calculate the surface 
energy of the three habits using Equation [3.22]. Ducker et. al reported the surface energy 
for the basal plane near the IEP (pH 5.8) to be 0.48 mJ/m$^2$. The measurements by Ducker 
et al. were conducted in aqueous conditions at several pH values by surface force 
measurements. Due to a lack of surface energy data from the literature, on various
crystal facets of $\alpha$-$\text{Al}_2\text{O}_3$ in water or 1,4-butanediol, surface energies at the IEP for the rhombohedral and prismatic planes were estimated by calculating the ratio of the central distance for the experimentally observed morphologies at pH 9.5. Table 3.4 summarizes the surface energy at IEP with pure water as solvent. The changes in surface energy, for the three habits are plotted in Figure 3.5 (a). The surface energies have peak values at the isoelectric points for each habit. Moving away from the isoelectric point decreases the surface energy due to increased surface charging.

For illustrative purposes, pure water was replaced by a mixed solvent of 92.5%/7.5% volume fraction or 0.75/0.25 mole fraction of a 1,4-butanediol/water solvent mixture. Under these conditions the solvent will still support charged species and the proposed model is valid. A relative dielectric constant for the solvent mixture at 298°C of $\varepsilon = 36.14$, was taken from the literature [47]. Assuming there is no specific adsorption of charged groups at the interface, the IEP and the proton association constants are kept the same as pure water. The magnitude of charge developed under the mixed solvent conditions will decrease because the adsorption of 1,4-butanediol will limit the amount of surface sites available for surface charge generation. Under mixed solvent conditions it was assumed that only 1/1000 of the surface sites were actively engaged in surface charging. Due to a lack of adsorption data for 1,4-butanediol – water binary mixtures on alumina surfaces, estimates were made for the decrease of surface energy by specific adsorption of 1,4-butanediol over the three $\alpha$-$\text{Al}_2\text{O}_3$ habits. Since, the basal plane is stabilized by 1,4-butanediol and the rhombohedral plane is stabilized by water [36], it was assumed that maximum decrease in surface energy by surface adsorption of 1,4-
butanediol molecules will take place on the basal plane, followed by the prism and rhombohedral planes.

Table 3.4 summarizes the decreased surface energies as a function of habit at the IEP for the 0.925/0.075 volume fraction 1,4-butanediol/water binary solvent mixture. The estimated values of the surface energy for the basal, prism and rhombohedral planes were 0.12, 0.25 and 0.43 mJ/m², respectively. The changes in surface energy, for the three habits are plotted in Figure 3.5 (b). Similar to the previous solvent condition for pure water, the surface energies have maximum values at the IEP values. Solution pH values distant from the IEP decreased the surface energy due to increased charging on the surfaces. However, the magnitude of the surface charge was reduced due to lower charge generation in the mixed solvent conditions. Due to significant decreases in the surface energies, expected to occur by specific adsorption of 1,4-butanediol on the basal plane, the platelet and columnar morphologies dominated for the particles generated in the 1,4-butanediol/water mixed solvent conditions. From the model it can be predicted that platelet morphologies can be obtained only at higher 1,4-butanediol concentrations and basic solvent conditions. Columnar morphology can be obtained under acidic conditions and high 1,4-butanediol concentrations. Polyhedron morphology with prismatic and/or rhombohedral facets can be obtained under acidic and basic conditions and high water content in the solvent.
3.5 Comparison of Experimental and Theoretical Morphology of α-Al2O3

A comparison of the experimentally obtained and theoretically predicted morphologies of α-Al₂O₃ crystals, synthesized in the current research and by various other workers [48-50] is tabulated in Table 3.5. The theoretically predicted morphologies compare well to the hexagonal symmetry of the synthesized α-Al₂O₃ particles. However, the theoretical values for the central distances in all three forms vary from the experimental values. Furthermore, the predictions for the aqueous synthesis are generally more consistent with the experimental generated morphologies. The presence of water at concentration greater than 1 or 2 volume percent dominates morphological development. Only the samples in Table 3.5 (d) and (e) at low water concentrations are consistent with habit planes stabilized by 1,4-butanediol adsorption. Table 3.5 (a) & (b) shows a comparison between the theoretically predicted morphology at pH 14 and pH 13, respectively, and experimentally obtained morphologies under high alkaline aqueous condition [48, 49]. Both morphologies show hexagonal platelet particles with basal and rhombohedral planes, but experimentally obtained particles have higher aspect ratios compared to the theoretically predicted particles using water as the solvent.

Table 3.5 (c) compares theoretical and experimental morphologies obtained at pH 13.5 under glycothermal conditions using 1,4-butanediol as the solvent. The theoretically predicted morphology using 1,4-butanediol/water mixture produces platelet shaped particles. However the morphology produced experimentally resembles that predicted when water is the solvent. This can be explained by the fact that under very high basic conditions 1,4-butanediol rapidly degrades producing increased amounts of water. Thus,
the solvent composition changes to high water concentrations, resulting in particles with morphologies similar to that expected for water. The platelet morphologies experimentally obtained at pH 12.2 and pH 11.0, shown in Table 3.5 (d) and (e), compare closely to particle morphologies predicted under high 1,4-butanediol concentrations. The natural pH to synthesize $\alpha$-Al$_2$O$_3$ particles using 1,4-butanediol with minimal solvent degradation is between pH 9-12 [36]. At low water concentrations, the basal plane has the greatest stability followed by the prism plane. This is due to the specific adsorption of 1,4-butanediol molecules on surface sites. Morphologies of particles synthesized at pH 12.2 and pH 11.0 compare favorably with those predicted using 1,4-butanediol as the solvent. Under highly acidic conditions (pH 1.8), shown in Table 3.5 (f), solvent degradation is extreme, resulting in particles with morphologies similar to that expected for water.

3.6 Extension of the Theoretical Model

The proposed model to determine equilibrium morphology under solution conditions can be extended to the synthesis of metal, ceramic and polymeric materials so long as the solvent supports charged species. Depending on the type of surface groups at the solid-solvent interface, surface charging can be modeled by the MUSIC theoretical model. For any material that has multiple molecular terminations on the surface depending on the history (temperature, atmosphere and solvent conditions), degree of crystallinity, and cleavage at particular plane, the predictions of surface energy become
difficult with surface reconstructions, surface chemical reactions and adsorption from the atmosphere. Thus, proper experimental techniques simulating the solvent conditions during synthesis are essential when determining surface energy, surface adsorption and surface charging at the solid-solvent interface. It becomes impractical to simulate such experimental conditions, and simplifying assumptions are often required to fit experimental data to theoretical models.

The behavior of crystal surfaces in a solvent as a function of temperature even up to near synthesis temperatures can be evaluated through the integration of high temperature zeta potential measurements [51, 52], calculation of proton association constants of surface groups and interaction energies of solvent molecules with crystal surfaces. These measurements can be achieved by molecular dynamics or \textit{ab initio} simulation techniques. Molecular dynamic simulation of competitive adsorption of hydrocarbon and water on crystal surfaces aid explanation for the mechanism of adsorption, packing behavior and density of mixed solvent molecules. This will assist in accurately estimating the surface energies for various crystallographic facets of a crystal [53]. Differences in adsorption behavior on different crystallographic planes can be studied by combining adsorption density measurements and adsorption mechanism studies. This can be performed by combining instrumental techniques such as atomic force microscopy (AFM) [54], surface force apparatus (SFA) [55], contact angle measurements [56], inelastic electron tunneling spectroscopy (IETS) [57], Fourier transform infrared spectroscopy (FT-IR) [58] and internal reflection spectroscopy (FT-IR/IRS) [59]. The proposed theory can be extended to the required process and material conditions to obtain equilibrium surface energy for different low index forms and predict
equilibrium morphology of synthesized materials. The surface energy calculation based on integration of the Lippmann equation can be expanded to show the effects of adsorbed ionic and non-ionic species. Surface adsorption for mixed solvent systems, surfactants and ionic species can be predicted through a Langmuir type adsorption model [26, 35]. The decrease of surface energy with adsorption of various ionic and non-ionic species, solvent molecules and surface charging in solvent conditions has been reported for the mercury-solvent interface [26, 35, 60]. Better models such as the Stern, or the Gouy-Chapman-Stern-Grahame model can be adapted to accommodate specifically adsorbed species on the surface of the particles [26] as a function of habit plane. Proper application of the model also requires knowledge of the process variables including absolute temperature ($T$), ionic strength ($c$) and dielectric constant ($\varepsilon$) of the solvent medium. The integration constant representing surface energy at the IEP ($\gamma_{0(p)}$), should be determined by surface energy measurement techniques such as contact angle, Wilhemy balance or surface force measurements [26, 45, 55].

### 3.7 Limitations of the Theoretical Model

The proposed model is based only on experimentally observed *forms* (planes) of the synthesized $\alpha$-Al$_2$O$_3$ crystals. In order to use the proposed model for accurate prediction of particle morphology, the surface energy and surface charging characteristics for the material must be determined as a function of all low index planes. There is a need to successfully determine proton association constants for the surface groups at the oxide/solvent interface by experimental or simulation techniques to verify the predictions.
from the proposed model [22, 34, 61]. In addition, real crystal surfaces have structural defects, coordination imperfections, impurities, kinks and steps which will compromise the predictions by the model. Preferential adsorption at these defect sites on real crystals will not permit complete correlation to the predictions by the proposed theoretical model. Assumptions used in the derivation of the model require a monovalent background electrolyte, which will not be the case during precipitation of ceramic oxides due to the presence of higher valence cations. Additionally, the concentration of background electrolyte will vary with changing solubility of the material in solution.

3.8 Conclusions

In the current work it was shown that morphological development of crystals grown from solution are governed by solvent conditions such as pH, ionic strength and solvent interactions. $\alpha$-Al$_2$O$_3$ particles synthesized under glycothermal conditions are shown to be sensitive to the degradation of solvent causing changes in overall solvent composition [36]. For the first time, the proposed theoretical morphological prediction model accounts for solid/solvent interactions such as electrostatic and surface adsorption of solvent molecules. Comparing the experimentally synthesized and theoretically derived morphologies for $\alpha$-Al$_2$O$_3$ particles, synthesized under both aqueous and glycothermal conditions, provides a better understanding on how to control solvent conditions to tailor morphology of $\alpha$-Al$_2$O$_3$ particles under various solvent conditions. Specific adsorption of the solvent on certain crystal facets can considerably lower their surface energy for particular facets dictating the morphology of the crystals. In
particular, the role of water, solvent degradation, and processing to minimize water production due to solvent degradation on morphological forms produced has been validated in the current work.

3.9 References


Table 3.1. The predicted proton affinity constant ($\log K_{c,m}$) for various surface groups present on crystallographic planes of $\alpha$-Al$_2$O$_3$, calculated from revised MUSIC ( multisite complexation) model.

<table>
<thead>
<tr>
<th>Surface Species</th>
<th>Oxygen Coordination</th>
<th>$m$</th>
<th>$n$</th>
<th>Charge $s_{c,m}$</th>
<th>$v_{M-O}$</th>
<th>$\log K_{c,m}^*$</th>
<th>$\log K_{c,m}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-O</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>-1.5</td>
<td>0.5</td>
<td>21.8</td>
<td>--</td>
</tr>
<tr>
<td>Al-OH</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>-0.5</td>
<td>0.5</td>
<td>9.9</td>
<td>10.0</td>
</tr>
<tr>
<td>Al-OH$_2$</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>+0.5</td>
<td>0.5</td>
<td>-2.0</td>
<td>--</td>
</tr>
<tr>
<td>Al$_2$-O</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>-1.0</td>
<td>1.0</td>
<td>11.9</td>
<td>12.3</td>
</tr>
<tr>
<td>Al$_2$-OH</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
<td>--</td>
</tr>
<tr>
<td>Al$_2$-OH$_2$</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>+1.0</td>
<td>1.0</td>
<td>-11.9</td>
<td>--</td>
</tr>
<tr>
<td>Al$_3$-O$^+$</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>-0.5</td>
<td>1.5</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Al$_3$-O</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>-0.5</td>
<td>1.5</td>
<td>5.9</td>
<td>--</td>
</tr>
<tr>
<td>Al$_3$-OH</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>+0.5</td>
<td>1.5</td>
<td>-9.9</td>
<td>--</td>
</tr>
<tr>
<td>Al$_3$-OH$_2$</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>+1.5</td>
<td>1.5</td>
<td>-21.8</td>
<td>--</td>
</tr>
</tbody>
</table>
Table 3.2. Summary of parameters used to fit surface potential model to experimental zeta potential for {0001} basal plane, {1010} prismatic plane and {1012} rhombohedral plane of α-Al₂O₃. (F1- Primary site, F2- Secondary Site, Fa3- Tertiary site with $m + n = 2$, Fb3- Tertiary site with $m + n = 1$).

<table>
<thead>
<tr>
<th>Habit</th>
<th>Surface Site Density, $^*$ Al³⁺/m², $N_{(p)}$</th>
<th>Effective Site Density, $^{**}$ Al³⁺/m², $N_{s(p)}$</th>
<th>$F_{1(p)}$</th>
<th>$F_{2(p)}$</th>
<th>$F'_{3(p)}$</th>
<th>$F_{3(p)}$</th>
<th>Calculated Isoelectric Point pH$_{0(p)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>{0001}</td>
<td>$6.25 \times 10^{18}$</td>
<td>$6.25 \times 10^{15.5}$</td>
<td>0.14</td>
<td>0.00</td>
<td>0.30</td>
<td>0.56</td>
<td>6.0</td>
</tr>
<tr>
<td>{1010}</td>
<td>$7.5 \times 10^{18}$</td>
<td>$7.5 \times 10^{15.5}$</td>
<td>0.35</td>
<td>0.30</td>
<td>0.00</td>
<td>0.35</td>
<td>8.2</td>
</tr>
<tr>
<td>{1012}</td>
<td>$15.0 \times 10^{18}$</td>
<td>$15.0 \times 10^{15.5}$</td>
<td>0.45</td>
<td>0.45</td>
<td>0.05</td>
<td>0.05</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Table 3.3. Summary of area fraction contributed from individual crystallographic planes to various morphologies of α-Al₂O₃, and the isoelectric points measured experimentally and by the proposed model. ($f_{(B)}$ - area fraction {0001} basal plane; $f_{(P)}$ - area fraction {1010} prismatic plane; and $f_{(R)}$ - area fraction {1012} rhombohedral plane).

<table>
<thead>
<tr>
<th>Morphology</th>
<th>$f_{(B)}$</th>
<th>$f_{(P)}$</th>
<th>$f_{(R)}$</th>
<th>Experimental pH₀</th>
<th>Model pH₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platelet</td>
<td>0.85</td>
<td>0.15</td>
<td>--</td>
<td>5.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Columnar</td>
<td>0.4</td>
<td>0.6</td>
<td>--</td>
<td>7.0</td>
<td>6.8</td>
</tr>
<tr>
<td>Polyhedron</td>
<td>0.3</td>
<td>--</td>
<td>0.7</td>
<td>9.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>
Table 3.4. Summary of isoelectric point and surface energy at isoelectric point for various crystallographic planes (habits) used to calculate surface energy variation with varying solvent pH in 100% water and mixed 92.5%/7.5% 1,4-butanediol/water solvents at 298 °K.

<table>
<thead>
<tr>
<th>Habit</th>
<th>Calculated Isoelectric Point pH&lt;sub&gt;0&lt;/sub&gt;</th>
<th>γ&lt;sub&gt;0(p)&lt;/sub&gt; @ pH=pH&lt;sub&gt;0(p)&lt;/sub&gt; (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100% Water ε = 78.5 @ 298°K</td>
<td>92.5/7.5 vol.% 1,4-butanediol/water ε = 36.14 @ 298°K</td>
</tr>
<tr>
<td>{0001}</td>
<td>6.0</td>
<td>0.48*</td>
</tr>
<tr>
<td>{1010}</td>
<td>8.2</td>
<td>0.50</td>
</tr>
<tr>
<td>{1012}</td>
<td>10.0</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Table 3.5. Comparison of experimental morphologies of $\alpha$-Al$_2$O$_3$ with those predicted by proposed model for predicting equilibrium morphologies of crystals grown from solution.

