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Synthesis and Processing of Nanostructured Alumina Ceramics

By

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A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University
July 2013

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Abstract

The term “Nanoceramics” is well known in the ceramic field for at least two decades. In this project a detailed study was performed on the synthesis of $\alpha$-alumina nanopowders. High solids content nanoalumina suspensions were prepared and used to form green bodies using both wet and dry forming routes. The green bodies were then sintered using both conventional single and two-step sintering approaches.

Synthesis: Two different synthesis methods, viz. precipitation and hydrothermal treatment, were used to synthesize fine $\alpha$-alumina powders from aluminium chloride, ammonia solution and TEAH (Tetraethyl ammonium hydroxide). XRD, TEM and FEG-SEM were used to characterise the powders produced. The presence of commercial $\alpha$-alumina powder as seed particles did not affect the transformation to $\alpha$-alumina phase during the hydrothermal treatment at 220°C in either basic or acidic environments. The results obtained from the precipitation route showed that the combined effect of adding $\alpha$-alumina seeds and surfactants to the precursor solution could lower the transformation temperature of $\alpha$-alumina from about 1200°C for unseeded samples to 800°C, as well as reducing the level of agglomeration in the alumina powders. The difference in transformation temperature mainly resulted from the nucleation process by the $\alpha$-alumina seeds, which enhanced the $\theta \rightarrow \alpha$ transformation kinetics. The lower level of agglomeration present in the final powders could be due to the “surface modifying” role of the surfactants preventing the particles from growing together during the synthesis process. By introducing a further high-temperature step for a very short duration (1 minute) to the low-temperature heat treatment route (800°C/12 h), the unseeded sample with added surfactant transformed into pure $\alpha$-alumina phase. The newly-added step was shown to be an in-situ seeding step, followed by a conventional nucleation and growth process. The best final powder was compared with a commercial $\alpha$-alumina nanopowder.

Processing of alumina ceramics: The effect of low-molecular weight ammonium dispersants including Dispex-A40, Darvan-C and Dolapix-CE64, on high solids content nanoalumina suspensions was investigated. The nanosuspension prepared using the most suitable dispersant, Dolapix-CE64, was slip cast into ~53% dense, very homogeneous green bodies. This nanosuspension was also spray freeze dried into
crushable granules using Freon as a foaming agent. Green compacts with density of ~53.5% were then formed by dry pressing the 2 vol% Freon-added spray freeze dried granules at 40 MPa. Both slip cast and die pressed green bodies were sintered using conventional single-step and two-step routes followed by characterising the density and grain size measurement of final dense compacts. The results have been compared with that of a submicron alumina ceramic prepared using a commercial $\alpha$-alumina suspension. Highly dense alumina with an average grain size of ~0.6 $\mu$m was fabricated by means of spark plasma sintering at 1200°C. The application of 500 MPa allowed achieving almost fully dense alumina at temperature as low as 1200°C for 30 minutes with no significant grain growth.

**Keywords:** Nanopowder; Alumina; Hydrothermal; Precipitation; Slip casting; Spray freeze drying; Sintering; SPS
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</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>FAST</td>
<td>Field Assisted Sintering</td>
</tr>
<tr>
<td>FEG-SEM</td>
<td>Field Emission Gun – Scanning Electron Microscope</td>
</tr>
<tr>
<td>HP</td>
<td>Hot Press</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Isostatic Press</td>
</tr>
<tr>
<td>PoP</td>
<td>Plaster of Paris</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SC</td>
<td>Slip Cast</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electron</td>
</tr>
<tr>
<td>SFD</td>
<td>Spray Freeze Drying</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark Plasma Sintering</td>
</tr>
<tr>
<td>TEAH</td>
<td>Tetraethyl Ammonium Hydroxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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</table>
1. Introduction

Nanocrystalline ceramics refer to those ceramics with mean grain sizes less than 100 nm and are a subset of nanosized materials. The motivation for manufacturing and studying nanocrystalline ceramics lies in the unique properties they possess\textsuperscript{1-3}.

Nanotechnology was first introduced in the famous lecture of Nobel Laureate Richard P. Feynman, “There’s Plenty of Room at the Bottom,” given in 1959 at the California Institute of Technology\textsuperscript{4}. One of the earliest definitions of nanotechnology was given by Drexler\textsuperscript{5} as “the control of matter based on molecule-by-molecule control of products and by-products through high-precision systems as well as the products and processes of molecular manufacturing, including molecular machinery.” According to Whatmore and Corbett\textsuperscript{6} the term nanotechnology is used for “almost any materials or devices, which are structured on the nanometre scale in order to perform functions or obtain characteristics which could not otherwise be achieved”.

The subject of nanotechnology consists of designing, construction and utilization of materials with one or more dimensions in the nanometer range including (a) materials confined in three dimensions, e.g. nanoparticles and nanopores, (b) materials confined in two dimensions e.g. nanotubes and nanofilaments and (c) materials confined in one dimension, e.g. nanofilms and nanolayers. Nanomaterials can be designed to display considerably improved and interesting physical, mechanical and chemical properties due to the limited size of their constituents\textsuperscript{7, 8-9}. The reason for such novel behaviour of nanomaterials is that when the structural characteristics are in-between bulk materials and isolated atoms, i.e. in the 1-100 nm range, these materials may exhibit some different characteristics to those exhibited by bulk materials or their atoms\textsuperscript{10}.

Nanostructured materials can be made by numerous routes, however there is a broad classification dividing these methods into two categories: top-down and bottom-up\textsuperscript{10, 11}. In the top-down approach, the start is at a large scale, which is then reduced in size to approach the nanoscale level as in the preparation of microprocessors for computer industry. Top-down processes are in fact solid-state processing of materials including mechanical milling, machining and lithographic processes. Bottom-up processes mainly consist of chemical synthesis routes and highly controlled deposition/growth of materials. When nanoparticles are created using the bottom–up approach, the size
and the shape of a particle can be controlled by the production conditions. These particles can also be considered as nanocrystals. The atoms within the particle are ordered, or crystalline. As highlighted before, when the dimensions of a particulate material are decreased from microns to nanosize, significant changes in physical, chemical and mechanical properties may occur.