<table>
<thead>
<tr>
<th>Worker</th>
<th>Synthesis Conditions</th>
<th>Experimental Morphology</th>
<th>Theoretical Morphology (100 vol.% Water)</th>
<th>Theoretical Morphology (92.5/7.5 vol.% 1,4-butanediol / water)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(a)</strong> Kuznetsov, V. A. (1971)[48]</td>
<td>Hydrothermal Alkaline (K$_2$CO$_3$) 530-600ºC pH not reported</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 14</td>
<td>pH 14</td>
</tr>
<tr>
<td><strong>(b)</strong> Kuznetsov, V. A. (1971)[48]</td>
<td>Hydrothermal Alkaline (KHCO$_3$) 530-600ºC pH not reported</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 13</td>
<td>pH 13</td>
</tr>
<tr>
<td><strong>(c)</strong> Kumar, R. (Present)</td>
<td>Glycothermal 0.05M KOH pH 13.5 300ºC</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 13.5</td>
<td>pH 13.5</td>
</tr>
<tr>
<td><strong>(d)</strong> Bell, N. S. (1999)[50]</td>
<td>Glycothermal TEAOH pH 12.2 300ºC</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 12.2</td>
<td>pH 12.2</td>
</tr>
<tr>
<td><strong>(e)</strong> Kumar, R. (Present)</td>
<td>Glycothermal $10^{-6}$M KOH pH 11 275ºC</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 11.0</td>
<td>pH 11.0</td>
</tr>
<tr>
<td><strong>(f)</strong> Kumar, R. (Present)</td>
<td>Glycothermal $10^{-5}$M Oxalic Acid pH 1.8 275ºC</td>
<td><img src="image" alt="Experimental Morphology" /></td>
<td>pH 1.8</td>
<td>pH 1.8</td>
</tr>
</tbody>
</table>
Figure 3.1. SEM micrographs and equivalent crystal made from SHAPE© of (a) platelet, (b) columnar, and (c) polyhedron morphologies $\alpha$-Al$_2$O$_3$ particles synthesized by glycothermal synthesis method using 1,4-butanediol as solvent.
Figure 3.2. Zeta potential for (a) platelet, (b) columnar, and (c) polyhedron morphologies of $\alpha$-Al$_2$O$_3$ particles at 298 °K in 100% water as solvent and 10-3 M, 1:1 background electrolyte. The solid lines on the plots are surface potential calculated by the revised multi-complexation (MUSIC) model for the oxide/solvent interface and the Gouy-Chapman model for potential decay of the diffused ion layer from the oxide interface.
Figure 3.3. Arrangement of atoms on a 20Å x 20Å surface of (a) (0001) basal plane, (b) (10 T 0) prismatic plane, and (c) (T 012) rhombohedral plane, determined by making slices for each plane using ATOMS©.
Figure 3.4. Surface potential for the \{0001\} basal planes, \{10\overline{1}0\} prismatic planes and \{\overline{1}012\} rhombohedral planes of $\alpha$-Al$_2$O$_3$ in 100% water as solvent at 298 °K, calculated from the proposed model. Isoelectric point (IEP) calculated from proposed model for basal, prismatic and rhombohedral planes were at pH 6.0, pH 8.2 and pH 10.0 respectively.
Figure 3.5. Surface energy for the \{0001\} basal planes, \{10 \bar{1} 0\} prismatic planes and \{ \bar{1} 012\} rhombohedral planes of $\alpha$-Al$_2$O$_3$ in (a) 100 % water, and (b) 92.5 vol. % / 7.5 vol. % 1,4-butanediol/water, as solvent at 298 °K. Surface energy decreases as we move away from the isoelectric point of the corresponding planes.
Chapter 4

Synthesis of Alpha-Alumina Nanoparticles with Platelet Morphology under Glycothermal Conditions

4.1 Introduction

Alpha-alumina (α-Al₂O₃, corundum) is one of the most important ceramic materials [1, 2]. In addition to traditional applications, α-Al₂O₃ is finding new and advanced applications as a nanophase material in nanotechnology [3]. The ability to synthesize α-Al₂O₃ nanoparticles (1-100 nm) with controlled size and shape is important in continuing to establish new and unique applications [3]. Sub-micron particles with polyhedral morphology can pack up to 70% theoretical density in the green state. The high packing density facilitates porosity reduction in sintered ceramic bodies and reduces temperature and time for sintering [4, 5]. Particles with platelet morphology can form self-assembled structures for potential applications as photonic materials [6]. Introduction of platelet-like nanoparticles in ceramic materials can also introduce anisotropic electrical, optical and mechanical properties to the materials [7-10].

Nanoparticles of α-Al₂O₃ have been prepared by soild state and solution synthesis techniques [11-16]. The reported techniques usually employ a final calcination step that requires temperatures higher than 900 °C for the final transformation of the Boehmite and transition aluminas to α-Al₂O₃. Most of the reported high surface area α-Al₂O₃ (specific
surface area > 60 m²/gm), have some percentage of untransformed hydrated or transition alumina phases. There has been no report of a process that can produce sub-100 nm phase pure \( \alpha \)-\( \text{Al}_2\text{O}_3 \) with the capability of controlling particle morphology. This limitation requires a process that can produce sub-100 nm phase pure \( \alpha \)-\( \text{Al}_2\text{O}_3 \) nanoparticles, with an ability to control particle morphology and employ significantly lower temperatures for synthesis.

The glycothermal process has a proven ability to produce phase pure \( \alpha \)-\( \text{Al}_2\text{O}_3 \) with temperatures as low as 300 °C, without a final high temperature calcination step [17-22]. Lower synthesis temperatures results in low energy consumption and more economically feasible processes to synthesize high purity ceramic materials [23]. Avoiding high temperature calcinations steps can also reduce the degree and strength of agglomerates in a powder. The glycothermal synthesis process is similar to a hydrothermal process in which precipitation of the desired phase is in a heated solvent (a glycol) under autogenous pressure in a closed vessel. The ability to control and design glycothermal processes creates the potential to synthesize monosized ceramic particles at relatively lower temperatures. Control of \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particle size and morphology has been studied extensively under glycothermal conditions [18, 20, 21]. Control of experimental parameters including stirring speed, treatment temperature and solid loading, and use of chemicals as specific adsorbates give control over the morphology of the synthesized particles [18, 19, 21]. Recent work has shown that a range of particle morphologies can be obtained under glycothermal conditions by simply controlling the water content in the solvent [22, 24]. Sizes ranging from 200 nm to 4 µm have been prepared using \( \alpha \)-\( \text{Al}_2\text{O}_3 \).
and $\alpha$-Fe$_2$O$_3$ seed particles in various concentrations during glycothermal treatment of gibbsite, using 1,4-butanediol as the solvent [20].

Control in size of the particles precipitated by a solution synthesis method is dictated by the system thermodynamic and kinetic factors, including the rate of nucleation, and the level of supersaturation during precipitation. Nucleation mechanism and rate throughout the precipitation process controls the final number of particles and the particle size distribution of the product phase. The focus of the current work is to produce sub-100 nm $\alpha$-Al$_2$O$_3$ nanoparticles by increasing the final number of particles or nuclei density in the 1,4-butanediol/gibbsite system. Increasing the nuclei density produces smaller particles (sub-100 nm) by distributing the fixed amount of precipitated solid phase onto a higher number of particles.

The nuclei density can be increased by increasing the nucleation rate via introducing heterogeneities (vessel walls, dust, colloids, etc.) into the crystallizing system [25]. The effectiveness of a heterogeneity as a nuclei is determined by the crystallographic nature of its surface. Turnbull et al. have developed theoretical arguments quantifying the relationships between crystal structure and the effectiveness of seed materials as nuclei [26]. There should be a one to one registry between the heterogeneity and the nucleating crystallographic phase for a strong nucleating effect. A one to one registry provides a coherent interface with low interfacial stresses and promotes nucleation by decreasing the free energy barrier. If there is a lattice mismatch between the two phases, then the disregistry is given by the following equation,
\[ \delta = \frac{a_s - a_n}{a_s} \]  

[4.1]

where \( a_s \) and \( a_n \) are the lattice parameters for the substrate and the nucleating phase, respectively. A semi-coherent interface may form with localized regions of disregistry, but can still promote a strong nucleating effect. Experimental evidence has indicated that for the interface to be coherent or semi-coherent in order to have a strong nucleating effect, values of \( \delta \leq 0.15 \) is required [26]. If the crystallizing system is seeded with particles of the precipitating phase, as is the case in the current work, then \( \delta = 0 \). The interface is completely coherent and new crystallites are formed with a greatly reduced nucleation barrier [27]. To synthesize particles smaller than the intrinsic (unseeded) capability of a crystallizer, seed particle (heterogeneities) concentration must be at least an order of magnitude greater than the intrinsic nuclei density of the system [20].

The present article focuses on synthesizing nanosized \( \alpha \)-Al\(_2\)O\(_3\) particles with platelet morphology and sizes less than 100 nm, under glycothermal conditions. The increase in nuclei density was achieved through controlled seeding of the experiments [20, 27]. The role of (i) treatment temperature, (ii) seed concentration, (iii) stirring rate and (iv) solvent water content were investigated on size and aspect ratio of synthesized \( \alpha \)-Al\(_2\)O\(_3\) nanoparticles.
4.2 Materials and Methods

4.2.1 General Synthesis Method

The general method for the preparation of $\alpha$-$\text{Al}_2\text{O}_3$ nanoparticles under glycothermal conditions and the additives for the synthesis process are outlined in the flow-sheet in Figure 4.1. Precursor solid suspension was prepared in a 500 ml Enlenmeyer flask by dispersing 10 gm (equivalent to 0.5 M in 250 ml total volume) of commercial gibbsite powder,\(^{14}\) formula $\text{Al(OH)}_3$ or $\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$, in 100 ml of methanol by rapid stirring for 2 hrs. The gibbsite suspension in methanol was then sonicated for 90 seconds to break loose agglomerates and obtain monomodal 0.7 $\mu$m gibbsite particles in suspension. The resulting suspension was then added to 200 ml of 1,4-butanediol.\(^{15}\)

About 1 gm of either 100 nm or 75 nm $\alpha$-$\text{Al}_2\text{O}_3$ seed particles\(^{16}\) were added to the suspension. A TEM photomicrograph of 75 nm seed particles are shown in Figure 4.2. Seed particles were collected by repeated centrifugation and separation of fine particles. The exact seed size and concentrations for specific experiments are mentioned in Table 4.1. The suspension was then rapidly stirred under a nitrogen atmosphere for about 12 hrs at 60 °C to uniformly disperse gibbsite and seed particles in 1,4-butanediol, and evaporate the excess methanol. The precursor suspension thus obtained was transferred to a 1-liter hydrothermal pressure vessel.\(^{17}\) An additional 50 ml of 1,4-butanediol was

\(^{14}\) Spacerite II, ALCOA, Pittsburgh, PA

\(^{15}\) Sigma Aldrich, St. Louis, MO

\(^{16}\) Alumina 9245, Saint Gobain, Massachusetts

\(^{17}\) Parr Instrument Company, Moline, Illinois
used to rinse the flask of remaining precursor. The contents were transferred to the pressure vessel, and the pressure vessel was tightly sealed. A vacuum was applied via a roughing pump, through a pressure release valve for about 1 hr, to evacuate any oxidizing air inside the vessel. The vessel was then purged with nitrogen for 5 minutes through the sampling tube valve and filled with nitrogen gas with a slight over-pressure of 0.1 MPa (15 psi). The contents were stirred at the desired stirring speeds via a magnetically-coupled stirrer attached to the head of the pressure vessel. The vessel was heated to the desired treatment temperatures between 235 ºC – 300 ºC at 2.5 ºC/min. Seed particle concentrations, seed size, stirring speed and precursor pre-treatment were modified to control the size and aspect ratio of the synthesized nanoparticles. The autogenous pressure developed the pressure vessel remained between 1 - 4 MPa under the reaction conditions.

After the glycothermal treatment, the vessel was cooled at 2.5 ºC/min with any residual pressure released through the pressure relief valve. Solvent recovered for selected experiments were analyzed for water content using a Karl Fisher (KF) titrator. The reaction products were washed at least four times each, by centrifugation and re-dispersion in methanol and pH adjusted de-ionized water at pH 3 (pH adjusted by adding $10^{-3}$ M HNO$_3$). The contents were dried at 70 ºC for 24 hr. The powders obtained were characterized for phase by a Scintag X-ray diffractometer (XRD) and specific surface

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18 Denver Instrument Company, Arvada, Colorado
19 Scintag, USA, Cu Kα $\lambda = 1.54$ Å
Selected powders were viewed under a JEOL 2010F high-resolution transmission electron microscopy (HRTEM) for estimating particle size and shape. The aspect ratio for selected particles was measured by performing line scan analysis on AFM images of the particles. A quantitative trace element analysis of selected, synthesized $\alpha$-$\text{Al}_2\text{O}_3$ nanoparticles was performed using X-ray fluorescence spectrometry (XRF, performed at W. R. Grace & Co.-Conn., Columbia, Maryland). For comparison purposes, a sample of high purity $\alpha$-$\text{Al}_2\text{O}_3$ (AESAR, 99.99%), Ward Hill, MA) was analyzed by the same technique.

4.2.2 Kinetic Study of Glycothermal Synthesis of $\alpha$-$\text{Al}_2\text{O}_3$

Experiments were performed for a kinetic study of the transformation-crystallization of gibbsite to $\alpha$-$\text{Al}_2\text{O}_3$ under glycothermal conditions. The transformation kinetics were studied for a suspension with solids loading of 10 gm/250 ml having 100 nm seed particle concentration of $1.5 \times 10^{12}$ particles/ml, and treated for 12 hrs at 300 °C. Approximately 5 ml samples were extracted at regular time intervals through the sampling valve. Solids collected by centrifugation were washed with methanol to remove excess 1,4-butanediol and other organic byproducts. A few drops of concentrated powder suspension in methanol were placed on a zero-background single crystal silicon

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20 Micromeritics Instrument Corporation, Norcross, GA
21 Japanese Electronics and Optics Laboratory, Japan
(510)\textsuperscript{22} slide to perform XRD. The fraction of phases present in the recovered powder was found by integrating the peak area of the maximum intensity peaks for each the phases. Kinetic of transformation-crystallization was studied by analyzing the fraction of transformed $\alpha$-Al$_2$O$_3$ using a Johnson-Mehl-Avrami (JMA) plot, as modified by Hancock and Sharp [28] and implemented by Moon et al., Rosetti et. al., (1992) [29]

$$\ln[-\ln(1-f)] = \ln(r) + m \ln(t)$$

[4.2]

where $f$ is the fraction crystallized isothermally at time $t$, $r$ is a constant that partially depends on nucleation frequency and growth rate, and $m$ is a constant that varies with the system geometry. By obtaining a slope ($m$) from linear regression in the plot of $\ln[-\ln(1-f)]$ against $\ln(t)$ for $f = 0.15$ to 0.66, the controlling formation mechanism can be determined depending on the value of $m$.

### 4.2.3 Estimation of Primary Particle Size

Specific surface area (SSA) measurements were performed on all the synthesized $\alpha$-Al$_2$O$_3$ powders by the Brunauer-Emmett-Teller (BET) technique. Samples were preheated at 125 °C under nitrogen for 30 min. before performing the surface area measurements. An estimation of the primary particle size calculated as equivalent spherical diameter (ESD) was made using following equation [30]:

$$ESD(nm) = \frac{6}{SSA \times \rho} \times 1000$$

[4.3]

\[22\] Gem Dughout, State College, PA
where SSA is expressed in m²/gm, and \(\rho\) is the density (g/cm³) of the powder.

### 4.3 Results and Discussions

#### 4.3.1 Chemical Analysis of Nanosized Alumina

The chemical analyses via XRF on the glycothermally synthesized nanoscale alpha-alumina indicate that the relatively small amounts of impurities, typically at less than 0.04 weight percent (nominally 400 ppm) are not responsible for the tabular morphology observed for the nanoscale alpha-alumina that will be discussed below. A summary of the chemical analyses of a typical nanoscale alpha-alumina, the commercial precursor, and a certified commercial sample used as a control is given in Table 4.2. The precursor, Spacerite S11, had a nominal purity equal to 99.49±0.02 weight percent aluminum oxide. The precipitated nanoscale alpha-alumina had a purity equal to 99.96±0.02 weight percent aluminum oxide. The major common impurities for the precursor and precipitated alumina are Ga₂O₃, ZrO₂, and Pr₆O₁₁. As might be expected for the precipitated sample, the common impurities are all lower or equal to the concentrations present in the precursor sample. Only a small concentration of TiO₂ (30ppm) was present in the nanoscale alpha-alumina and not in the precursor. The nominally 99.99 weight percent certified sample was determined via XRF to be 99.93±0.02 weight percent pure with the primary impurities as BaO (320ppm), Cs₂O (150 ppm), and Cl (140 ppm) with a trace (60ppm) amount of P₂O₅ present. It is likely that a relatively small amount of cross contamination of at least 0.03 weight percent was
present in the samples because of the slightly lower concentration than expected for the
certified sample used as a control. In any case the concentration of impurities at 0.04
weight percent (400 ppm) can not account for the platelet morphology presented below.
The specific surface area of a nanoscale alpha-alumina at 40m²/g would have ~2 impurity
atom approximately every nm². Thus, the relatively low concentration of impurities is
unlikely to drastically influence the nucleation or growth kinetics of the alpha-alumina in
the 1,4-butanediol.

4.3.2 Effect of Treatment Temperature

The effect of treatment temperature on nanosized α-Al₂O₃ synthesis was
investigated and the experiments performed are summarized in Table 4.1. Trials 1, 2 and
3 were treated at 300 °C, 250 °C and 235 °C for 1 hr, 18 hr and 72 hr, respectively. The
synthesis was performed in the same way as outlined in Figure 4.1 with 3.3x10¹²
particles/ml of 75 nm α-Al₂O₃ seed particles. Phase pure α-Al₂O₃ particles were
synthesized at all temperatures. The X-ray diffraction pattern of powder synthesized at
235 °C (trial 3), shown in Figure 4.3, confirmed that phase pure α-Al₂O₃ could be
synthesized at temperatures as low as 235 °C. The powders obtained from all the three
trials had a SSA of 28 m²/gm, corresponding to a primary particle ESD of 55 nm.
Decreasing the synthesis temperature did not decrease the size of the nanoparticles by
increasing the nuclei density in the system. Instead, long synthesis times were required to
obtain phase pure α-Al₂O₃ at lower temperatures.
The presence of seed particles of the same phase as the product phase decreased the free energy for nucleation and promoted formation of $\alpha$-$\text{Al}_2\text{O}_3$ at lower temperatures [26, 27]. The high energy nuclei-solvent (primary nucleation) or nuclei-substrate (heterogeneous nucleation on impurity or alternate phase material) interface is replaced by a low energy nuclei-substrate (heterogeneous nucleation on same phase material) interface by the presence of seed particles. Decreasing the free energy of nucleation has been known to crystallize particles at much lower superstoauration levels and transformation temperatures [26, 31, 32].

4.3.3 Kinetic of Transformation with Seeding

Changes in gibbsite (Al(OH)$_3$), boehmite (AlOOH) and $\alpha$-alumina ($\alpha$-$\text{Al}_2\text{O}_3$) phase concentrations with treatment time are plotted in Figure 4.4. The kinetic plot for fraction of crystallized $\alpha$-$\text{Al}_2\text{O}_3$ under seeded condition is shown in Figure 4.5. The straight line fitted to the data point on the plot has a slope $m = 1.3$, suggesting that under seeded conditions the transformation of gibbsite to $\alpha$-$\text{Al}_2\text{O}_3$ occurs by a zero order mechanism. This finding is similar to an earlier study on PbTiO$_3$ crystallization by Rossetti et al. [33]. Transformation by zero order mechanism indicates that the formation of $\alpha$-$\text{Al}_2\text{O}_3$ nanoparticles under seeded conditions does not depend on supersaturation via the feedstock or phase boundary reactions, but on variables such as relative solubility of the precursor phases and the final $\alpha$-$\text{Al}_2\text{O}_3$. To verify or refute this analysis, the concentration of [Al] in solution during the course of the glycothermal treatment was determined. If the relative solubilities of precursor and final phase are providing a
relative supersaturation to drive the precipitation process, there should be a correlation between solubility of phases. As shown in Figure 4.6, the Al solubility diminishes by almost three orders of magnitude while the $\alpha$-$\text{Al}_2\text{O}_3$ phase fraction increases from zero to about 90% over the course of the glycothermal treatment. The temperature range that the reaction time covers is from 200°C for up to 0.2 hours followed by a rapid temperature increase to $275^\circ\text{C}\pm0.5^\circ\text{C}$ at 0.2 hr. There was no significant change in solution pH (not shown) over the entire reaction time from 0.01 to 72 hours with solution pH relatively stable from pH 9 to pH 10. The correlation between Al solubility and $\alpha$-$\text{Al}_2\text{O}_3$ phase development in this unseeded study supports the kinetic results that zero order reaction kinetics are controlling the formation of $\alpha$-$\text{Al}_2\text{O}_3$. Thus, the solid precursor materials, whether Boehmite or pseudo-Boehmite, are merely acting as a reservoir to maintain the Al solubility while the driving force for precipitation of $\alpha$-$\text{Al}_2\text{O}_3$ is the difference in solubility between the precursor phases(s) and the $\alpha$-$\text{Al}_2\text{O}_3$ as originally described by Rossetti et al. [33] and also observed by Moon et al. [29]. Since, the analysis is based on a very limited kinetic study; a more complete kinetic study is required by further varying solid loading, seed sizes and concentrations to suggest models for optimizing the seed size, concentration and time of reaction to achieve finer nanoparticles at lower transformation temperatures and less time.

4.3.4 Effect of Seed Concentration & Size

The experimental trials to determine the effect of seed size and concentration are shown in Table 4.1. Seeding with finer $\alpha$-$\text{Al}_2\text{O}_3$ seed particles and higher seed
concentrations increases the SSA and thus decreases the primary particle size of synthesized \(\alpha\)-Al\(_2\)O\(_3\) particles. Use of finer seed particles of the same mass gave a higher density of nuclei particles. Trials 5, 6 and 7 seeded with \(7.5\times10^{11}\) particles/ml (100 nm), \(1.5\times10^{12}\) particles/ml (100 nm) and \(3.3\times10^{12}\) particles/ml (75 nm), respectively, produced powders with SSA of 16 \(\text{m}^2/\text{gm}\), 20 \(\text{m}^2/\text{gm}\) and 23 \(\text{m}^2/\text{gm}\), respectively. The corresponding ESD of the synthesized \(\alpha\)-Al\(_2\)O\(_3\) particles for trials 5, 6 and 7 were calculated to be 95 nm, 75 nm and 65 nm, respectively. A control experiment was performed to observe the primary particle size without any seed addition. Synthesis without seeding (trial 4) produced powder with SSA of 4 \(\text{m}^2/\text{gm}\) corresponding to primary particle ESD of 375 nm.

The results indicate that the ESD measured for the precipitated \(\alpha\)-Al\(_2\)O\(_3\) particles are smaller than the seed size introduced into the system. If each seed particle serves as a nuclei, then introducing \(3.3\times10^{12}\) particles/ml of 75 nm seed particles should produce primary particles with an average ESD ~ 160 nm. However, primary particle ESD for all the experiments was below 160 nm. This indicates that there was an increase in the density of nuclei, relative to the seeds that were introduced, under the synthesis conditions. The increase in nucleation density can occur either by dissolution and re-precipitation of \(\alpha\)-Al\(_2\)O\(_3\) to finer particles or by introduction of new seed particles via secondary nucleation. The former scenario is not likely since dissolution re-precipitation in a batch crystallizer generally causes the particles to increase in size by Ostwald ripening from this dissolution of smaller particles and growth of larger particles. However, secondary nucleation is known to occur in stirred reaction vessels [25, 34, 35].
The mechanism of nuclei formation due to the presence of crystals in supersaturated solutions has been generally termed as secondary nucleation. The nucleation mechanisms can be separated into three categories [25];

a) **Apparent secondary nucleation**- The crystals introduced into the system are a source of nucleation

b) **True secondary nucleation**- crystal nuclei are formed by interaction of the crystals and the solution

c) **Contact secondary nucleation**- interaction between the crystal and another solid surface is necessary (e.g. with another crystal, stirrer or crystallizer (vessel))

Many workers have studied various aspects of secondary nucleation with a detailed description of the mechanisms of secondary nucleation summarized by Nyvlt et al. [25]. In a crystallizing system, it is difficult to separate the three categories of secondary nucleation and it is likely that two or more of these mechanisms are active in a crystallizing system.

In the initial stages, it is believed that *apparent secondary nucleation* takes place. The small crystallites adhering to each other as agglomerates are dispersed in the suspension. These serve as coherent nucleating sites for the precipitating particles. As soon as new crystallites are formed on the surface of the seed particles *true secondary nucleation* and *contact secondary nucleation* are believe to dominate. A control experiment was designed in which larger $\alpha$-Al$_2$O$_3$ particles (~ 1 $\mu$m) were used as seed particles, to check the phenomena of *true secondary nucleation*. Observation of particles
recovered after synthesis under SEM show multiple particles growing over the seed particles, as shown in Figure 4.7. It is proposed that the new crystallites formed on the surface of the mother seed crystal are broken off by the shear of flowing solution and/or the collision of the seed particle with another particle, stirrer or the vessel wall. As long as the suspension supersaturation is high enough for the broken crystallite to survive, these can serve as secondary nuclei for growing into individual particles or serve as a source for next generation of secondary nuclei.

As a whole, the secondary nucleation rate $N_N$ has been expressed by [25],

$$N_N = (E_t).(F_1).(F_2)$$  \[4.4\]

where $E_t$ is the energy transferred during the collision, $F_1$ is the number of particles formed per unit transferred energy and $F_2$ is the fraction of surviving particles. To produce even smaller-sized nanoparticles, the generation of nuclei by secondary nucleation can be increased by increasing $E_t$ and the frequency of collision by increasing the stirring intensity [35]. This will increase the collisions among the crystal-stirrer, crystal-crystallizer (vessel) and crystal-crystal. Thus, the next logical step is to optimize the maximum stirring rate that could give the highest degree of secondary nucleation and the smallest possible $\alpha$-$\text{Al}_2\text{O}_3$ particles with the same amount of seed particles and precursor material.
4.3.5 Effect of Stirring Speed

The effect of stirring speed on nanosized $\alpha$-Al$_2$O$_3$ synthesis was investigated and the experiments performed are summarized in Table 4.1. Synthesis in these experiments were performed as shown in Figure 4.1, by seeding with $3.3\times10^{12}$ particles/ml of 75 nm $\alpha$-Al$_2$O$_3$ seed particles. Stirring speed for trials 8, 9, 10 and 11 were varied as 0 rpm, 60 rpm, 240 rpm and 740 rpm, respectively. Powders obtained under these conditions were phase pure $\alpha$-Al$_2$O$_3$ with SSA of 23 m$^2$/gm, 28 m$^2$/gm, 28 m$^2$/gm and 23 m$^2$/gm corresponding to primary particle ESD of 65 nm, 55 nm, 55 nm and 65 nm, respectively.

The results suggest that increasing stirring rate initially increases the secondary nucleation rate, but at the highest stirring rates investigated the rate of secondary nucleation decreases. Similar behavior has been reported by Ottens et al. [35]. It was demonstrated experimentally that the number of newly formed crystals increases with increasing collision energy up to a certain energy level above which there is no increase in the number of crystals formed. It has been found that after a certain critical limit, the collisions are ineffective in producing increased secondary nuclei. Increasing the stirring rate above this critical limit may even lead to a decrease in the rate of secondary nucleation [25]. Thus, for further experiments a constant stirring rate of 240 rpm was used, since increasing stirring rate beyond this limit did not increase the secondary nucleation rate.
4.3.6 Effect of Solvent Water Content

Control of particle morphology by controlling the solvent water content during glycothermal synthesis of unseeded α-Al₂O₃ particles was reported earlier [24, 36]. The solvent 1,4-butanediol specifically adsorbs and stabilizes on the \{0001\} basal plane of α-Al₂O₃ particles. Thus, under high 1,4-butanediol and low water concentrations in the solvent, α-Al₂O₃ particles with platelet morphology are formed. Based on this earlier study, a similar approach was adopted towards controlling the aspect ratio of platelet shaped α-Al₂O₃ particles under seeded conditions. The approach involved holding the precursor suspension at 200 °C for 1 hr before heating to the treatment temperature of 300 °C, with introduction of an additional 10 ml of de-ionized water to the precursor suspension. Holding at 200 °C before heating to the final treatment temperature has been shown to release the initial water of dehydration, from the gibbsite precursor and from the solvent phase into the empty head space of the vessel, thus reducing the overall water content in the solvent.

Table 4.1 summarizes the experimental parameters for experiments performed to investigate the role of solvent water content in controlling the aspect ratio of synthesized α-Al₂O₃ particles. All the experiments were seeded with the same seed concentration of 3.3x10¹² particles/ml and were stirred at 240 rpm. In trial 12, an additional 10 ml of de-ionized water was added to the precursor suspension and the contents were glycothermally treated at 300 °C without holding at 200 °C. In trial 13, no additional water was added to the precursor suspension and the contents were glycothermally treated at 300 °C without holding at 200 °C. Finally for trial 14, no additional water was
added to the precursor suspension and the contents were held at 200 °C before

glycothermally treating at 300 °C.

The volume percent of water in the solvent, measured by KF titration, recovered
after treatments glycothermal was 3.5%, 2.6% and 1.75 % for trials 12, 13 and 14,
respectively. The measured SSA of the synthesized α-Al₂O₃ particles increased with
lower amounts of water in the solvent. SSA was measured to be 18 m²/gm, 28 m²/gm
and 35 m²/gm corresponding to primary particle ESD of 85 nm, 55 nm and 40 nm for
trials 12, 13 and 14, respectively. As an initial estimate, the increase in SSA and
reduction in corresponding primary particle size can be interpreted as an increase in
secondary nucleation rate. But observing the synthesized particles under TEM
(Figure 4.8 and Figure 4.9) and AFM (Figure 4.10) shows that the ESD estimated from
SSA were different from the actual size of the particles. Also, the aspect ratio of the
particles changed considerably at the various water contents in the solvent. Changes in
aspect ratio can contribute to inconsistencies in the estimated ESD because of the
assumption of spherical particle is invalid.

A simple geometrical calculation was made to explain the changes in surface area
of the particles with changing aspect ratio of the platelet shaped particles. The
assumption was made that the platelet particles are hexagonal in shape, as reported for
seeded and unseeded α-Al₂O₃ particles synthesized under glycothermal conditions [20,
36]. Figure 4.11 show a schematic of a hexagonal particle with face diameter D and
height h. Aspect ratio AR is expressed as the ratio of the face diameter to the height of
the crystal such that,

The surface area for the basal plane (top and bottom faces) can be expressed by,

\[ A_{Basal} = \frac{3\sqrt{3}}{4} D^2 \]  \hspace{1cm} [4.6]

And the surface area for the prism plane (6 side faces) is given by,

\[ A_{Prism} = 3Dh \]  \hspace{1cm} [4.7]

The volume of the platelet particle is,

\[ V_{platelet} = \frac{3\sqrt{3}}{8} D^2 h \]  \hspace{1cm} [4.8]

Assuming there is no change in the nucleation density and the average volume per particle remains the same, we can derive an expression for the SSA for the particle,

\[ SSA = \frac{A_{Basal} + A_{Prism}}{V\rho} \]  \hspace{1cm} [4.9]

where \( \rho \) is the density of the particle (\( \rho = 3.98 \text{ gm/cc} \) for \( \alpha-\text{Al}_2\text{O}_3 \)). MathCAD version 11\(^{23}\) was used to calculate the change in SSA for changing aspect ratio of the particle plotted in Figure 4.11. For particles with a fixed volume but changing aspect ratio, there exists a minimum in SSA for more equiaxed particles with \( AR_e = 1 \). An increase in anisotropy by reducing the aspect ratio below \( AR_e \) gives more needle shaped particles

\(^{23}\) Mathsoft Eng. & Education, Inc., Cambridge, MA
with increased SSA, and increasing the aspect ratio above $AR_c$ produced particles with platelet morphology.