There are already products containing nanoparticles available on the market. Sunscreens contain nanoparticles designed to give better protection from the harmful rays of the sun; there are fabrics with nanoparticles that make the fabric liquid and stain repellent. In medicine, nanoceramics are already being used in drug delivery and as bone replacement agents. In the paint industry, nanostructured molecules are used to preserve the integrity of the paint. Modern mobile phone batteries use nanotechnology for longer battery life. At present the two dominant market sectors for nanotechnology appear to be information and communication technology (ICT) and medicine, although other niche applications include cosmetics, sunscreens, self-cleaning windows, ultra-strong lightweight materials, low-cost solar power generation, miniature fuel cell technology and environmental pollution monitoring and remediation. ICT applications include ultra-high density information storage – terabyte range, ultra-fast conventional computers, novel ultra-powerful “quantum computers”, ultra-broadband communication systems, high-definition, low-energy consumption flat-screen display technologies and a new generation of fully integrated communication and information systems. Medical applications include diagnostics, e.g. “lab-on-a-chip” technology for rapid identification of pathogens; patient monitoring, e.g. real-time sensing of physiological and biochemical parameters; “smart” drug delivery systems, e.g. providing swift and timely delivery of just the right amount of pharmaceutical product to where it is needed in the body; and targeted treatment of disease using “designer” nanoparticles which attach themselves selectively to specific sites, etc.

Nanocrystalline ceramics have been used in fuel cells and oxygen sensors due to the diffusion occurring along the grain boundaries instead of the lattice in these materials. This accelerated diffusion results in increased ionic conductivity as the oxygen ions can simply migrate using the grain boundaries rather than passing through the lattice. Another application of nanoceramics is in producing deformable ceramics due to the superplasticity characteristic as a consequence of the presence of nanosized grains.
The superplasticity behaviour can lead to the possibility of ceramics being formed directly by general metal forming methods such as rolling, extrusion and etc. from solid ceramic pieces.7

Thus, in each and every field we can identify the use of nanomaterials and the influence of these materials in the miniaturisation of various products and the evolution of new products with better performance. For example, ductile behaviour has been reported for nanophase ceramics such as titania and alumina processed by consolidation of ceramic nanoparticles.11 New nanomaterials based on oxides of zirconium, silicon and germanium have demonstrated superplastic behaviour, undergoing 100–1000% elongation before failure.11,13

With the exception of some nanostructured ceramics made by crystallising glass, which results in a mixture of 90% crystalline and 10% glass in the microstructure, bulk nanocrystalline ceramics are mostly fabricated by the compaction and densification of nanosized particles.

There are several major complications in the fabrication of nanoceramics by compaction and sintering of nanosized powders. First and foremost there is a need to eliminate agglomerates in the nanocrystalline powders. The second challenge is the production of sufficient quantities of the nanopowders whilst a third challenge is the difficulty in retaining a nanostructure during sintering. It is difficult to control grain growth; hence the optimisation of sintering cycles for different nanoceramics is essential. The final issue is the lack of data about the properties of nanoceramics. Even though many researchers have reported the sintering of nanoceramics, only a very few were successful in sintering them to full density whilst keeping the mean grain size below 100 nm. Also, in many cases the sample size was too small to make any meaningful property measurements.

With its unique combination of high hardness, corrosion resistance, thermodynamic stability and economic advantages, alumina is a material that has gained wide acceptance by industry. It is used for hip implants, sliding and sealing elements, thread guides, cutting tools, grinding grits and other applications.14 The influence of grain size on these properties is not predictable at the nanoscale, but smaller submicron grain sizes give rise to a higher hardness as decreasing the grain size limits the space for motion and multiplication of the lattice elements of microplasticity, e.g.
dislocations and twins \(^{15}\). Therefore, as investigated by Krell \(^{16}\), sintered sub-micron alumina showed a Vickers microhardness of \(~20\) GPa.

These hard ceramics become transparent when densified to the final density of \(\geq 99.95\%\) theoretical density with the average grain size of smaller than 1 \(\mu m\) \(^{17}\). Therefore, submicron alumina is one of the hard transparent armour materials, which can be used for compact windows. However, the light transmission in polycrystalline alumina, unlike some other transparent ceramics, is affected by losses through birefringent splitting of the beam. To minimize the scattering losses in these polycrystal materials, one solution is to retain the average grain size small (with reference to the light wave length) \(^{15}\). Krell, et al. fabricated highly dense alumina components with \(99.9\%\) theoretical density with average grain size of \(~0.5\) \(\mu m\). The components exhibited the real in-line transmission (RIT) of 60\% with a wavelength of 650 nm at 0.8 mm thickness \(^{18}\). Due to the improved properties mentioned above, the demand for ultrafine alumina compacts is currently increasing and material scientists all over the world are trying to synthesise and process this material to investigate its novel and potential applications.

In this work nanosized alumina powders were synthesised via simple chemical routes including precipitation and hydrothermal treatment and characterised by several different characterisation facilities. Both wet and dry forming methods were used to produce alumina bodies of high green density. Both pressureless and pressure-assisted sintering have been employed to densify the green alumina bodies followed by measuring the density and grain size of the densified compacts. Once sintered alumina bodies are evaluated, they can be compared to the present submicron alumina products or to develop new products with improved performance. Thus the deliverables of the present work are quite significant and the impact could be high.

Six Chapters are included in this thesis; the overall objectives and report structure are outlined in this chapter.

In Chapter 2, the background knowledge and the relevant literature review are presented. The structure, properties and applications of alumina are reviewed as well as the synthesis methods for nanosized alumina powders, including precipitation and hydrothermal routes. In addition, a comprehensive survey of the literature on the
processing of fine and ultrafine alumina powders into ceramic compacts, including different forming and densification methods is reported.

Chapter 3 summarizes the experimental work performed: the chemicals used in the experiments and the details of the synthesis routes employed to produce alumina nanoparticles and fabricate densified alumina bodies. Different characterization and measurement techniques involved at various stages of the work are also given in detail in this chapter.

The results of the experimental work on synthesis of nanoalumina powders using the precipitation and hydrothermal routes are included in chapter 4. The details of the effects of synthesis conditions including starting salt, adding seed and surfactants, process time and temperature on the morphology and size of the synthesised particles are discussed in this chapter. It also includes the results and discussion on attempts to process the resulting powders into densified alumina compacts.

In chapter 5 the important conclusions of the present project are highlighted and finally chapter 6 provides the possible directions for future work in this challenging and rewarding field of study.
2. Literature review

2.1. Alumina Ceramics

Alumina is the most widely used ceramic and it is the same to the ceramic industry as steel is to the metallurgical industry. Alumina ceramics have found various technological applications because of their distinctive combination of physicochemical properties including hardness, resistance to aggressive media and refractory properties.

Alumina naturally exists in abundant amounts, mostly as aluminium hydroxides in bauxite ores, which are impure mixtures of gibbsite, Al(OH)$_3$, boehmite and diaspore, polymorphs of AlO(OH). Most of raw bauxite ores need to be refined by the Bayer process after being mined. This process removes the impurities leaving a nominal 99.5% alumina after calcination at temperatures as high as 1600ºC. High temperature calcination leads to nearly 100% $\alpha$-alumina, whereas lowering this temperature, while resulting in finer powders, may retain some transition alumina phases shown in. This may cause some difficulties in the further processing of the powder, since the transition aluminas have partially disordered crystal structures, unlike the $\alpha$-alumina phase.

Aluminas are used in various applications, which range from dense alumina hip prostheses with high purity to the calcined bauxite for anti-skid road products. The size of the alumina powders used to manufacture these products can clearly change from sub-micron powders to large lumps depending on the type of the application. Other products prepared by using alumina include computer substrates, refractory products, grinding media, fibre insulation and many more.

2.2. Crystallography

Alumina is a classic oxide exhibiting metastable behaviour with several transition aluminas existing before final rearrangement into the stable $\alpha$ phase. It is a polymorphic material existing in various phases; the transformation of transition alumina being the topic of an extensive literature. The transition phases of
alumina are of particular importance because of their application as catalysts and catalyst supports\textsuperscript{20, 27-30} and are indicated as $\gamma$, $\eta$, $\chi$, $\delta$, $\theta$, $\kappa$, $\iota$, $\varepsilon$\textsuperscript{19, 31}; shown in Table 2-1. The transition aluminas consist of disordered crystal structures, which are based on a close-packed oxygen sublattice with varying interstitial aluminium configurations. These structures become more ordered, forming a hexagonal oxygen sublattice, as equilibrium is approached until stable $\alpha$-alumina is formed\textsuperscript{19}. The crystallographic structures for different transition aluminas ($\gamma$- and $\theta$-alumina) are presented in Figure 2-1 and Figure 2-2.

**Table 2-1** Crystallographic structures for transition alumina\textsuperscript{19}.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Gamma</th>
<th>Eta</th>
<th>Chi</th>
<th>Delta</th>
<th>Theta</th>
<th>Kappa</th>
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<td>$\theta$</td>
<td>$\kappa$</td>
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<td>4-875</td>
<td>34-4930</td>
<td>16-394</td>
<td>37-1462</td>
<td>4-878</td>
<td>26-31</td>
</tr>
</tbody>
</table>

**Figure 2-1** Schematic of the first two layers in the $\gamma$-alumina structure. The aluminium ions occupy both octahedral and tetrahedral positions. Octahedral and tetrahedral Al ions are in black and grey, respectively\textsuperscript{32,32}. 
The formation sequence of transition aluminas depends strongly on the starting materials and how they were formed. For instance, if the starting material is gibbsite, Al(OH)$_3$, the most probable transition order is $\chi \rightarrow \tau \rightarrow \kappa \rightarrow \theta \rightarrow \alpha$. However if the starting material is boehmite, AlOOH, formed from solution or amorphous gel/precipitate, then the sequence can be described as $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$, where $\alpha$-alumina forms at temperatures as high as 1200ºC.

The crystal structure of $\alpha$-alumina or corundum structure, as shown in Figure 2-3, is composed of close packed planes (A and B) of oxygen anions and aluminium cations, which occupy only two-thirds of the octahedral sites of the basic array. This results in three different types of layers of aluminium cation layers termed a, b, and c planes. In the complete stacking sequence of oxygen and aluminum layers A-a-B-b-A-c-B-a-A-b-B-c-A is displayed in Figure 2-4.

During the $\theta \rightarrow \alpha$ transformation, $\alpha$-alumina nuclei form within the ultra-fine $\theta$-alumina matrix (with more ordered cubic close packed lattice compared to $\gamma$-alumina). The nuclei then grow quickly to produce $\alpha$-alumina colonies. Due to the low intrinsic nucleation density and the shrinkage associated with the phase transformation as a result of the lower specific volume of $\alpha$-alumina (0.251 cm$^3$g$^{-1}$ for $\alpha$-alumina and 0.276 cm$^3$g$^{-1}$ for $\gamma$-alumina), the $\alpha$-alumina colonies recede from the matrix and will subsequently form a network of pore channels and $\alpha$-alumina “dendrites”. Generally the temperature required to remove these pores depends on their size, but it can be in

![Schematic of the structure of $\theta$-alumina, in which half of the Al ions occupy the tetrahedral sites](image)
excess of 1600°C in order to achieve high densities. This can have a very negative impact on the final grain size by yielding a severely coarsened ceramic. Another polymorph of AlOOH, diaspore, transforms directly to $\alpha$-alumina.

Figure 2-3 Schematic drawing of a) the corundum structure in $\alpha$-alumina, b) top view of this structure and c) octahedral structure of $\alpha$-alumina.

Figure 2-4 Schematic of the structure of $\alpha$-alumina.

2.3. Nanocrystalline Ceramics and their Properties

Nanocrystalline ceramics, materials with mean grain sizes smaller than 100 nm, have been receiving much attention recently due to their potential to display unusual
physical and mechanical properties. As the grain size becomes smaller, a higher fraction of the atoms reside in the grain boundaries, which results in the behaviour of the nanocrystalline ceramics being dominated by events at the grain boundaries\(^1\). For instance, nanocrystalline ceramics can display both plastic and extensive deformation at elevated temperatures by grain-boundary sliding\(^8, 36-39\). Although ceramics are brittle materials in general, some nanocrystalline ceramics have the ability to exhibit superplasticity at significantly high strain rates. Superplastic behaviour was reported for the first time in ceramics in fine grained tetragonal zirconia partially stabilised with 3 mol% yttria in 1986 by Wakai and co-workers\(^36\), Figure 2-5. The research on the superplasticity behaviour of ceramics has since extended to other ceramics such as silicon nitride\(^40, 41\).

![Figure 2-5](image)

**Figure 2-5** Yttria stabilised zirconia (Y-TZP) samples before and after superplastic deformation\(^37\).

There have also been suggestions that nanostructured ceramics can have very low thermal conductivities\(^42\). The thermal conductivity depends directly on the mean free path length of phonons; normally this is restricted by phonon-phonon scattering events and is of the order of a few nanometres\(^42, 43\). However in nanosized grains, the distance between grain boundaries is in the nanometer range, so these boundaries can contribute meaningfully to the scattering processes as well\(^42\). In addition, nanoceramics have been used as solid-state sintering aids to join together other larger grained commercial ceramics at moderate temperatures, as a result of their high fraction of grain boundaries and short diffusion paths\(^44\).