TEM images shown in Figure 4.8 (a) show that trial 12 with additional water added to the solvent gave particles with an aspect ratio of $\sim 1.5$. Trial 13 with intermediate water content (no additional water added and no hold at 200°C) gave particles with an aspect ratio of $\sim 2.2$, as shown in Figure 4.8 (b) Finally, Trial 14 with the least water content (no additional water added and suspension held at 200°C for 1 hr) gave particles with an aspect ratio of $\sim 5.0$, as shown in Figure 4.8 (c) A high resolution TEM image of a particle from trial 14, shown in Figure 4.4 confirmed that the particles had the large face as (0001) basal plane of $\alpha$-$\text{Al}_2\text{O}_3$. Section analysis of multiple images obtained by tapping mode AFM (one such analysis is shown in Figure 4.5), confirmed that the particles obtained in trial 14 had a face diameter of $70 \pm 10$ nm and a thickness equal to $15 \pm 5$ nm, thus having platelet morphology with aspect ratio of $5 \pm 1$.

The plot for aspect ratio against SSA (Figure 4.11) correlates to the observation that SSA for the platelet particles increases with anisotropy. As shown in the TEM micrographs, the anisotropy in the synthesized nanoparticles increases with decreasing water content. Trials 14 had the least water content and a maximum SSA of $35 \text{ m}^2/\text{gm}$ and maximum anisotropy of $AR \sim 5.0$. Trial 13 had an intermediate water content, an intermediate SSA of $28 \text{ m}^2/\text{gm}$ and an intermediate anisotropy of $AR \sim 2.2$. Trial 12 had the maximum water content, the least surface area of $18 \text{ m}^2/\text{gm}$ and the least anisotropy of $AR \sim 1.5$ for the synthetic conditions used for this study.
4.4 Conclusions

Phase pure alpha-alumina was produced under glycothermal conditions with sizes less than 100 nm by seeding with $\alpha$-$\text{Al}_2\text{O}_3$ particles. It is probable that secondary nucleation takes place during the synthesis process, producing additional seed particles. Under seeded conditions $\alpha$-$\text{Al}_2\text{O}_3$ particles can be produced at temperatures as low as 235 °C, but the reaction time required at low temperatures are as long as 72 hr. An optimum stirring speed of 240 rpm was found, with stirring rate above this limit having no additional effect on the rate of secondary nucleation. A more complete kinetic study is required with varying seed size and concentration to suggest models for optimizing the seed size, concentration and time of reaction to achieve finer nanoparticles at lower transformation temperatures and less time. However, the zero order mechanism indicated by the preliminary kinetic study is consistent with prior studies by Rossetti et al. and Moon et al. on similar systems. Further studies of the experimental parameters should be carried out to more fully develop a theoretical model specific to secondary nucleation under glycothermal synthesis conditions.

Control of particle morphology is obtained by controlling the water content in the solvent. The work reported on morphology control under seeded conditions is shows the feasibility of the process for nanoscale alpha-alumina. Since, the transformation mechanisms and kinetics have changed between the unseeded and seeded experiments; a more detailed investigation is required to control the morphology of particles synthesized under seeded conditions. Schemes should be developed to recover well dispersed nanoparticles after synthesis. This will aid in characterizing individual particles by TEM.
and AFM techniques and will help obtain statistically significant data from multiple particles to determine particle size and aspect ratio.

4.5 References


Table 4.1. Summary of synthesis conditions to investigate the role of treatment temperature. The corresponding specific surface area (SSA) of the powder measured by BET, and the primary particle size calculated as equivalent spherical diameter (ESD). All trials had a solids loading of 10gm/250ml of gibbsite/1, 4-butanediol.

<table>
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<th>Trial</th>
<th>Precursor Pre-treatment (KF Water, vol%)</th>
<th>Temp. (oC)</th>
<th>Time (hrs)</th>
<th>Stirring Speed (rpm)</th>
<th>Seed Size (nm)</th>
<th>Seed Conc. (No. particles/ml)</th>
<th>SSA (m²/gm)</th>
<th>ESD (nm)</th>
<th>Width, D (nm)</th>
<th>Height, H (nm)</th>
<th>AR=D/h (Aspect Ratio)</th>
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Table 4.2. A quantitative trace element analysis by XRF. The results indicate that the glycothermally synthesized $\alpha$-Al$_2$O$_3$ had an average purity of 99.96±0.02 w/o (w/o-weight percent).

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<th>Impurity (ppm)</th>
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$^*$ Impurity from precursor gibbsite
Figure 4.1. Flow sheet showing the additives and methodology in the synthesis of α-Al₂O₃ nanoparticles under glycothermal conditions.
Figure 4.2. TEM micrograph of 75 nm seed particles, collected after repeated centrifugation and collection of fine particles from commercial slurry of α-Al₂O₃ nanoparticles from Saint Gobain (Grade: Alumina 9245).
Figure 4.3. X-ray diffraction pattern for $\alpha$-Al$_2$O$_3$ nanoparticles glycothermally synthesized at 235$^\circ$C.
Figure 4.4. Change in gibbsite (Al(OH)$_3$), boehmite (AlOOH) and $\alpha$-alumina ($\alpha$-Al$_2$O$_3$) concentration with treatment time under glycothermal condition for synthesis of $\alpha$-alumina from 0.5 M gibbsite in 1,4-butanediol at 300 °C with 1.5x10$^{12}$ seeds/ml. (The lines on the plot are just to guide the eyes)
Figure 4.5. Johnson-Mehl-Avrami (JMA) plot for fraction of crystallized $\alpha$-Al$_2$O$_3$ synthesized under glycothermal condition from 0.5 M gibbsite in 1, 4-butanediol at 300 °C with 1.5x10$^{12}$ seeds/ml. It is observed that the transformation of gibbsite to $\alpha$-Al$_2$O$_3$ under seeded condition is by a zero order mechanism.
Figure 4.6. Solubility and alpha alumina phase fraction as a function of time. The materials were held for 6 hours at 200°C followed by a rapid temperature increase to 275 °C for the duration of the experiment. (The lines are used for guidance)
Figure 4.7. Seeding with large sized (~ 1 µm) α-Al₂O₃ particles with 3.3x10¹² seed/ml, show multiple nucleation taking place over the seed particles. Synthesis was done for 36 hrs at 300ºC with stirring speed of 480 rpm.
Figure 4.8. Selected TEM micrographs of $\alpha$-Al$_2$O$_3$ nanoparticles obtained from: (a) Trial 12- Additional 10 ml DI Water, No hold @ 200 °C ($H_2O$: 3.5%), (b) Trial 13- No additional DI Water, No hold @ 200 °C ($H_2O$: 2.6%), and (c) Trial 14- No additional DI Water, 1 hr hold @ 200 °C ($H_2O$: 1.75%).
Figure 4.9. Type Caption Here High resolution TEM micrograph of $\alpha$-Al$_2$O$_3$ nanoparticle obtained from trial 14, confirming the presence of (0001) basal plane as the large face.
Figure 4.10. Platelet morphology of $\alpha$-Al$_2$O$_3$ nanoparticles, obtained from trial 14, was confirmed by AFM section analysis.
Figure 4.11. Type Caption Here Schematic of hexagonal platelet particle and plot for change in specific surface area (SSA) changing aspect ratio (AR) for particles having same volume. Minimum in aspect ratio is shown at the critical aspect ratio $AR_c \sim 1.0$. 
Chapter 5

Effect of Surface Hydration on Aggregation of Nanophase Alumina

5.1 Introduction

Understanding the aggregation of nanophase materials is a crucial step towards commercializing the promises of nanotechnology based on nanoparticles [1-3]. Aggregation is a critical issue in the processing and handling of nanophase materials in commercially viable volumes, and poses challenges towards fabrication of bulk materials and devices [1, 3-5]. Typical problems in handling nanoparticles in bulk quantities are clogging of pipelines, loss of rheological properties, flocculation and gelation. Consolidation of aggregated materials compromises the packing density of green bodies and the final microstructure of the bulk materials [1, 6], thus compromising the advantages of “nano-properties” from fabricated materials and devices. The work reported here is a step towards understating aggregation in nanophase materials by combining theoretical modeling with experimental results. We propose that surface hydration in nanophase materials, especially metals, metal-oxides and metal-hydroxides (collectively addressed as metal/hydr(oxides) in this article), enhances aggregation with aging or shelf life of nanophase materials, even under ambient conditions. Understanding the aggregation mechanism and the chemical nature of the aggregates are required to develop de-aggregation and dispersion schemes for nanophase alumina particles. The de-
aggregation and dispersion schemes were developed based on the current study as will be explained in a separate follow up article [7].

As a universal rule, all inorganic materials have some degree of hydration from absorbed moisture from the atmosphere or residual water from the synthesis and processing that are trapped in their pores or chemical structure [8-11]. The degree of surface hydration increases with the surface area of the material; therefore nanophase metal/hydr(oxides) particles can have a significant weight percent of H$_2$O on their surface [12, 13]. Coverage of OH groups on the surface of metal/hydr(oxides) has been shown to largely determine their adsorption behavior and surface reactivity [8, 14-18]. The presence of labile hydroxyl groups on the surface of metal/hydr(oxides) has been shown to increase the connectivity of particle networks in sol-gel derived silica by condensation reactions at the surface of the particles [14, 19]. Water present on the surface of the particles can act as an adhesive in joining two particles. Several bonds can form due to the surface water, water between the particles can hydrogen bond neighboring particles, hydroxyl groups from adjacent particles can hydrogen bond with each other, or form ester type oxide bridges (M-O-M) by condensation of a water molecule, forming aggregated network of particles. The proposed scenarios are depicted in terms of the chemical reactions:

\[ \text{M-O + H}_2\text{O} + \text{M-O} = \text{M-O----H}_2\text{O----O-M} \]  \hspace{1cm} [5.1 (a)]

\[ \text{M-OH} + \text{M-OH} = \text{M-OH----HO-M} \]  \hspace{1cm} [5.1 (b)]

\[ \text{M-OH} + \text{M-OH} = \text{M-O-M + H}_2\text{O} \]  \hspace{1cm} [5.1 (c)]
These reactions, at the surface of adjacent particles with surface hydration, can go on for months during storage of the particles, increasing the state of aggregation of the powder [19].

Alumina is one of the most widely used inorganic materials. Due to its abundance in nature, occurrence in various allotropic and hydrated forms, and availability in wide range of shapes and sizes, alumina finds applications in a wide range of industries [20]. Thus, for the current study, we chose nanophase alumina to be ideally suited for the development of fundamental understanding on the nature of surface interactions causing aggregation in nanophase metal/hydr(oxides). Aggregation in nanophase aluminas is a critical problem that occurs during processing and fabrication of bulk materials. Peptization or dispersion of alumina particles to a stable colloidal state is a key step in the preparation of wash-coat slurries, attrition-resistance spray dried microspheres, catalytic extrudates and beads and bulk ceramic components through powder processing [21-24].

The present article focuses on understanding the aggregation behavior in alumina nanoparticles. The state of surface hydration and aggregation were experimentally determined for different nanophase aluminas. A series of semi-emperical calculations were used to study the interactions of water molecules with cluster models of alumina. The modeling of hydration and aggregation of alumina clusters was done using PM5 semiempirical parameters as implemented in CAChe worksystem. Theoretical infrared (IR) spectra were generated for different cluster sizes with and without surface hydration,

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for bridged alumina clusters, and were compared to the experimental IR spectra to show the existence of particle-particle bridges between alumina nanoparticles with excess surface hydration.

5.2 Computational Method

Molecular dynamics simational technique was used to generate the theoretical transmission IR spectra for alumina clusters using, CAChe™ worksystem version 5.1.25 The molecular dynamics simulation method is based on Newton’s second law or the equation of motion, \( F = ma \), where \( F \) is the force exerted on the particle, \( m \) is its mass and \( a \) is its acceleration [25]. From knowledge of the force on each atom, it is possible to determine the acceleration of each atom in the system. Integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time. The method is deterministic; once the positions and velocities of each atom are known, the state of the system can be predicted at any time.

From this trajectory, the average values of properties can be determined. The MOPAC (Molecular Orbital Package) application containing PM5 semi-empirical parameters was used for the calculations. MOPAC is a quantum-mechanical method that uses the Schrödinger equation to determine bond strengths, atomic hybridizations, partial charges, and orbitals from the positions of the atoms and the net charge. The molecular orbitals, heat of formation, and molecular geometry derivatives obtained can be used to

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calculate vibrational spectra, molecular geometries, force constants, and other properties of molecules, radicals, and ions. These quantities are used to calculate reaction trajectories and to investigate chemical reactions by locating transition states. The thermodynamic data on free energy of formation ($G_f$), heat capacity ($C_p$), enthalpy of formation ($H_f$) and entropy of formation ($S_f$), obtained by MOPAC, can be used to calculate an operational free energy ($G$) with the formula:

$$\Delta G^o = \Delta H^o - T \Delta S^o$$  \[5.2\]

where, $T$ is temperature in °K [26, 27].

CAChe also plots the vibrational spectra for a molecule, created by coordinated motions of the atoms, as electromagnetic radiation in the IR region is absorbed by the molecule. Absorption bands observed in the IR region are associated with the bending and stretching of particular types of bonds, so the IR vibrational spectra aid the analysis of molecular structure. CAChe uses quantum mechanics to compute the force necessary to distort the molecule from its equilibrium geometry and predict the frequency of vibrational transitions. When a point is selected on the vibrational spectrum, motion vectors for every atom appear in the workspace. For a more detailed discussion on CAChe computational software and quantum-mechanical method of calculations readers are referred to CAChe user guide, provided by Fujitsu Limited [26].

### 5.3 Materials and Methods

Nanophase aluminum hydr(oxides) with varying state of hydration and allotropic forms, were provided by W. R. Grace & Co.-Conn., Columbia, Maryland. The powders
were characterized for phase by Scintag X-ray diffractometer\textsuperscript{26} (XRD), specific surface area (SSA) by Gemini 2370 BET,\textsuperscript{27} and particle size by light scattering using Malvern Mastersizer.\textsuperscript{28} Degree of surface hydration was characterized by thermogravimetric analysis using Simultaneous Differential Techniques (SDT),\textsuperscript{29} capable of performing simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) / differential thermal analysis (DTA) at high temperatures.

5.3.1 Estimation of Degree of Excess Hydration

The degree of excess hydration was estimated as \textit{excess water content} ($W_x$) in the powder. TGA was used to determine the weight loss in powders by heating in air from room temperature to 1200 °C at 5 °C/min. Weight loss from room temperature to 125 °C was attributed to evolution of physically adsorbed water and weight loss between 125 °C – 1200 °C was attributed to the evolution of chemically adsorbed water and stoichiometric water of hydration that was, present as hydroxyl groups in the lattice structure. Heating of hydrated phases to the stable phase of $\alpha$-Al$_2$O$_3$, existing above about 1100 °C, releases water of dehydration by condensation of hydroxyl groups [20]. The \textit{total weight loss} ($W_\theta$), between room temperature to 1200 °C, was adjusted to the \textit{dry weight of powder} ($P_\delta$) i.e. \textit{weight of completely hydrated alumina} ($A_\delta$) + \textit{weight loss due to dehydration of stoichiometric water} ($W_\delta$) of lattice hydroxyls. Stoichiometric

\textsuperscript{26} Scintag, USA, Cu K$\alpha$, $\lambda$ = 1.54 Å
\textsuperscript{27} Micromeritics Instrument Corporation, Norcross, GA
\textsuperscript{28} Malvern Instruments Ltd. Malvern, UK
\textsuperscript{29} TA Instruments, New Castle, DE
weight loss from Boehmite and alpha-alumina were taken as 15% and 0%, respectively. The Degree of excess surface hydration \( (W_x) \) was calculated by subtracting stoichiometric weight loss \( (W_s') \) from adjusted total weight loss \( (W_t') \) between room temperature to 1200 °C, as equations represented below:

\[
W_x = W_t' - W_s' \quad [5.4]
\]

\[
W_t' = \frac{W_t}{A_s + W_s} \quad [5.3]
\]

5.3.2 Estimation of Primary Particle Size

SSA measurements were performed on all the alumina samples by Brunauer-Emmett-Teller (BET) technique. Samples were preheated at 125°C under nitrogen before performing the surface area measurements. An estimation of the primary particle size calculated as equivalent spherical diameter (ESD) was made using following equation:[28]

\[
ESD(nm) = \frac{6}{SSA(m^2 / gm) \times \rho (g / cm^3)} \times 1000 \quad [5.5]
\]

where, \( \rho \) is the density of the powder.