As mentioned previously, nanocrystalline ceramics have shown signs of improved physical and mechanical properties in comparison with conventional polycrystalline materials. Some of these properties such as transparency, super-plasticity, hardness, toughness and wear resistance are described briefly in the following section.
2.3.1. Transparency

High transmission of light in ceramics can be achieved by both very low porosities (<0.05%) and small grain sizes (<1 μm). Only 0.1% of residual porosity can affect the transparency of a ceramic compact, and large grains can also result in light scattering in birefringent ceramics such as alumina, as shown in Figure 2-6. Therefore, nanocrystalline ceramics have attracted much attention recently and researchers are investigating different techniques to prepare transparent ceramic compacts. Figure 2-6(c) shows alumina compacts produced by Apetz and van Bruggen 45; the average grain sizes of these compacts are 20 μm and 0.5 μm, respectively for the translucent body (left) and the transparent one (right). Both alumina samples are of 0.8 mm thickness and polished on both sides 45.

![Figure 2-6](image)

**Figure 2-6** Comparison of the light transmission of polycrystalline alumina with a) large grains (translucent) a low in-line transmission and b) fine grains (transparent) with a high in-line transmission and c) the translucent (left) and transparent (right) alumina bodies 45.

2.3.2. Mechanical Properties

Hardness, fracture toughness and bending strength are properties that influence the performance of structural materials. These properties are mainly used to predict and explain the ability of ceramic materials to resist any kind of deformation and also crack initiation and propagation. There are a large number of reports about the mechanical properties of submicron alumina, but unfortunately there is not enough report on the mechanical properties of nanocrystalline alumina ceramics.

The hardness of a material is described as the resistance to plastic deformation when being indented. The principle of indentation involves application of a given load to a
sample followed by measuring the dimensions of the residual impression left on the material once the indenter is removed. The hardness value is defined as the ratio of the indentation load and a parameter representing the area of the residual impression, depending on the shape of the indenter and the technique employed for the hardness. The Vickers hardness number (VHN), which is generally used, can be calculated using the formula 46:

\[
VHN = \frac{P}{0.002 \times d^2 \times \sin \frac{\psi}{2}} (= 1.8544 \frac{P}{d^2})
\]

Where VHN is in MPa, \( P \) (the applied load) in N, and \( d \) (the diagonal of the indent) in mm. \( \psi \) is the angle between the two opposite sides of the indenter, 136° for a pyramidal indenter and \( A_{TAC} \) represents the true area of contact.

However making quantitative predictions about hardness of materials with different mean grain sizes is unlikely. Skrovanek and Bradt 47 investigated this matter using hot-pressed alumina samples (+ 0.5% MgO), with grain sizes in the range of 1.5-8 μm achieved by annealing. They showed there was a rise in Knoop hardness (applied load = 4 N) as the grain size decreased from 8 μm to 3-4 μm, whilst an additional decrease in the grain sizes did not cause more improvement in hardness value. Krell and Blank reported a hardness value of around 22.5 GPa for pressureless sintered alumina compacts with a sub-micrometer structure and a grain size range of 0.4-0.5 μm 48. This value even exceeds the hardness of hot-pressed composites of Al₂O₃-TiC (Figure 2-7). The combination of reduced dislocation mobility (because of the fine grain size), high and homogeneous density are the requirements for the high value of hardness in alumina sub-micron compacts.
Fracture toughness of ceramics can be measured by the indentation microfracture method, which correlates the toughness with the length of cracks appearing from the corners of the Vickers indentation results. The application of the Vickers indentation fracture toughness test for brittle materials has become common due to its advantages including: (a) it can be used even on small samples, which is not true for other fracture toughness tests, (b) preparing the specimen is fairly simple requiring only a clean, polished, reflective plane surface, (c) the Vickers diamond indenter used to form the hardness indentation is a standard universal item, (d) in many cases the crack lengths can be measured optically without too much difficulty, and (e) finally it is a fast and cost effective method. However this technique has some disadvantages as well, such as (a) the accuracy when measuring the crack lengths, (b) the variety of equations used to calculate the indentation fracture toughness reported in the literature, and (c) different values been reported for the fracture toughness of a material calculated by indentation technique and its fracture toughness as measured by conventional methods.

Krell et al. studied the mechanical properties of sintered sub-micrometer α-alumina ceramics of densities over 99% as displayed in Table 2-2. It can be observed that the sub-micron alumina compacts with their improved hardness and strength exhibit

![Figure 2-7 Grain size dependence of the Vickers hardness of sintered alumina bodies](image_url)
fracture toughness values similar to or even below the values measured for conventional alumina ceramics.

**Table 2-2** Grain size and mechanical properties of materials studied by Krell et al.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Relative density / %</th>
<th>Average grain size / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure alumina</td>
<td>99.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Commercial reference</td>
<td>99.8</td>
<td>4-6</td>
</tr>
</tbody>
</table>

The hardness and fracture toughness of nanostructured alumina ceramics have not been studied widely, even though there are many reports on the mechanical properties of fine-grained alumina ceramics, a well organised study to find the effects of nanosized grains on these properties of the product material is missing in the literature.

### 2.4. Synthesis of Alumina Powders

With the exception of some nanostructured ceramics such as thin films, bulk nanostructured ceramics are almost always produced by powder compaction and sintering the formed bodies. Therefore, there have been numerous routes to synthesis ceramic powders ¹ ⁸. Powders of α-alumina can be synthesized by several well-
established synthesis methods, which can be divided into four major categories: (i) conventional synthesis. (ii) chemical methods (iii) mechanical milling and (iv) thermophysical techniques ¹.

2.4.1. Conventional Synthesis

The conventional synthesis of ceramic powders includes reaction between oxide and/or carbonate precursors. Thus for α-alumina, in the Bayer process, bauxite is hydrothermally dissolved in sodium hydroxide to form sodium aluminate solution. An aggregated gibbsite powder is produced by seeding the solution with gibbsite crystals and it is converted to α-alumina at around 1600 °C ⁵¹.