5.3.3 Estimation of State of Dispersion

States of dispersion of as-received powders were estimated by calculating average agglomeration number (AAN). AAN gives an estimation of the number of primary particles in an agglomerate/aggregate. AAN is calculated by taking the ratio of the
volume of the agglomerate/aggregate to the volume of the primary particle [29]. Volume of agglomerate/aggregate is calculated from its median size, represented as D50%, estimated from particle size distribution obtained by light scattering using a Malvern Mastersizer. Volume of a primary particle is calculated from the ESD by BET. Both D50% and ESD should have the same units. The equation for AAN can be simplified as shown below:

\[
AAN = \frac{(D50\%)^3}{(ESD)^3}
\]  

\[5.6\]

5.3.4 Determination of Experimental FTIR Spectra

Transmission IR spectra of the nanophase alumina samples were collected using a nitrogen gas purged Nicolet Nexus 470 FT-IR spectrometer. Spectra were measured between 4000-650 cm\(^{-1}\) at 2 cm\(^{-1}\) resolution. To optimize the signal to noise ratio, 128 scans were averaged per spectrum. Background spectra were measured by transmitting an IR beam through a KBr pellet approximately 1 mm thick, which were pressed from 0.3 gm of vacuum dried (12 hr at 200°C) KBr powder. Alumina samples were prepared by thoroughly mixing 0.003 gm of nanophase alumina powder and 0.297 gm of KBr by using a mortar and pestle. The ground powder mix was pressed into translucent discs about 1 mm thick. IR spectra were obtained immediately after pellets were removed from the press, to avoid moisture pickup from environment.
5.3.5 Optimization and Determination of Theoretical IR Spectra for Alumina Clusters

The alumina raw clusters were generated by cropping a larger $\alpha$-Al$_2$O$_3$ cell, but maintaining the $\alpha$-Al$_2$O$_3$ lattice structure. The clusters were chosen such that they assumed a nearly spherical configuration avoiding sharp edges or protrusions to minimize lattice distortions on relaxation. The raw clusters, shown in Figure 5.1 (Column I), are represented as R2, R4, R12 and R16 and have the formula Al$_n$O$_{3n/2}$; where, n = 2, 4, 12 & 16 (number of Al atoms), respectively. Theoretical calculations of larger alumina clusters, comparable to the size of nanoparticles (~10nm), were limited by the computational cost including both computer capability and simulation time. The individual clusters were optimized and IR spectra were generated using the MOPAC-PM5 application as implemented in the CAChé worksystem.

A water molecule was brought near to the surface of the optimized clusters and allowed to relax, followed by generation of IR spectra. The individual clusters with the same number of Al atoms were then bridged to simulate aggregated nanoparticles. The clusters were bridged in two ways as proposed in the hypothesis represented as Equations 5.1 (a) and (c). First, by condensation of a water molecule from individual hydrated clusters, and secondly, by dissociation of a water molecule between two optimized unhydrated clusters. The chemical reactions for bridge formation between the clusters are listed in Table 5.1. The cluster arrangements were then relaxed to obtain optimized geometry and generate IR spectra by using -PM5 optimization in CAChé™ worksystem.
5.4 Results and Discussions

5.4.1 Degree of Excess Hydration and Aggregation/Agglomeration in Nanophase Aluminas

Characterization of powders, provided by W. R. Grace & Co.-Conn., Columbia, Maryland, for phase, degree of excess hydration, ESD, D50%, and AAN, are provided in Table 5.2. XRD data indicated that the sample precipitated at 200°C (S200) was Boehmite ($\gamma$-AlOOH) and further calcinations at 700°C (S700), 1000°C (S1000) and 1300°C (S1300) transformed this material to gamma-alumina ($\gamma$-Al$_2$O$_3$), a mixture of gamma-alumina ($\gamma$-Al$_2$O$_3$) and delta-alumina ($\delta$-Al$_2$O$_3$), and alpha-alumina ($\alpha$-Al$_2$O$_3$), respectively. The degree of excess hydration measured as excess water content from TGA data show that the excess water content in the nanophase powders decreased as the sample was heated to higher temperatures. Sample S200, precipitated at 200°C, had excess water content of 23.9%. Excess water content decreased to 7.2%, 4.3% and 0.8% upon calcination to 700°C, 1000°C and 1300°C, for samples S700, S1000 and S1300, respectively. Samples with higher degree of excess hydration show higher degree of aggregation/agglomeration. Samples S200, S700, S1000 and S1300 had AAN measured as $7.0 \times 10^{11}$, $1.3 \times 10^9$, $3.2 \times 10^8$ and $6.7 \times 10^4$, respectively.

Due to high surface area, nanoparticles have high surface hydroxyl to mass ratio [12, 14, 19], giving more reactive sites for the particle-particle bridge formation, as proposed in the current work. Also, the high solubility of the nanoparticles due to high capillarity or curvature effects leads to dissolution and precipitation of hydroxides species on the surface of the metal/hyd(oxides) particles [1, 30]. Precipitation of dissolved
species is favored between the crevices and necks between the particles, due to their negative curvature. Upon aging, the precipitated hydroxides can form strong bridges among the particles, causing them to aggregate into a stiff network of particles. The extent of aggregation in nanoparticles has been known to depend on the history of the particles, temperature, pH, concentration and the type of solvent [14, 19].

5.4.2 Optimization and Determination of Theoretical IR Spectra for Alumina Clusters

5.4.2.1 Individual Alumina Clusters

Individual alumina clusters with formula AlₙO₃ₙ/₂, where n = 2, 4, 12 and 16, were optimized using the MOPAC-PM5 semiempirical parameter as implemented in the CAChe™ worksystem. The optimized alumina clusters are shown in Figure 5.1 (column II). Theoretical transmission IR spectra for optimized alumina clusters are shown in Figure 5.2, and the vibration peak assignments are listed in Table 5.3. For the optimized alumina clusters, multiple vibration peaks were generated between 85-933 cm⁻¹, corresponding to the bending and stretching of Al-O type bonds in the bulk and surface of alumina clusters. The theoretically determined vibration range for Al-O bonds correspond closely to the experimentally observed range of 400-1200 cm⁻¹ for various aluminas reported in literature [20, 31]. As the cluster size increases, the absorbing wave numbers start overlapping one another, making the absorption peaks more continuous. The range of adsorption wavelength also increased with increasing cluster size. This may
be due to increased contribution from higher number of atoms on the surface of the clusters and changes in the local environment of the atoms [32].

5.4.2.2 Alumina Clusters with Surface Hydration

One water molecule was brought close to each of the optimized clusters, shown in Figure 5.1 (column II) and the structures allowed to relax and optimize to a new geometry as shown in Figure 5.1 (column III). Upon relaxation the water molecule dissociated forming two hydroxyl groups on the surface of the cluster. The hydroxyl group of dissociated water (O_w-H, w→ oxygen from water) adsorbs the Lewis acid site of the surface Al atom. The second hydroxyl group (O_s-H, s→ oxygen from alumina surface) is created by adsorption of the dissociated proton, from water, on to the Lewis base site of surface O atoms [8, 33, 34]. Molecularly adsorbed water on the oxide surfaces has been reported to be metastable and dissociates readily, even in the absence of defects, to give two distinct types of surface hydroxyl groups [9, 35].

The optimized cluster geometries with surface hydroxyls are shown in Figure 5.1 (column III). The corresponding theoretical transmission IR spectra for hydrated alumina clusters are shown in Figure 5.3, and the vibration peak assignments are listed in Table 5.3. Bending and stretching modes for Al-O bonds were generated below 922 cm⁻¹, similar to those generated for optimized alumina clusters (Figure 5.2). New IR vibration peaks were generated due to the presence of hydroxyl groups. Adsorption peaks due to stretching of hydroxyl groups on the surface of alumina clusters were generated between 3171-3326 cm⁻¹. The hydroxyl stretching modes for O_s-H and O_w-H bonds were
separated by approximately 50 cm\(^{-1}\) for each cluster, and were observed between 3171-3267 cm\(^{-1}\) and 3288-3326 cm\(^{-1}\), respectively, depending on the location of the hydroxyl group and the geometry of the alumina clusters. The hydroxyl bending modes were generated below 900 cm\(^{-1}\) and overlapped with the bending and stretching modes of bulk and surface Al-O bonds. Also, Al-O\(_n\) (bond between Al on cluster surface and O from hydroxyl group adsorbed after dissociation of water) stretching modes were generated between 907-980 cm\(^{-1}\).

The experimentally observed hydroxyl stretching modes for hydrated alumina phases have been reported between 3000-3800 cm\(^{-1}\) and the bending modes are reported between 950-1100 cm\(^{-1}\) [20, 31, 35, 36]. The experimentally measured wave numbers have a broad range due to variations in the length of the O-H bonds. The length of the O-H bonds is dependent on the type of coordination of surface atoms, which determines the extent of Lewis acidity or basicity of the surface Al and O atoms, respectively [32, 37].

### 5.4.2.3 Bridged Alumina Clusters

Optimized alumina clusters were bridged by either condensation of a water molecule between two hydroxylated clusters of the same size or dissociation of a water molecule between two optimized alumina clusters of the same size. The reactions for bridging alumina clusters and the standard free energy calculated for the reactions from thermodynamic values obtained by CAChe calculations are listed in Table 5.1. The standard free energy for bridge formation by condensation was calculated between –86 to –36 KJ/mol, and that for bridge formation by dissociation was calculated between –762
to –386 KJ/mol. Since the standard free energies for all the reactions were negative at 298 °K, the bridge formation between alumina clusters can take place at ambient conditions in the presence of surface hydration. Thus, it can be deduced that the presence of water molecules between nano-alumina particles can cause bridging between nanoparticles and lead to aggregation of particles.

The optimized cluster geometry for the bridged alumina clusters formed by condensation and dissociation are shown in Figure 5.4 (Column I and Column II), respectively. The corresponding theoretical transmission IR spectra for the bridged alumina clusters are shown in Figure 5.6, and the vibration peak assignments are listed in Table 5.3. Bending and stretching of Al-O bonds were generated below 1027 cm\(^{-1}\), similar to those generated for optimized alumina clusters and hydrated alumina clusters. Bending modes for O-H bonds were generated below 909 cm\(^{-1}\), also similar to those for hydrated alumina clusters. The stretching mode for O\(_{w}\)-H was lost in bridged clusters formed by condensed H\(_2\)O between O\(_{w}\)-H groups on bridging clusters. But, new IR peaks were observed between 1035-1049 cm\(^{-1}\) for stretching of the Al-O\(_{w}\)-Al bonds bridging the two clusters. The Al-O\(_{w}\)-Al vibration peak did not change much with the size of the cluster, and can be said to be characteristic for Al-O\(_{w}\)-Al ester type bonds between the clusters. The stretching of O\(_s\)-H bonds remained the same between 3169-3266 cm\(^{-1}\) for clusters bridged by condensation of O-H groups on surface of clusters.

Dissociation of a water molecule between two clusters generated new IR vibration peaks between 3128-3160 cm\(^{-1}\) due to stretching of Al-(O\(_{w}\)H)-Al bonds joining two clusters. The O\(_s\)-H bonds on the alumina clusters were shifted to 2685 cm\(^{-1}\) and 3076 cm\(^{-1}\) for clusters D12 and D16, respectively, as the proton on the hydroxyl group was shared
between the bridging clusters. For cluster D4, the symmetry of the two joining alumina clusters equally shared the proton between the two clusters, giving three splitting peaks for stretching and bending of $\text{O}_2\text{H-O}_3$ bonds at 991, 1305 and 1471 cm$^{-1}$. Also, multiple stretching modes for Al-O bonds bridging two clusters were observed below 779 cm$^{-1}$, overlapping with multiple surface O-H bending modes and bulk and surface Al-O stretching and bending modes.

5.4.3 Comparing Experimental and Theoretical IR Spectra for Nanophase Alumina

Experimentally determined transmission IR spectra for the nanophase alumina powders, listed in Table 5.2, are shown in Figure 5.6. Observation from the IR spectra for nanophase aluminas shows that, heating of hydrated powder causes a gradual loss of intensity for vibration modes to lose intensity due to hydroxyl groups. Thus, the spectra give evidence for dehydration and dehydroxylation of the samples with heat treatment. The IR spectrum becomes very smooth for sample S1300, heated to 1300 °C, except for absorption below 1000 cm$^{-1}$, characteristic of stretching and bending modes for Al-O type bonds in bulk and surface of alumina. The multiple peaks observed between 900-1600 cm$^{-1}$, for samples S200, S700 and S1000 can be assigned to surface hydration and bridge formation between nanophase alumina particles. For sample S200, broad adsorption peaks observed between 1800-2500 cm$^{-1}$ and 3050-3200 cm$^{-1}$ and the split peaks at 1070 cm$^{-1}$ and 1150 cm$^{-1}$ correspond to multiple adsorption peaks for vibration modes of O-H groups present in the bulk of boehmite particles [31, 36, 38].
Though the vibration peaks for the experimental IR spectra are not as definitive as for theoretically calculated spectra, we can find evidence of the role of excess hydration in causing aggregation in nanophase alumina particles. The varying degree of hydration on individual particles, distribution in size of primary particles and the varying degree of bridging between the particles can produce multiple adsorption peaks spread over a wide range, making it difficult to identify individual vibration peaks in experimental data. The adsorption peak observed between 1300-1600 cm$^{-1}$ for samples S200, S700 and S1000 is due to the presence of free and physisorbed water molecules on the surface of the nanoparticles [20, 38].

Theoretical IR spectra for bridged clusters have shown that the presence of water between alumina clusters can bridge the two clusters by dissociation of a water molecule and formation of Al-(O$_w$H)-Al type bonds, and sharing of a proton between the two clusters. These bonds have characteristic IR peaks between 2685-3160 cm$^{-1}$ and around 1400 cm$^{-1}$, similar to those observed in experimental IR spectra for nanophase alumina powders. Small shoulders are seen around 1040 cm$^{-1}$ for samples S700 and S1300 and medium to weak adsorption peaks, around the same wave number, are observed for samples S200 and S1000 in experimental IR spectra of nanophase alumina powders. These adsorption peaks correspond to Al-O$_w$-Al ester type bonds formed on bridging two hydrated alumina clusters by condensation of a water molecule, as determined by theoretical IR calculations. Thus, comparing the experimental to theoretical spectra for nanophase aluminas in unhydrated and hydrated states show evidence of bridge formation between alumina nanoparticles in the presence of excess hydration.
5.5 Conclusions

Physical characterization of nanophase alumina powders shows evidence of aggregation in nanoparticles. Increased amounts of excess hydration in the powder have been related to increased aggregation in nanophase aluminas. Theoretical calculations using MOPAC-PM5 optimization in CAChe worksystem have shown evidence that bridge formation in nanoparticles can take place under ambient conditions by either condensation of water molecules by joining hydroxyl groups on the surface of adjacent nanoparticles or by dissociation of water between the unhydrated nanoparticles. Evidence of bridge formation between the nanoparticles has been found by comparing IR vibration peaks for theoretically calculated IR spectra for unhydrated, hydrated and bridged alumina clusters, and experimentally observed IR spectra for nanophase alumina powders heat treated to different temperatures. Theoretical calculations of larger alumina clusters, comparable to the size of nanoparticles (~10nm), were limited by the computational cost including both computer capability and simulation time. Nonetheless, the approach to characterize the state of aggregation and mechanism of aggregation in nanophase materials using a combination of experimental and theoretical simulation techniques has been established. Future work will be focused towards making theoretical calculations on larger metal/hydr(oxides) clusters with multiple hydration and bridging sites to simulate more realistic nanoparticles.
5.6 References


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Table 5.1. List of reactions forming bridged alumina clusters by (a) Condensation of a water molecule by joining two adjacent hydrated clusters, and (b) Dissociation of a water molecule between two alumina clusters. The bridged clusters are shown in Figure 5.4. The standard free energy for the reactions (calculated from thermodynamic data obtained by MOPAC-PM5 optimization using CAChe™ worksystem) is negative for all cluster sizes at room temperature (298 °K), indicating that these bridges can form under ambient conditions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Condensation of Water</strong></td>
<td></td>
</tr>
<tr>
<td>$2 \text{Al}_2\text{O}_2 (\text{OH})_2 \rightarrow (\text{HO})\text{Al}_2\text{O}_2--\text{O}--\text{Al}_2\text{O}_2(\text{OH}) + \text{H}_2\text{O}$</td>
<td>-41</td>
</tr>
<tr>
<td>$2 \text{Al}_4\text{O}_5 (\text{OH})_2 \rightarrow (\text{HO})\text{Al}_4\text{O}_5--\text{O}--\text{Al}_4\text{O}_5(\text{OH}) + \text{H}_2\text{O}$</td>
<td>-48</td>
</tr>
<tr>
<td>$2 \text{Al}<em>{12}\text{O}</em>{17} (\text{OH})<em>2 \rightarrow (\text{HO})\text{Al}</em>{12}\text{O}<em>{17}--\text{O}--\text{Al}</em>{12}\text{O}_{17}(\text{OH}) + \text{H}_2\text{O}$</td>
<td>-36</td>
</tr>
<tr>
<td>$2 \text{Al}<em>{16}\text{O}</em>{23} (\text{OH})<em>2 \rightarrow (\text{HO})\text{Al}</em>{16}\text{O}<em>{23}--\text{O}--\text{Al}</em>{16}\text{O}_{23}(\text{OH}) + \text{H}_2\text{O}$</td>
<td>-86</td>
</tr>
<tr>
<td><strong>Dissociation of Water</strong></td>
<td></td>
</tr>
<tr>
<td>$2 \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow (\text{HO})\text{Al}_2\text{O}_2--\text{Al}_2\text{O}_3(\text{OH})$</td>
<td>-762</td>
</tr>
<tr>
<td>$2 \text{Al}_4\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{Al}_4\text{O}_6--(\text{HOH})--\text{Al}_4\text{O}_6$</td>
<td>-474</td>
</tr>
<tr>
<td>$2 \text{Al}<em>{12}\text{O}</em>{18} + \text{H}<em>2\text{O} \rightarrow \text{Al}</em>{12}\text{O}<em>{18}--(\text{OH})--\text{Al}</em>{12}\text{O}_{17}(\text{OH})$</td>
<td>-386</td>
</tr>
<tr>
<td>$2 \text{Al}<em>{16}\text{O}</em>{24} + \text{H}<em>2\text{O} \rightarrow \text{Al}</em>{16}\text{O}<em>{24}--(\text{OH})--\text{Al}</em>{16}\text{O}_{23}(\text{OH})$</td>
<td>-601</td>
</tr>
</tbody>
</table>
Table 5.2. List of alumina samples obtained form Grace (Columbia, Maryland), treatment temperature, phase identified by XRD, excess water content or degree of excess hydration measured by TGA, equivalent spherical diameter (ESD), median particle size (D50%) measured by light scattering and average agglomeration number (AAN). Powders with higher water content have higher degree of agglomeration.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Treatment Temp. (°C)</th>
<th>Powder Phase</th>
<th>Excess Water (%wt)</th>
<th>Equivalent Spherical Diameter, ESD (nm)</th>
<th>Median Particle Size, D50% (µm)</th>
<th>Average Agglomeration Number (AAN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S200</td>
<td>200</td>
<td>Boehmite</td>
<td>23.9</td>
<td>9</td>
<td>78</td>
<td>7.0 x 10^{11}</td>
</tr>
<tr>
<td>S700</td>
<td>700</td>
<td>γ−Alumina</td>
<td>7.2</td>
<td>9</td>
<td>10</td>
<td>1.3 x 10^{9}</td>
</tr>
<tr>
<td>S1000</td>
<td>1000</td>
<td>δ−Alumina + γ−Alumina</td>
<td>4.3</td>
<td>16</td>
<td>11</td>
<td>3.2 x 10^{8}</td>
</tr>
<tr>
<td>S1300</td>
<td>1300</td>
<td>α−Alumina</td>
<td>0.8</td>
<td>320</td>
<td>13</td>
<td>6.7 x 10^{4}</td>
</tr>
</tbody>
</table>
Table 5.3. Assignment of infrared vibrational peaks for optimized, hydrated and bridged alumina clusters. Please refer to Figure 1 and Figure 4 for the corresponding cluster codes.

<table>
<thead>
<tr>
<th>Cluster Code</th>
<th>Vibration Modes, Wave Number (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OₙH (S)</td>
</tr>
<tr>
<td><strong>Optimized Clusters</strong></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>-</td>
</tr>
<tr>
<td>O₄</td>
<td>-</td>
</tr>
<tr>
<td>O₁₂</td>
<td>-</td>
</tr>
<tr>
<td>O₁₆</td>
<td>-</td>
</tr>
<tr>
<td><strong>Surface Hydrated with 1 H₂O</strong></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>3326</td>
</tr>
<tr>
<td>H₄</td>
<td>3299</td>
</tr>
<tr>
<td>H₁₂</td>
<td>3288</td>
</tr>
<tr>
<td>H₁₆</td>
<td>3319</td>
</tr>
<tr>
<td><strong>Bridged by Condensation of 1 H₂O</strong></td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
</tr>
<tr>
<td><strong>Bridged by Dissociation of 1 H₂O</strong></td>
<td></td>
</tr>
<tr>
<td>D₂</td>
<td>3294</td>
</tr>
<tr>
<td>D₄</td>
<td>-</td>
</tr>
<tr>
<td>D₁₂</td>
<td>-</td>
</tr>
<tr>
<td>D₁₆</td>
<td>-</td>
</tr>
</tbody>
</table>

Oₙ → Oxygen from Water
O₂ → Oxygen from alumina surface
S → Stretching Mode
B → Bending Mode
M → Multiple peaks
<table>
<thead>
<tr>
<th>COLUMN I</th>
<th>COLUMN II</th>
<th>COLUMN III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Cluster</td>
<td>Optimized Cluster</td>
<td>Surface Hydrated with 1 H2O</td>
</tr>
<tr>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>R2: Al2O3</td>
<td>O2: Al2O3</td>
<td>H2: Al2O2 (OH)2</td>
</tr>
<tr>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>R4: Al4O6</td>
<td>O4: Al4O6</td>
<td>H4: Al4O5 (OH)2</td>
</tr>
<tr>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
<tr>
<td>R12: Al12O18</td>
<td>O12: Al12O18</td>
<td>H12: Al12O17 (OH)2</td>
</tr>
<tr>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
<tr>
<td>R16: Al16O24</td>
<td>O16: Al16O24</td>
<td>H16: Al16O24 (OH)2</td>
</tr>
<tr>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 5.1. The geometry for \( \text{Al}_2\text{O}_3 \) clusters with formula \( \text{Al}_n\text{O}_{3n/2} \) (\( n = 2, 4, 12 \) & 16; number of Al atoms); Column I: Raw Cluster, Column II: Optimized Cluster, and Column III: Surface Hydrated with 1 H2O. Clusters were generated and optimized; using MOPAC
Figure 5.2. Theoretical transmission infrared (IR) spectra generated using, using MOPAC as implemented in CAChe software, for unhydrated alumina clusters shown in Figure 1, Column II. IR peaks below 933 cm\(^{-1}\) are due to stretching and bending of Al-O type of bonds in the bulk and surface of alumina clusters.
Figure 5.3. Theoretical transmission infrared spectra generated, using MOPAC as implemented in CAChe software, for alumina clusters with hydroxyl groups on the surface, shown in Figure 1, Column III. IR peaks above 3171 cm$^{-1}$ are due to stretching and bending of hydroxyl groups on the surface of alumina.
<table>
<thead>
<tr>
<th>COLUMN I</th>
<th>COLUMN II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensation of 1 H₂O</td>
<td>Dissociation of 1 H₂O</td>
</tr>
<tr>
<td>C2: (HO)Al₂O₂--O--Al₂O₂(OH)</td>
<td>D2: (HO) Al₂O₃--Al₂O₂(OH)</td>
</tr>
<tr>
<td>C4: (HO)Al₄O₅--O--Al₄O₅(OH)</td>
<td>D4: Al₄O₆--(HOH)-- Al₄O₆</td>
</tr>
<tr>
<td>C12: (HO)Al₁₂O₁₇--O--Al₁₂O₁₇(OH)</td>
<td>D12: Al₁₂O₁₈ --(OH)-- Al₁₂O₁₇(OH)</td>
</tr>
<tr>
<td>C16: (HO)Al₁₆O₂₄--O--Al₁₆O₂₄(OH)</td>
<td>D16: Al₁₆O₂₄ --(OH)-- Al₁₆O₂₃(OH)</td>
</tr>
</tbody>
</table>

![Aluminium Oxygen Hydrogen](image)

**Figure 5.4.** The optimized geometry of the bridged alumina clusters caused by condensation (*Column I*) or dissociation (*Column II*) of water on the surface of the clusters.
Figure 5.5. Theoretical transmission infrared spectra for bridged alumina clusters, shown in Figure 4. IR peaks between 1000 cm$^{-1}$ to 2500 cm$^{-1}$ are due to stretching of hydroxyl groups or Al-O$_x$-Al bonds, bridging two clusters.
Figure 5.6. Experimental transmission infrared spectra for aggregated nanophase alumina powders summarized in Table 5.2. Heating of hydrated powder to higher temperatures gradually looses intensity for vibration modes due to surface hydration or bridging.
Chapter 6

Optimized De-aggregation and Dispersion of High Concentration Slurry of Nanophase Alumina by Chemically Aided Attrition Milling

6.1 Introduction

Bulk quantities of aggregate/agglomerate-free nanoparticles are needed to advance the commercialization of nanotechnology via powder routes [1-3]. Nanoparticles are successfully being synthesized in bulk quantities using solution, solid-state, and plasma arc synthesis techniques [4-9]. Unfortunately, the synthesized nanoparticles are rarely stored or transported in the dispersing medium, but the powders are dried before storage and transportation. The end user then tries to re-disperse the powder into a dispersing medium such as water, alcohol, or oil before processing to form the final product [10]. Drying affects the concentration of surface hydroxyl groups, the precipitation of surface hydroxyl species and the degree of bonding among the particles leading to agglomerated powders[11-13]. High surface area nanophase powders adsorb significant amounts of water and other gases that affects the reactivity of surface hydroxyl groups [14, 15]. Aging of nanophase powder under such conditions forms permanent bridges between the particles, even under relatively low temperature ambient conditions [16]. Bridging can lead to neck formation, which results in aggregated particles impossible to process into bulk materials.
The challenge comes in re-dispersing, processing and handling nanophase powder in highly concentrated slurries for processing in manufacturing plants. Clogged pipelines, poor flow properties, flocculation and gelation are some of the typical problems in processing aggregated nanoparticles. Aggregation is also a critical issue in compaction and densification of starting powder fabricated bulk materials and devices [1, 3, 17, 18]. Consolidation of aggregated materials compromises the packing density of green bodies and the final microstructure of the bulk materials [1, 19, 20].

The objective of the current research is to achieve highly concentrated slurries of well-dispersed nanoparticles with near primary particle dimensions. Alumina was chosen as the material for current research since it is one of the most widely used commercial inorganic materials [21]. In first part of this study, the influence of surface hydration on aggregation of nano-alumina particles was explored through molecular dynamic simulation of nano-alumina clusters and infrared (IR) investigation of aggregated nano-alumina powders [16]. It was concluded that nanoparticles have strong bridging oxygen by condensation and/or dissociation of water molecules between the nanoparticles, even under ambient conditions. The second part of the research is focused towards breaking the bridges among the nanoparticles using a chemically aided milling (CAM) technique.

Ultrafine milling/de-aggregation of ceramic particles by a CAM process has been reviewed by Mandanas et al. [22]. The two main advantages of CAM are (i) increased feed rate, and (ii) production of finer particles at constant feed rate [23]. The mechanism of de-aggregation in a CAM processes is similar to that of “stress corrosion cracking.” Experimental and theoretical studies have shown that reactive species (e.g. water or ammonia), can attack at strained bonds in pre-existing surface flaws. Preferential
dissolution at the highly strained crack tips can promote crack growth to a critical flaw size, at which point the flaw becomes unstable and rapid crack propagation can cause the material to fail [24-26]. However, flow density arguments maintain that it is impossible for milling to produce particles less than about 1 µm. In the current work, we will show that the combination of good colloidal dispersion of the aggregated powder combined with the optimized milling variables can lead to a rapid reduction in the aggregated particle size. In a CAM process, grain boundary cleavage at strained bridges among the aggregated particles, promotes de-aggregation under suitable chemomechanical environments. Therefore, solvent chemistry during CAM should be selected such that the material being milled has some degree of elevated solubility in the solvent [10, 22].

In preliminary milling trials, the process condition to achieve the best dispersed state for partially calcined alumina were established, but milling below about 1 micron particle sizes was not achieved. The multiple factors that contribute to successful milling are almost all inter-dependent. Thus, a design of experiment approach was taken to sort out the variables that can produce a main effect on the ability to reduce particle size in polycrystalline aggregates of nanoscale powders. DOE was also found to be useful to establish the interdependence among the variables. Milling is a complicated dynamic process that involves simultaneous events including breakage of particles, breakage of aggregates and agglomeration. The resulting particle sizes obtained by milling are controlled by the material and aggregate properties. The available breakage mechanisms, and the energy or power input during milling [27-29]. The most important conceptual advantage of “attrition milling” is that all the energy or power input is used directly to agitate the media and the suspension, and not used in rotating or vibrating the heavy tank
along with the media, as in vibratory mill or conventional ball mill [30]. The random tumbling of media created inside the attrition mill causes irregular movement instead of group movement, giving more action during milling. A combination of impact, abrasion and shear from collision, flow, rotation and tumbling of media, and similar interaction between the particles results in size reduction as well as good dispersion in much shorter time [30].

The grinding time \( t \) in an attritor is related to the media size \( (MS) \) and agitator shaft speed \( (RPM) \) by the following equation [30]:

\[
t = \frac{K(MS)^3}{\sqrt{RPM}}
\]

where, \( K \) is a constant depending upon the type of slurry, type of media, and equipment being used. From Equation [6.1], decreasing the media size decreases grinding time. Since there are more media in a given volume, there are more surface collisions, abrasion and shear actions occurring during milling. However, using extremely small media may not be very efficient as the impact force of the media is proportional to the mass of the media. Also, the cost of milling and contamination are expected to increase due to larger surface area available for media wear. Equation [6.1] also suggests that increasing the shaft RPM can decrease the milling time. However, energy efficiency may be compromised by using a RPM that is too high requiring additional power to run the mill.

The addition rate of aggregated powder is also a critical parameter in optimizing a milling process. High addition rates compromise the initial de-aggregation of the powder by occluding the solvent and increasing viscosity. Large aggregates trap a large volume of dispersing medium (e.g., water or alcohol in their pores) and restrict free movement of
the particles and the media. This compromises the maximum capacity of the load and can lead to gelation of the load which increases the suspension viscosity. Low fill volume and high viscosity compromise milling efficiency by consuming more energy to move the media, instead of being directed towards reducing the particle size. This also results in fewer particle-particle interactions, restricted media movement, and a longer time for milling time to a given particle size [23, 31, 32]. In contrast, a slower addition rate requires a longer time for powder addition, which compromises milling efficiency and increases the media, shaft and container wear. Thus, the powder addition rate must be optimized to de-aggregate the powder in an efficient way.