2.4.2. Chemical Synthesis

Chemical methods generally use direct and relatively simple chemical reactions to fabricate a product in powder form. With most of the chemical techniques the powders produced are often in “precursor” form, which means they are chemically close to the final required composition but they need to be heated to remove water and other volatiles. The size of the final particles depends on the size of particles within the precursor powder, however these particles will usually grow or even bond to each other during the calcination process because of the high temperature. Therefore lowering this temperature is a vital first step in preparing finer powders by chemical techniques.

2.4.2.1. Sol-Gel Synthesis

The phrase sol-gel has been recently used for all wet chemical synthesis methods; however there are only two sol-gel techniques. Colloidal sol-gel processing is the first technique, which can be divided into several stages. The starting material, for example a metal salt, is initially converted to a dispersible oxide on addition to dilute acid or H₂O in a chemical process, which forms a colloidal dispersion (sol). By removing H₂O and/or anions from the sol a stiff gel in the form of spheres, fibres, fragments or
coatings is produced. Calcination of the gel in air leads to an oxide product after decomposition of the salts 51.

The second sol-gel technique includes hydrolysis of metal-organic compounds particularly metal alkoxides, M(OR)ₓ, where R is an alkyl group. To prepare ceramic oxides, metal alkoxide is mixed with alcohol and the hydrolysis is carried out under controlled conditions resulting in a solid monolithic gel (an alcogel). This gel is dried and calcined to an oxide powder 51.

2.4.2.2. Precipitation Synthesis

Precipitation is a convenient chemical method, which has been used to synthesise nanopowders 52. The aim in a precipitation route is to produce ceramic oxides through forming intermediate precipitates such as hydrous oxides or oxalates, with the intention that an intimate mixture of components is formed throughout the precipitation and chemical homogeneity is maintained during following calcination processes 51. This method has been used to produce BaTiO₃ powder with mean particle size of 0.4-1 μm, nanocrystalline YSZ with average particle size of <100 nm and α-Al₂O₃ nanopowder of <90 nm particle size 51, 52.

Precipitation of hydroxides from salts is a technique relying on the fact that salts are water soluble. After a solution containing metal cations M⁺ is prepared directly from salts, the cation can be introduced to a hydroxide ion from another solution to form metal hydroxide M(OH)ₓ, as shown in Eq. 2-2:

\[
M^{x^+} + n(OH)^{-} \rightarrow M(OH)_x
\]

Eq. 2-2

If the metal hydroxide, M(OH)ₓ, has a moderate to low solubility, it will precipitate as a fine product. Increasing the concentration of one or both of cations and anions can lead to achieve supersaturation 8, 53. For instance, enhancing the concentration of the OH⁻ ion in the second solution, i.e. increasing the pH, results in lowering the final particle size. The possibility of controlling the particle size is one of the many advantages offered by chemical synthesis routes 8.
2.4.2.3. Hydrothermal Synthesis

Hydrothermal synthesis is a low-temperature and environmentally friendly alternative to the methods mentioned earlier with the advantage of being a single-step, low energy consumption and time saving process with no need for high-temperature calcination and extensive milling \(^{54}\). Further advantages of this method include high chemical and phase purity, low aggregation levels and narrow crystallite size distributions for the resulting material, in addition to excellent control of particle morphology. It is possible to produce a wide range of particle shapes, both equiaxed, such as cubes, spheres, diamonds, bipyramids, and elongated, such as fibres, whiskers, nanorods, nanotubes and also platelets, nanoribbons, nanobelts, etc \(^{20, 55-60}\). The particle size can also range from a few nanometers to large single crystals.

The phase relationships in the \(\text{Al}_2\text{O}_3–\text{H}_2\text{O}\) system, which were established initially by Laubengayer and Weisz \(^{61, 61}\), and subsequently studied by several other investigators such as Ervin and Osborn \(^{62}\) and Kennedy \(^{63, 64}\) revealed the presence of only four phases in the temperature range of 0\(^{\circ}\)–500\(^{\circ}\)C and pressure range of 1–100 MPa. These phases include gibbsite \(\text{Al(OH)}_3\), boehmite \(\gamma\)-\(\text{AlOOH}\), diaspore \(\alpha\)-\(\text{AlOOH}\) and \(\alpha\)-alumina, Figure 2-8.

![Figure 2-8](image)

**Figure 2-8** Hydrothermal \(\text{Al}_2\text{O}_3–\text{H}_2\text{O}\) phase diagram \(^{65}\).

By increasing the temperature under hydrothermal conditions boehmite transforms either directly into the \(\alpha\)-alumina phase at 380\(^{\circ}\)C and pressures between 1-15 MPa or into the intermediate diaspore phase from 210\(^{\circ}\)C and then into \(\alpha\)-alumina from 360\(^{\circ}\)C.
at higher pressures, without forming transition aluminas \(^65\). The following reactions occur under hydrothermal conditions at pressures in the range of 1-15 MPa:

\[
\begin{align*}
\text{Al(OH)}_3 & \rightarrow \gamma-\text{AlOOH} + \text{H}_2\text{O} \quad \text{at } \sim 100{\degree}\text{C} \quad \text{Eq. 2-3} \\
2\gamma-\text{AlOOH} & \rightarrow \alpha-\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad \text{at } \sim 380{\degree}\text{C} \quad \text{Eq. 2-4}
\end{align*}
\]

### 2.4.3. Thermophysical Synthesis

The other common technique to produce ceramic particles is via thermophysical methods, in which materials with relatively large particles are used as a source. Subsequently by applying thermal energy, sometimes combined with mechanical stress, these materials are reduced to a powder form without having any change in their chemical composition. The major technique to be used in this category is gas phase condensation. This method involves evaporation of solid by Joule heating to form a supersaturated vapour, from which fine-scaled particles condense. This supersaturated vapour can be achieved by other means as well including electron beam evaporation or laser ablation, which lead to a wide range of particle sizes, shapes and compositions depending on the precise thermophysical route \(^1,66-68\).