Based on conventional notion of milling dynamics, fragmentation of aggregates initiates at the larger defects that exist in the original material, and propagate leaving finer defects in smaller particles. Consequently, the probability of finding a critical flaw in finer particles decreases with particle size. As fragmentation of large aggregates continues, the required stress for crack propagation in small aggregates becomes overwhelming and a “grind limit” is reached [33]. Also, when planning a milling experiment, one must consider the grinding media wear as that can contribute to the total impurity concentration and life of the grinding media [34]. Longer milling time or a larger number of media collisions can lead to increased media wear and contamination in the milled material. Thus, proper control of the CAM process variables is required to achieve ultra-fine milling of micron-sized aggregates to nanometer dimensions, at the same time minimizing media wear and grinding time.

The present article reports the use of design of experiment (DOE) to identify the main effects that dominate the de-aggregation process as a function of time. DOE also
helps to determine and establish any interacting synergistic effects between the variables. The information gained from DOE can be used to improve performance, reduce cost and time, and build mathematical models that can approximate the relationship between the output(s) and inputs [35]. Optimum milling conditions will be proposed from the DOE analysis to obtain efficient milling of nanophase alumina powder from about 11 µm in size to near primary particle dimensions of 20-50 nm. The media material and shape, powder solid loading, media to powder ratio and slurry pH were fixed for the DOE study. The parameters studied by DOE were media size, shaft RPM and powder addition rate. Table 6.1 summarizes the fixed and unfixed experimental factors (milling variables) considered for the DOE.

6.2 Materials and Methods

6.2.1 Chemically Aided Attrition Milling

The nanophase alumina powder for de-aggregation studies by CAM was provided by W. R. Grace & Co.-Conn., Columbia, Maryland. The Al₂O₃ powder had mixed phases of γ-Al₂O₃ + δ-Al₂O₃ powders obtained by calcination of precipitated boehmite at 1000 °C for 3 hr. The powder had a specific surface area of 116 m²/gm, as measured by the Brunauer-Emmett-Teller (BET) technique, with an equivalent spherical diameter of 16 nm [16]. A typical milling process started by taking 1007 gm (2.22 lb) of high purity zirconia (yttria stabilized) milling media in a 750 cc grinding tank coated with
polyethylene and jacketed for cooling water circulation. Media size for a particular experiment was selected from the DOE, summarized in Table 6. A Halar coated stainless steel shaft having plastic disc spacers agitated the contents inside the grinding tank.

Suspensions with 25vol% (50wt%) solids loading were prepared by slowly adding 160 gm of powder to 150 ml of de-ionized water adjusted to pH 4, while having the agitator speed set to 700 rpm. After all of the powder was added, the milling shaft speed for a particular experiment was changed to the shaft speed selected from the DOE summarized in Table 6.2. Suspension pH was selected to have slightly elevated solubility of the alumina to promote dissolution at the crack tips to promote stress corrosion cracking. The solubility-pH diagram or “predominance area diagram” for alumina is shown in Figure 6.1. The shaded region in the diagram, showing elevated solubility with decreasing pH (acidic side of the solubility curve), was explored for de-aggregation by the CAM process. Optimum pH was set to pH 4.0±0.25 by the elimination method, since under this pH range the slurry remained free flowing throughout the milling process and the suspension could be easily loaded up to 25 to 30 vol% (50 to 60 wt%) solids loading. The suspension pH was checked every 5 min using a SENTRON ARGUS probe and pH-meter. Suspension pH drifted towards the basic side as powder addition and milling proceeded. Small amounts of concentrated hydrochloric acid (HCl) was added every 5 min. to readjust the pH and limit pH drift.

1 Union Process Inc., Akron, OH
2 SENTRON Inc., Gig Harbor, WA
within pH 3.75-4.25. A total amount of 4.5-5.5 ml (equivalent to 0.35-0.45 M) HCl was added throughout the powder addition and milling period.

### 6.2.2 Characterization of Milled Suspension

Small amounts of suspension were extracted after 1, 2, 3 and 4 hr of milling (milling time started \( t = 0 \ hr \) after complete addition of the powder) to measure particle size distribution by quasi-elastic light scattering using a Malvern Zetasizer.\(^3\) Small amounts of sample recovered after 4 hr of milling were air dried at 70 °C for 24 hrs and analyzed for ZrO\(_2\) and Y\(_2\)O\(_3\) content by X-Ray Fluorescence\(^4\) (XRF) technique to evaluate impurity pickup from media wear. The effect of milling was also observed by comparing electron micrographs obtained for selected samples before and after milling using a Hitachi S-3500N scanning electron microscopy\(^5\) (SEM) and a JEOL 2010F high-resolution transmission electron microscopy\(^6\) (HRTEM).

### 6.2.3 Figure of Merit: Average Agglomeration Number (AAN)

The state of dispersion of the milled suspensions was estimated by calculating average agglomeration number (AAN). The AAN gives an approximate estimation of the number of primary particles in an agglomerate/aggregate. An AAN of 10 or less was

\(^3\) Malvern Instruments Ltd. Malvern, UK  
\(^4\) Philips Analytical, Natick, MA  
\(^5\) Hitachi Instruments Inc., Japan  
\(^6\) Japanese Electronics and Optics Laboratory, Japan
considered to be a well-dispersed suspension. AAN is calculated by taking the ratio of the volume of the agglomerate/aggregate to the volume of the primary particle [36]. The volume of agglomerate/aggregate is calculated from its median size \( \text{D50\%} \) estimated from particle size distribution obtained by light scattering using a Malvern Mastersizer. Volume of a primary particle is calculated from the equivalent spherical diameter (ESD) as calculated from SSA measured by the BET technique, assuming spherical particles.

The equations for ESD and AAN can be simplified as shown below [37]:

\[
ESD(\text{nm}) = \frac{6}{\text{SSA(m}^2 / \text{gm}) \times \rho(\text{g} / \text{cm}^3)} \times 1000
\]

where, \( \rho \) is the density of the powder.

\[
AAN = \frac{(\text{D50\%})^3}{(ESD)^3}
\]

Both D50\% and ESD have the same units.

6.2.4 Design of Experiment (DOE) for CAM

Design of Experiments (DOE) was used to determine which of the milling conditions (factors, process inputs) were important to certain milling outcomes (responses, process outputs). Three factors were considered for the current work: powder addition rate, media size, and shaft speed. Each factor was assigned two levels i.e. the maximum and the minimum values set on the basis of preliminary trials. A three factor \((k = 3)\), two-level \((l = 2)\), full factorial design was used [38]. Three center points \( (CP) \) were added for replication, providing an estimate of experimental error, and to detect
curvature in responses. The number of experiments \((N)\) required by the DOE is given by the following equation:

\[
N = t^k + CP = 2^3 + 3 = 11 \quad [6.4]
\]

The structure of the experimental design is illustrated as a “Cube Plot” shown in Figure 6.2. The experimental parameters chosen for the DOE are listed in Table 6.2. *Standard Order* gives the order in which the experiments were designed by changing the three factors. The order in which the experiments were executed is represented as *Run Order*. The Run Order was randomized to avoid possible uncontrolled/unknown factor effects like changes in humidity and room temperature from becoming confounded with experimental factor effects. Center point experiments are identified with a zero \((0)\) in the *Center Point* column. The last three columns *Addition Rate (AR)*, *Media Size (MS)*, and *Shaft Speed (RPM)* specify the factor level to be used in each experiment.

The *AAN* was calculated for the milled suspensions and was reported as milling responses for the following conditions:

- **Response 1**: 1 hr of milling  
  *(AAN-1 hr)*
- **Response 2**: 2 hr of milling  
  *(AAN-2hr)*
- **Response 3**: 3 hr of milling  
  *(AAN-3hr)*
- **Response 4**: 4 hr of milling  
  *(AAN-4hr)*

Impurity pick up recorded as parts per million (ppm) increases in \(\text{ZrO}_2\) and \(\text{Y}_2\text{O}_3\) content, due to media wear, were also reported as responses:

- **Response 5**: 4 hr of milling  
  *(ZrO\(_2\) ppm-4hr)*
- **Response 6**: 4 hr of milling  
  *(Y\(_2\text{O}_3\) ppm-4hr)*
6.2.5 Statistical Analysis

Each response was analyzed by statistical software-Minitab\(^7\) using a combination of factorial analysis of variance (ANOVA) and multiple regressions. The regression equation for the matrix was represented as:

\[ R = C_0 + C_1F_1 + C_2F_2 + C_3F_3 + C_{12}F_1F_2 + C_{23}F_2F_3 + C_{31}F_3F_1 + C_{123}F_1F_2F_3 \quad [6.5] \]

where \( R \) is the response; \( F_1, F_2 \) and \( F_3 \) are the three factors powder addition rate, media size and shaft rpm, respectively; \( C_0 \) is the constant; \( C_1, C_2 \) and \( C_3 \) are coefficients for individual milling factors; \( C_{12}, C_{23} \) and \( C_{31} \) are coefficients for two-way interactions between the milling factors; and \( C_{123} \) is the coefficient for three-way interaction between the milling factors. The significance of the individual milling factors and also two-way or three-way interactions between multiple factors was calculated as probability or \( p \)-values. The tests of hypothesis were structured as [38, 39]:

Type 1: The null hypothesis- factor or combination of factors has no detectable effect. Any observed effect apart from zero, when compared to the estimate of experimental error, is fully explained as mere noise.

Type 2: The alternate hypothesis- factor or combination of factors has some detectable effect. At least some part of the observed effect is not explained by the error term. The effect is different from zero.

Hypothesis testing was carried out at a 95\% level of confidence, or a level of significance of alpha = 0.05. The \( p \)-value is an estimate of the risk of committing a Type I error in rejecting the null hypothesis, and considering the factor to be significant when

\(^7\) Minitab Inc., State College, PA
in reality it is not. When the \emph{p-value} is 0.05 or lower, the null hypothesis (Type 1) is rejected, and the factor is considered significant, unless otherwise mentioned for specific responses.

\section*{6.3 Results and Discussions}

\subsection*{6.3.1 State of Dispersion on Milling}

The change in median particle size (D50\%) with milling time, for experiments tabulated in Table 6.2, is shown in Figure 6.3. It can be observed that for \textit{Run # 4} and \textit{Run # 5} de-aggregation below a median size of 35 nm, corresponding to AAN below 10 (\emph{Figure of Merit}) could be achieved after only 1 hr of milling. The viscosity of the slurry decreased significantly as milling proceeded. For a typical milling run, slurry viscosity after 0 hr and 4 hr of milling were measured to be $> 600$ mPa-sec and $< 10$ mPa-sec, respectively. The particle size distributions of the as-received and 1 hr milled alumina suspensions (parameters same as Run # 5) dispersed in pH 4.0 aqueous suspension, are shown in Figure 6.4. The as-received powder shows a broad distribution between 1 – 100 \(\mu\)m, with D50\% $\sim 11\ \mu\text{m}$. The 1 hr milled suspension show two peaks, major peak at $\sim 30$ nm and a minor peak ($\sim 10$ vol\%) at $\sim 250$ nm. The effect of CAM on alumina can also be verified from the selected SEM and TEM micrographs shown before and after milling in Figure 6.5 and Figure 6.6 respectively. The SEM micrograph of as-received alumina powder corresponds well to the median particle size of 11 \(\mu\)m shown in Figure 6.4. The TEM micrographs for alumina obtained after 1 hr milling with parameters same
as Run #5, show dispersed alumina nanoparticles in clusters of 1-20 primary particles with size ranging from 10 – 50 nm, and few big clusters about 250 nm in size, also corresponding well to the particle size distribution shown in Figure 6.4.

6.3.2 Analysis of DOE on CAM

Milling performance for DOE analysis was recorded as average agglomeration number (AAN) and ZrO₂ and Y₂O₃ pickup, reported in Table 6.. The milling factors in Table 6.3 are coded as “+1”, “-1”, and “0” for high, low and center point factor levels, respectively. Analysis of variance (ANOVA) was performed on each response to identify the main, two-way, three way and curvature effects. No curvature effects were detected for any of the responses indicating a linear response. Test of the hypothesis based on the F-statistic was used to identify the p-values obtained from the ANOVA analysis, tabulated in Table 6.. A p-value ≤ 0.05 was considered to be significant, except for response 1 (AAN-1 hr) where the p-values ≤ 0.1 were considered to be significant (all the considered effects had the border line case with p-value between 0.04 – 0.07). The variables or combination of variables that were not significant are represented with a “0” (zero). The effect on response was considered to be positive (+) or negative (−) by observing the slope on the main effects plot [38]. A positive effect was represented with a “+” (plus) sign and a negative effect were represented with a “−” (minus) sign. A main effects plot is made by plotting the mean response for each factor level. A line connects the mean responses for each factor, and the slope of the line is give by dividing the difference in mean response of the two levels by the difference in magnitude of the factor level [38].
Since, the DOE in the present work is a two level factorial, each factor or combination of factor has two values, a high $F_{+1}$ and a low $F_{-1}$. Responses for high factor are represented as $R_{+1,n}$ and for low factors are represented as $R_{-1,n}$, where $n$ is the number of observations/responses with high or low factors.

$$\text{Effects Slope} = \frac{\sum_{n} R_{+1,n} - \sum_{n} R_{-1,n}}{F_{+1} - F_{-1}}$$  \hspace{1cm} [6.6]

### 6.3.2.1 Analysis of Response 1 (AAN-1 hr)

Analysis of results for response 1 (AAN-1 hr) indicate that all the factors had $p$-value on the borderline case of 0.04 – 0.07. The effects of the entire one, two or three-way interactions were significant and could be rejected with a confidence level of below 10%. This indicates that during the first hour of milling all the factors, addition rate, media size and shaft rpm, are important. A positive dependence of addition rate indicates that a slower addition rate will de-aggregate to a lower AAN. Slower addition rates give more residence time for initial de-aggregation of large aggregates to finer aggregates, which is beneficial for further de-aggregation to near primary particle dimensions. A negative dependence of shaft rpm indicates that higher shaft speed will also de-aggregate to lower AAN. This dependence is in agreement with Equation 6.1, showing the inverse dependence of de-aggregation time $t$ to the square root of shaft rpm $N$. Higher shaft rpm transmits more energy to the media and the suspension for increased de-aggregation through impact, abrasion and shear.
A negative dependence of media size to AAN during the first hour of milling is contradictory to the positive dependence of the same for 2, 3 and 4 hr of milling. A negative dependence means that larger media size will give lower AAN and vice versa. This dependence results from the dominating effect that Run # 7 has on the media size main effect. In the 2, 3 and 4 hr AAN responses, the effects slope is positive due to the low AAN’s for Run # 4, 5 and 11, and the moderate to low AAN for Run # 7. However, in the 1 hr response Run # 7 results in an AAN two orders of magnitude larger that the 2 hr AAN. The large value dominates the main effect of media size, yielding a negative effects slope. The high AAN after 1 hr of milling in Run # 7 can be explained by considering the milling parameters. At the start of milling there are large aggregates due to a high addition rate. The efficiency of the small media in breaking up the large aggregates is low; therefore, more collisions are required [30]. Since the RPM is low, milling does not occur until longer milling times. The AAN data for Run # 4 and 5 after 1 hr, AAN ~ 10 in both cases, show that a high RPM is enough to achieve efficient milling with the small media in less than an hour compared to 3 – 4 hr for the low rpm. Despite the negative media size effect slope, for 1 hr of milling, it is still better to use small media at a high RPM (AAN ~ 10) compared to large media at any RPM or powder addition rate (minimum AAN ~ 6400).

6.3.2.2 Analysis of Responses 2 - 4 (AAN-2, 3, and 4 hr)

The results for responses 2 – 4 (AAN-2hr, 3hr and 4 hr) indicate that media size (MS) has the only significant effect, and has a positive dependence. Thus, finer media is
required to achieve de-aggregate to a lower AAN. To understand the positive effect of grinding media size on the AAN of milled suspension, we need to take a look at the physical events and energy dissipation from the powder input to the final product. The energy or power input to the mill is transferred to the stirrer shaft and from the shaft to the grinding media and suspension. The events that actually de-aggregate the particles are: (i) the energy transfer from two colliding media to particles trapped between the collision, (ii) energy transfer from colliding particles to critical flaws (cracks and crevices), (iii) energy transfer from the abrasion and shear forces between the media, and (iv) energy transfer from abrasion & shear forces inside the suspension created by the movement of the shaft [33]. During, these events a good part of the energy is consumed in moving the media and suspension without any de-aggregation, such as collision events failing to trap particles between them, deformation or wear of grinding media and container walls and also dissipation of energy as heat due to friction. Thus, only a very small fraction of the input power is actually consumed in de-aggregation of the particles [27]. Using the same quantity of media but smaller in size creates increased collision and shear events with trapped aggregate particles, resulting in increased de-aggregation of the particles. Thus, the same amount of power or energy is transferred into an increased number of positive de-aggregating events with finer media. The underlying assumption to the above explanation is that the finer media has enough mass to generate momentum that can produce the minimum stress on the particles required to create a positive de-aggregation event. Correlating the relative effects of MS and RPM as given in Equation 6.1. The milling time is directly related to MS with a power of 3, but has only square
dependence on RPM. Thus, the media size effect dominates over the main effects and show the strongest dependence.

6.3.2.3 Analysis of Responses 5 and 6 (Impurity pickup- 4 hr)

Responses 5 and 6 (ZrO₂ ppm-4hr and Y₂O₃ ppm-4hr) indicate that the impurity pickup has a positive dependence on \textit{shaft rpm (RPM)} only. Increasing shaft rpm will increase the energy being transmitted to the media creating more collision abrasion and shear of the media. This will also increase the events that will not result in de-aggregation of the particles, but will only contribute to media wear by impact with each other, agitator shaft and the wall of the container. Since shaft rpm was not a significant factor in milling over 1 hr to achieve particles with AAN < 10 shaft rpm could be kept at lower speeds to reduce media wear and cost. Also, lower rpm will require lower energy input and will be beneficial in maintaining energy efficiency of the CAM process.

6.4 Conclusions

CAM of nanophase alumina powder was optimized using DOE. Powder addition rate, media size and shaft rpm were studied as milling variables in the DOE. The results indicate that within the range of variables studied, the media size was the most significant factor in achieving de-aggregation to near primary particle size with an AAN below 10. During the first hour of milling, all the individual and multiple factors were significant, but the effect of media size was undermined by the robustness of events in the first hour.
Experiments with the smallest media size (0.2 mm) and maximum shaft rpm (2000 rpm) were able to achieve AAN < 10 in just 1 hr of milling. Analysis of impurity pickup after 4 hr of milling indicate that only shaft rpm had positive dependence, and to reduce impurity pick up we should mill at low rpm or over a shorter time period. Depending on the type of application, the DOE suggests several options in choosing the optimized milling condition (within the range of parameters studied). Option 1- for applications not critical to impurity content but requiring faster milling rates, the optimized variables can be achieved under fast addition rate, high shaft speed and small media size. Option 2- for application requiring low impurity content but can handle long milling time, the optimized variables can be achieved under fast addition rate, low shaft speed and small media size. Option 3- for applications requiring low impurity content but intermediate milling time, the optimized variables can be achieved under slow addition rate, low shaft speed and small media size.

The milling conditions mentioned above have been proposed with the assumption that the suspension chemistry (e.g., pH and physical state of initial powder) remains the same. Any change in these two conditions may change the significance by one or several factors with milling time. Future work will involve testing the proposed options and developing CAM protocols for different metal and metal oxide powders with varying chemical and physical state.
6.5 References


Table 6.1. Summary of fixed and unfixed experimental factors (milling variables) for the design of experiment (DOE) developed for optimizing the chemically aided milling (CAM) of nanophase alumina.

<table>
<thead>
<tr>
<th>Milling Variable</th>
<th>Fixed/Unfixed</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder solid loading</td>
<td>Fixed</td>
<td>25 vol.% (50 wt.%)</td>
</tr>
<tr>
<td>Quantity of media</td>
<td>Fixed</td>
<td>1007 gm</td>
</tr>
<tr>
<td>Media material</td>
<td>Fixed</td>
<td>Zirconia (Yttria doped)</td>
</tr>
<tr>
<td>Media shape</td>
<td>Fixed</td>
<td>Round</td>
</tr>
<tr>
<td>Media size</td>
<td>Unfixed</td>
<td>2.0, 1.0, 0.2 (mm)</td>
</tr>
<tr>
<td>Agitator speed</td>
<td>Unfixed</td>
<td>700, 1350, 2000 (rpm)</td>
</tr>
<tr>
<td>Powder addition rate</td>
<td>Unfixed</td>
<td>0.25, 1.5, 2.0 (gm/min)</td>
</tr>
<tr>
<td>Slurry pH</td>
<td>Fixed</td>
<td>4.0±0.25</td>
</tr>
</tbody>
</table>
Table 6.2, Summary of experimental Factors for the design of experiment (DOE) developed for optimizing the chemically aided attrition milling (CAM) of nanophase alumina. The DOE was generated by statistical software- Minitab.

<table>
<thead>
<tr>
<th>Standard Order</th>
<th>Run Order</th>
<th>Center Point</th>
<th>Addition Rate (AR), gm/min</th>
<th>Media Size (MS), mm</th>
<th>Shaft Speed (RPM)</th>
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</thead>
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<td>1.25</td>
<td>1.0</td>
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Table 6.3. Summary of Factors (Coded as “+1” for high, “-1” for low, and “0” for center point) and Responses 1 – 6 for the design of experiment (DOE) developed for optimizing chemically aided attrition milling (CAM) of nanophase alumina. The DOE was generated by statistical software- Minitab.

<table>
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<tr>
<th>Run Order</th>
<th>Factors</th>
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<td>AAN-1hr</td>
<td>AAN-2hr</td>
<td>AAN-3hr</td>
<td>AAN-4hr</td>
<td>ZrO₂ ppm-4hr</td>
<td>Y₂O₃ ppm-4hr</td>
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Table 6.4. Significance chart for the individual milling factors and also two-way or three-way interactions between multiple factors for Responses 1 – 6. Significant hypothesis was applied to the p-value (p≤ 0.1 considered significant) obtained from the ANOVA analysis, performed by statistical software Minitab. (“+” (plus) positive effect; “-” (minus) negative effect; “0” (zero) Not significant)

<table>
<thead>
<tr>
<th>Effect</th>
<th>Response 1 AAN-1hr</th>
<th>Response 2 AAN-2hr</th>
<th>Response 3 AAN-3hr</th>
<th>Response 4 AAN-4hr</th>
<th>Response 5 ZrO₂ ppm-4hr</th>
<th>Response 1 Y₂O₃ ppm-4hr</th>
</tr>
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<tr>
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<td>p≤0.05</td>
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</tr>
<tr>
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<td>0</td>
</tr>
<tr>
<td>MS</td>
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</tr>
<tr>
<td>RPM</td>
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<tr>
<td>AR x MS</td>
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<td>AR x RPM</td>
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<tr>
<td>MS x RPM</td>
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<tr>
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**Figure 6.1.** Theoretical solubility vs. pH plot (Predominance Area Diagram) of alumina. Thermodynamic data taken from Baes & Meser [40]. The shaded region in the diagram, showing elevated solubility with decreasing pH, was explored for de-aggregation by CAM process. Optimum milling pH was set to pH 4.0±0.25.
Figure 6.2. Cube plot illustrating the structure of the design of experiment (DOE) developed for optimizing chemically aided attrition milling (CAM) of nanophase alumina.
Figure 6.3. Average agglomeration number (AAN) of the particles in suspension collected after milling at pH 4.0±0.25 for 1, 2, 3 and 4 hr, under milling conditions as planned for DOE tabulated in Table 1. (The lines in the plot are merely to connect the data points)
Figure 6.4. Particle size measurement by light scattering for as-received aggregated nanophase alumina (AAN ~ 300,000,000); and suspension obtained after CAM at pH 4.0±0.25 for 1 hr (AAN ~ 10) with parameters same as Run # 5.
Figure 6.5. SEM micrograph of as-received nanophase alumina (before milling) with AAN \( \sim 300,000,000 \).
Figure 6.6. TEM micrographs for chemically aided attrition milled (CAM) nanophase alumina with AAN ~ 10. Sample collected after 1 hr of milling at pH 4.0±0.25, with parameters same as Run # 5. About 10 vol% of suspension has ~ 250 nm aggregates, also seen in TEM micrograph.
Chapter 7

Conclusions and Suggested Future Work

7.1 Morphological Control of Particle Grown from Solution

The role of solvent degradation and water on morphological control of $\alpha$-Al$_2$O$_3$ particle synthesized under glycothermal conditions has been resolved. Specific adsorption/reactivity of solvent on certain crystallographic facets can considerably lower the surface energy for particular facets causing them to dictate the morphology of the crystals. The impurity analysis on samples with different morphologies eliminated the possibility of morphological forms being dominant due to presence of particular impurities. The formation of platelet morphology can be explained through specific adsorption of 1,4-butanediol molecules over the {0001} basal plane. On the other hand, formation of polyhedron morphology can be explained by the stabilization of {1012} rhombohedral plane by relatively high reactivity of water molecules over the surface.

There is a need to investigate the mechanisms proposed for the effect of solvent on controlling morphology through a combination of experimental and computational techniques. Integration of techniques such as infrared spectroscopy, contact angle measurements and atomic force microscopy, with simulative methods for calculating dissociation constants of surface groups and interaction energies of solvent molecules with crystal surfaces, can help to accurately estimate the behavior of crystal surfaces in solvent.
In the current work it was shown that morphological development of crystals grown from solution are governed by solvent conditions such as pH, ionic strength and solvent interactions. The proposed theoretical model accounts for solid/solvent interactions such as electrostatic and surface adsorption of solvent molecules. Comparing the experimentally synthesized and theoretically derived morphologies for \( \alpha-\text{Al}_2\text{O}_3 \) particles, synthesized under both aqueous and glycothermal conditions, has given a better understanding on how to control solvent conditions to tailor the morphology of \( \alpha-\text{Al}_2\text{O}_3 \) particles under various solvent conditions. Specific adsorption of the solvent on certain crystal facets can considerably lower the surface energy for particular facets causing them to dictate the morphology of the crystals.

The proposed model for determining equilibrium morphology under solution conditions can be successfully extended to the synthesis of metallic, ceramic and polymeric materials as long as the solvent supports charged species. Depending on the type of surface groups at the solid-solvent interface, surface charging can be modeled by the proposed theoretical model. The behavior of crystal surfaces in a solvent can be evaluated through the integration of high temperature zeta potential measurements [1, 2], calculations of proton association constants of surface groups, and interaction energies of solvent molecules with crystal surfaces. These measurements can be achieved by molecular dynamics or \textit{Ab Initio} simulation techniques. Molecular dynamics simulation of the competitive adsorption of hydrocarbon and water on crystal surfaces will help explain the mechanism of adsorption, packing behavior and density of mixed solvent molecules. This will assist in accurately estimating the surface energies for various crystallographic facets of a crystal [3].
Surface chemical models such as Stern, or the Gouy-Chapman-Stern-Grahane model can be adopted to accommodate for the specifically adsorbed species on the surface of the particles [4]. Proper application of the model requires knowledge of process variables such as absolute temperature ($T$), ionic strength ($c$) and dielectric constant ($\varepsilon$) of the solvent medium. The integration constant representing surface energy at the IEP ($\gamma_0(p)$), should be determined by surface energy measurement techniques like contact angle, Wilhemy balance or surface force measurements [4-6].

7.2 Synthesis of Alpha-alumina Nanoparticles

Phase pure alpha-alumina can be produced under glycothermal conditions with sizes less than 100 nm through seeding with $\alpha$-$\text{Al}_2\text{O}_3$ particles. It is proposed that secondary nucleation takes place during the synthesis process, producing additional seed particles. Under seeded conditions $\alpha$-$\text{Al}_2\text{O}_3$ particles can be produced at temperatures as low as 235 °C, but the reaction time required under low temperature conditions can be as long as 72 hr. An optimum stirring speed of 240 rpm was determined, but increasing stirring rate above this limit had no effect on the rate of secondary nucleation. Further studies of the experimental parameters should be carried out to quantify and propose a theoretical model specific to secondary nucleation under glycothermal synthesis conditions.

Alpha-alumina particles smaller than 40 nm could be synthesized by using 40 nm or smaller particles, synthesized under glycothermal conditions, as seed particles. Control of particle morphology can be obtained by controlling the water content in the
solvent. The work reported on morphology control under seeded conditions is a preliminary work to show the feasibility of the process. Since, the transformation mechanisms and the transformation kinetics have changed between the unseeded and seeded experiments; a more detailed investigation is required to properly understand how to control the morphology of particles synthesized under seeded conditions. Schemes should be developed for recovering well dispersed nanoparticles after synthesis. This will help in better imaging of individual particles by TEM and AFM techniques and will help develop statistically precise data for several particles while measuring particle size and aspect ratio. Future work should also focus towards re-cycling the synthesized nanoparticles as seed particles and scaling up the batch size for improved yields producing commercially viable quantities of > 10 wt%.

7.3 De-aggregation and dispersion of nanoparticles

Physical characterization of nanophase alumina powders shows evidence of aggregation in nanoparticles. Increased amounts of excess hydration in the powder have been related to increased aggregation in nanophase aluminas. Theoretical calculations using PM5 semi-empirical parameters as implemented in CAChe Worksystem have shown evidence that bridge formation in nanoparticles can take place under ambient conditions by either condensation or by dissociation of water between the hydrated nanoparticles.

Theoretical calculations of larger alumina clusters, comparable to the size of nanoparticles (~ 10nm), were limited by the computational cost including both computer
capability and simulation time. But, the approach to characterize the state of aggregation and mechanism of aggregation in nanophase materials using a combination of experimental and theoretical simulation techniques has been established. Future work will be focused towards making theoretical calculations on larger metal/hyd(roxides) clusters with multiple hydration and bridging sites to simulate more realistic nanoparticles.

Chemically aided milling (CAM) of nanophase alumina powder has shown the potential to produce bulk quantities of aggregate free suspension of nanophase materials for commercial applications. These results indicate that within the range of variables studied, the media size was the most significant factor in achieving de-aggregation to near primary particles size with an AAN below 10. Depending on the type of application, several options were proposed in choosing optimized milling condition for de-aggregation to near primary particle size dimensions.

The milling conditions mentioned above have been proposed with assumption that the suspension chemistry e.g. pH and physical state of initial powder stays the same. Any change in these two conditions may change the significance by one or several factors with milling time. Future work should involve testing the proposed options and developing CAM protocols for different ceramic and metal powders with varying chemical and physical states.
7.4 Compaction, Sintering to Bulk Nanograin Materials

Preliminary work has shown that nanophase alumina, zirconia and yttria can be compacted and sintered to bulk nanograin materials with near theoretical densities. But, a thorough understanding of compaction and sintering of nanophase ceramics needs to be developed. Compaction of dry nanoparticles can reintroduce aggregation in the powder. Formation of green bodies by consolidation of nanoparticles from liquid medium face challenges in achieving crack free green bodies, formation of complex shapes and high through put rate from the process. Future work should also focus towards developing processes and models for fast and reliable consolidation of ceramic nanoparticles from high-density slurries of well-dispersed nanophase materials. Models and protocols should be developed for low temperature sintering of green bodies, made from consolidation of nanoparticles, to bulk nanograin materials.

7.5 References


VITA

Rajneesh Kumar

Rajneesh Kumar was born on February 1, 1975 in Roukela, India. He obtained his Bachelor’s degree in Metallurgical and Materials Engineering from Visvesvaraya Regional College of Engineering, Nagpur, India in 1998. After graduation he joined the graduate program in Materials Engineering and Science at South Dakota School of Mines and Technology in 1998, and obtained his Master’s degree in June 2000. From there Rajneesh proceeded to the Penn State University to pursue doctoral degree in Materials Science and Engineering. Rajneesh will be employed as a Packaging Development Engineer at IBM, East Fishkill, NY. Rajneesh is a member of the American Ceramic Society and was inducted into and remains an active member of Keramos.