### 2.4.4. Mechanochemical Synthesis

In addition to the methods mentioned above, mechanical milling can be used as a cost-effective and simple technique to create ceramic nanopowders such as alumina in large scales \(^69\). Many researchers have used this technique to produce nanocrystalline particles by milling one or more precursors together and reaction of them either during milling or in a post-milling heat treatment to achieve a product with nanocrystalline particles within a soluble salt matrix. When the reaction is completed, the nanopowder can be obtained by removal of the matrix phase by washing with appropriate solvents \(^1,69,70\). Ultra-fine powder of pure \(\alpha\)-alumina with mean particle size of \(\sim 130\) nm was synthesised by mechanochemical treatment of a mixture of anhydrous AlCl\(_3\) and CaO, followed by heat treatment at 1300\(^{\circ}\)C.
2.4.5. Comparison of Different Synthesis Approaches

There are advantages and disadvantages for each of the synthesis techniques described above. The chemical methods can be used to produce chemically pure powders in large amounts; their degree of purity is limited only by the purity of the reactants. Moreover having a great knowledge of chemical, thermodynamic and kinetic theories will also help to manipulate these chemical reactions, particularly when preparing nanocrystalline powders using conventional and relatively simple routes. For instance, oxidation (burning) of magnesium and zinc has been used to produce nanocrystals of MgO and nanofibrils of ZnO. However chemical routes have some drawbacks including: (i) the surfaces of the resulting powders have a tendency to become contaminated by the medium they are produced in, (ii) a new reaction is needed to achieve each new composition desired in nanocrystalline powder, which requires changing and optimising the starting chemicals, the reaction kinetics and relationships between reaction conditions and powder characteristics.

Mechanical milling does not have the limitations mentioned above, as theoretically almost every material can be ground into a fine powder and the basic procedure does not need to be changed to make new powders and just minor adjustments will be adequate. However this method is not able to manufacture discrete nanoparticles in ultra-fine ranges. Moreover this technique does not support a high level of control over the formation of phases in multi-phase systems and it also increases the possibility of contaminating the powders with the milling media.

Similar to milling, the thermophysical approaches can be applied to most of the material systems and they are believed to be the cleanest of all the nanoceramics synthesis methods, for example sputtering, electron beam evaporation and ablation procedures are normally carried out in a vacuum chamber with a well-controlled environment. However, the need to evaporate in a low vapour pressure atmosphere makes this method an expensive and slow production process, for instance electron beam evaporation of a target material in a laboratory reactor results in about 8 gram per day of nanoceramic powder. Therefore the thermophysical techniques have been used only in laboratory conditions to investigate the synthesis of different nanocrystalline ceramics, although these methods have been used in industry by construction of multiple parallel reactors or moving from batch to semi-continuous processing. A major drawback of these
approaches is in preparing multi-component systems with different vapour pressures, which results in the need to modify the energy inputs to the sources or targets during the synthesis.

Conventional synthesis produces powders that are not particularly suited for the fabrication of coatings and fibres. Chemical routes are attracting attention for ceramic synthesis because some of them allow direct fabrication of coatings, fibres and monoliths without powder intermediates. These routes have the potential to achieve improved chemical homogeneity on the molecular scale, when an addition of small amounts of chemicals is needed, as well as achieving better mechanical properties such as strength by allowing preparation of un-aggregated powders. These potential advantages to improve the performance of ceramic components have increased the application of chemical synthesis methods, also known as soft chemistry routes, for developing ceramic materials. Among the chemical methods, increasing attention has been focused on sol-gel processing with aqueous oxide colloids, which has the practical advantage of avoiding the use of organic solvents and involves low cost precursors. Although different from the practical viewpoint, sol-gel processing and hydrothermal synthesis both include hydrolysis of solution species. Hydrothermal synthesis is a well-known industrial process offering a direct route to ceramic oxide powders; however it has not been the centre of attention as sol-gel or precipitation methods, even though controlling agglomeration level needs to be considered critically when carrying out a precipitation synthesis. The use of chemical methods can also lead to production of powders with ultra-fine size range.

2.4.6. Synthesis of Nanosized Alumina Powders

As previously mentioned, powders of α-alumina can be synthesized by several well-established synthesis methods, however in most of these methods temperatures above 1200°C are required to produce the crystalline α-alumina phase. The exceptions require calcination in specific atmospheres such as a hydrogen halide atmosphere, which raises costs.

Mechanical milling has been used for manufacturing nanoparticles by initially mixing the chemical reactants AlCl₃ and CaO. After milling, the mixture was heated to produce γ-
Al₂O₃ and CaCl₂, and then the soluble CaCl₂ matrix was leached away to release discrete nano-scaled particles of γ-Al₂O₃. Followed by calcining at 1250ºC, the γ-Al₂O₃ nanoparticles were transformed to ultra-fine but agglomerated α-alumina powder as can be seen in Figure 2-9.

![Figure 2-9](image)

**Figure 2-9** TEM micrograph of α-alumina powder formed by mechanical milling method ⁷⁰.

Figure 2-10 displays an example of an alumina nanopowder produced by a thermophysical technique using electron beam evaporation of an aluminium source in an oxygen atmosphere ⁶⁸. At low magnification, large agglomerates of alumina (300 nm-1 μm) can be observed clearly; by increasing the magnification TEM micrograph shows extremely fine alumina crystallites (25 nm) formed by the thermophysical route.

![Figure 2-10](image)

**Figure 2-10** Low magnification TEM (left) and high magnification (left), dark field TEM micrographs of the powder morphology resulting from electron beam evaporation ⁶⁸.
A number of researchers have attempted to use $\alpha$-alumina particles for seeding to act as nuclei and increase the kinetics of the $\theta \rightarrow \alpha$ transformation and, hence, to control the development of the $\alpha$-phase. The concept of applying nucleation in a transformation originated from glass-ceramics, however, seeding refers to the intentional introduction of particles with the aim of acting as nuclei in the transformation process rather than relying upon growth during heating as in glass-ceramics. Kumagai and Messing $^{22,23}$ studied the transformation, microstructural development and densification of boehmite gels, formed via a sol-gel process, with added $\alpha$-alumina seeds. The concept of seeding a transformation had been widely practiced by that time, but had not been applied in the ceramic industry broadly $^{21,21,22,22,23}$. They reported that by introducing 0.5-10 wt% of a commercial $\alpha$-alumina powder, on a dry weight basis, as seed to boehmite gel, both the kinetics of the transformation and the microstructure of the final product could be improved. Seeded gels fragments with 1.5 wt% seed could be sintered to almost full density at 1200°C. Sintered densities as a function of sintering temperature for the unseeded and seeded samples are presented in Figure 2-11.

![Figure 2-11](image)

**Figure 2-11** Density of gel fragments sintered for 100 minutes as a function of temperature $^{22}$.

The density of all samples was higher than 65% of theoretical at 1050°C and in the case of the 1.5 wt% seeded sample, it was about 75%. This difference is due to the fact that the seeded samples have already commenced sintering, whilst the unseeded sample was still transforming. The microstructures of polished and etched surfaces of
samples sintered at 1200°C are shown in Figure 2-12. Because of the relatively low density of the 0.15 wt% seeded sample, there was a considerable amount of grain pullout during polishing. The sample seeded with 1.5 wt% seeded was almost fully dense with mean grain size of <1 μm.

**Figure 2-12** SEM micrographs of a) 0.15 wt% and b) 1.5 wt% seeded samples.

In order to maintain continuity at the transforming interface during growth of α-alumina, the seed particles are required to be in intimate contact with numerous particles. Thus, the dispersion of individual seed particles in the boehmite gel matrix and the number of seeds is critical in controlling the transformation. For example, adding 0.15 wt% seed slightly influenced the transformation of boehmite to α-alumina whereas 1.5 wt% represented more suitable concentration for this transformation, based on the sintering experiments and also Differential thermal analysis (DTA) results, Figure 2-13. DTA along with XRD provided an experimentally expedient method to determine the effectiveness of seeding on phase transformations in the study and it was proved that seeding just affected the exotherm associated with the θ-to α-alumina transformation. As shown in Figure 2-13, the transformation for unseeded samples temperature was 1215°C, which reduced to 1050°C with 10 wt% seeding, whereas only 1.5 wt% seeding decreases the transformation temperature to 1075°C.

Dynys and Halloran have investigated the addition of 0.4 wt% MgO, Cr₂O₃, and Fe₂O₃ via water-soluble salts to aluminum secbutoxide (Al(OC₄H₉)₃) derived boehmite. They revealed that adding Fe₂O₃ increased the transformation in kinetics to achieve α-Al₂O₃, whilst MgO and Cr₂O₃ seeds did not affect the transition.
The seeding concept was also studied by Rajendran \(^2^6\) during the synthesis of ultra-fine \(\alpha\)-alumina powders via precipitation. The unseeded samples transformed to \(\alpha\)-alumina powder at 1200°C, Figure 2-14(a), resulting in powders with an average particle size of 200 nm after undergoing the usual transition phase changes during heat treatment. Seeding the precipitate lowered the transformation temperature to 1120°C, which was decreased further by 170°C to 950°C, Figure 2-14(b), by the presence of nitrate ions, predominantly as ammonium nitrate, which is a by-product of the precipitation of aluminium nitrate and ammonia solution, in the precipitate. This powder had the average particle size of \(\leq 60\) nm along with less than 5 wt% of \(\theta\)-alumina particles of \(~10\) nm.

As shown in Figure 2-15, the ammonium nitrate present in nitrated/seeded samples has affected the transformation temperature and also the particle size. The nitrate decomposes during calcination releasing a large amount of energy, \(210\) kJmol\(^{-1}\) \(^7^4\), and oxides of nitrogen and nitric acid evolve from the powder at 320°C by the reaction of oxides of nitrogen with the hydroxyl ions of the precipitate. This reaction and the evolution of a large amount of energy may:

1. Introduce a considerable amount of high energy defects in the transition alumina matrix, which can release some energy when partially or fully destroyed. This energy can contribute to the energy required for overcoming the activation energy barrier for nucleation of alpha alumina \(^7^5\).
2. Induce the transformation of a fraction of the transition alumina to α-phase at a relatively low temperature, so the nitrate containing samples have a few extra α-alumina particles, which can lower the transformation temperature.

3. Affect the arrangement of atoms in boehmite and other transition alumina phases resulting in a highly disordered structure. These disordered metastable phases can be transformed to a stable corundum structure by obtaining minimum, but sufficient energy.

Li and Sun investigated the effect of the presence of ammonium nitrate and α-alumina seeding on the transformation temperature to the α-phase. It was shown that addition of 5 wt% α-alumina seeds along with the presence of 44 wt% ammonium nitrate could lower the temperature of the θ-alumina → α-alumina transition from around 1200°C to 900°C, although there was no change in the formation temperatures of the transition phases. The final α-alumina powder calcined at 900°C had a mean particle size of ~10 nm, though it also contained the seeds, Figure 2-16.
Figure 2-15  TEM image of nitrated/seeded powder heat treated at 950°C. The arrows show the theta alumina particles present \(^{26}\).

Figure 2-16  a) XRD pattern and b) TEM micrograph of \(\alpha\)-alumina powder obtained by calcination at 900°C \(^{25}\).

DTA results, Figure 2-17, show that for the unseeded sample, two endothermic peaks exist at around 110 and 200-600°C. The former is due to the evaporation of absorbed water and the latter is caused by the continuous loss of the structural water in aluminium hydroxides. There are two exothermic peaks as well: the first at 695°C is probably associated with the burning off of the organic materials and the second at
1193°C is due to the $\theta$-alumina $\rightarrow$ $\alpha$-alumina phase transformation. For the sample with residual NH$_4$NO$_3$, there is a sharp exothermic peak at 334°C. This is due to the decomposition of ammonium nitrate, which releases a large amount of heat, 210 kJ/mol$^{26}$. Here, the $\theta$-alumina $\rightarrow$ $\alpha$-alumina transformation temperature was decreased to 1127°C. The related TG analysis shows that there was about 44 wt% NH$_4$NO$_3$ in the sample. The addition of 5 wt% $\alpha$-alumina seed further lowered the $\theta$-alumina $\rightarrow$ $\alpha$-alumina transformation temperature to 918°C. This means that the combined effect of 44 wt% NH$_4$NO$_3$ and 5 wt% $\alpha$-alumina seed reduced the transformation temperature by 275°C.

![Figure 2-17 DTA curves of the a) unseeded, b) with residual NH$_4$NO$_3$, d) seeded samples and c) TG curve of the sample with residual NH$_4$NO$_3$]({image})

As the phase diagram in Figure 2-8 and related reactions indicate, under low-pressure hydrothermal conditions, $\alpha$-alumina can be crystallized directly from boehmite at temperatures around 380°C. A number of researchers have attempted to lower the phase boundary of the $\alpha$-alumina phase to $\leq$380°C by adding seeds to increase the kinetics of the $\alpha$-alumina transformation and control the development of the desired $\alpha$-phase$^{20, 60, 65}$.

Sharma and co-workers$^{20}$ reported the synthesis of $\alpha$-alumina with a small amount of boehmite by using 4 wt% of seed with respect to Al$_2$O$_3$ via a co-precipitation method.
(pH~10) followed by a hydrothermal treatment under a saturated water vapour pressure at 190°C. A mixture of two different types of surfactants (surface active agents) was also used during the precipitation of precursors in this work in order to modify the surface of growing particles during the precipitation process, so the growth reaction is allowed to take place but not the “growing together” process. The surface free energy of these particulates can be reduced to an appropriate level by using a surface-active agent (so called “surface modifier”), which interacts with the generated particle surface. This method has been experienced earlier for synthesizing Eu-doped yttria powder. As shown in Figure 2-18, boehmite was obtained for the unseeded sample after hydrothermal treatment whereas α-alumina with 4 wt% boehmite was obtained after seeding the initial gel.

![XRD patterns of synthesised powders: a) unseeded, b) seeded, and c) seeded after being calcined at 950°C; showing boehmite and α-alumina peaks.](image)

Figure 2-18 XRD patterns of synthesised powders: a) unseeded, b) seeded, and c) seeded after being calcined at 950°C; showing boehmite and α-alumina peaks.

Figure 2-19 shows the FTIR spectra of different samples. For the unseeded sample, Figure 2-19(a), a broad peak exists at 3385 cm\(^{-1}\), which is due to OH stretching and can be caused by M–OH stretching. Two peaks at 1355 and 1450 cm\(^{-1}\) are due to C=C and C–C stretching bands. The peaks at 1530 and 1420 cm\(^{-1}\) are caused by stretching and bending of C–O bonds, respectively. The humps existing at around 2900 cm\(^{-1}\) are attributed to C–H stretching. These spectra represent the main components of the surfactants, Tween-80 and β-alanine. The intensity of these peaks reduced in the seeded powder, Figure 2-19(b). It could be due to their dissolution while washing the
powder in acetic acid. The two bands at 1700 and 1255 cm\(^{-1}\) are respectively associated with the asymmetric and symmetric vibrations of the COO of acetic acid. There is a peak at 3385 cm\(^{-1}\) on the FTIR spectra of the seeded powder, which is very weak and can be assigned to either surface-adsorbed water or OH groups because of the existence of trace AIOOH. The remaining peaks at 750 to 1000 cm\(^{-1}\) can be caused by Al–O vibrational modes.

![FTIR spectra of synthesised powders: a) unseeded, b) seeded, and c) seeded after being calcined at 950°C](image)

**Figure 2-19** FTIR spectra of synthesised powders: a) unseeded, b) seeded, and c) seeded after being calcined at 950°C.

Finally on the FTIR of the seeded powder after being heat treated at 950°C in Figure 2-19(c), the peaks associated with C=C, C–C, C–H, C–O, and acetate bonds have disappeared. This is probably because of the removal of organic materials during the heat treatment process. Further DTA study also confirmed that the organics were eliminated at temperatures above 350°C. Additional characterizations showed that the synthesized \(\alpha\)-alumina particles were about 60 nm in size, calculated by the Scherrer formula, with a surface area of 245 m\(^2\)g\(^{-1}\).

Hydrothermal synthesis of fine \(\alpha\)-alumina powders by using seed peptized with tetraethylammonium hydroxide (TEAH) in an acidic environment at 200°C was investigated by Yang, et al.\(^{60}\). After characterization by XRD the results illustrated that \(\alpha\)-alumina powders could be obtained by adding 4 wt% seed relative to the amount of the starting aluminium salt without forming the transition aluminas. Figure 2-20 shows the XRD patterns of various samples after being hydrothermally treated.
For the seeded samples, $\alpha$-alumina with some amount of boehmite was achieved, whilst the only phase detected in the unseeded sample was boehmite. The crystallite size of the powder resulted from hydrothermal treatment of 4 wt%-seeded sample was 32 nm, calculated using the Scherrer formula, with the specific surface area of 8.0 $\text{gm}^{-2}$. This low value of the surface area could be due to agglomeration of the ultra-fine particles of $\alpha$-alumina.

![Figure 2-20](image)

**Figure 2-20** XRD patterns of unseeded and seeded samples after hydrothermal treatment $^{60}$.

The SEM micrographs of the different powders after being hydrothermally treated at 200°C, are demonstrated in Figure 2-21.

![Figure 2-21](image)

**Figure 2-21** SEM morphologies of the a) unseeded and b) 1 wt% seeded powders after hydrothermal treatment $^{60}$.

The unseeded sample shows the typical needle-like boehmite particles, which were distributed homogeneously. Addition of the seeds resulted in the formation of a
bimodal morphology, consisting of agglomerates of needle-like particles and $\alpha$-alumina particles. The particles of $\alpha$-alumina were embedded into the agglomerates of boehmite, particularly for the samples with 1 and 2 wt% $\alpha$-alumina seed. This has been less significant for the sample with 3 wt% seeds, where individual $\alpha$-alumina particles could be observed. In the case of the 4 wt% seeded sample, traces of boehmite were rarely seen using the SEM.

So far, to our knowledge, most of the researches have concentrated on applying seeds to different chemical routes to obtain $\alpha$-alumina at lower temperatures. However, the phase transformation process to $\alpha$ phase in reaction-formed seeded particles has rarely been reported. The main focus of the present work is to study in detail the effects of $\alpha$-alumina seeding in combination with the use of different chemical additives such as surfactants for both precipitation and hydrothermal synthesis methods with a view to controlling the size, phase and morphology of resulting alumina nanoparticles.

### 2.5. Processing of Nanoceramics

The recent interest in the potential for novel properties arising from ceramic materials with grain sizes smaller than 100 nm has resulted in a need for processing routes to manufacture these ceramics. In the coming section different techniques for fabrication of starting powders, forming them into required shapes, and finally their densification process will be briefly reviewed.

#### 2.5.1. Issues Related to the Fabrication of Nanoceramics from Nanocrystalline Powders

So far the potential advantages of nanoceramics and their synthesis routes have been discussed, but there are a minimum of four major issues that need to be addressed for the successful preparation of nanostructured ceramics by the compaction and sintering of ultrafine starting powders, including $^1$:

- Producing sufficient quantities of nanocrystalline powder
- Controlling agglomeration in the nanocrystalline powder
- Compaction of the ultrafine particles to achieve flawless dense packing before sintering
- The minimisation of grain growth during sintering.

The first two issues will be explained below and other two will be discussed in subsequent sections.

### 2.5.1.1. Producing Sufficient Quantities of Ultrafine Powder

In the early years the production of ultrafine powder was a key obstacle in the preparation of nanoceramics. In 1984 Gleiter et al. 78 reported a “gas phase condensation” technique for preparing iron nanoparticles with less than 10 nm particle size. Later the technique has been used for the preparation of ceramic nanoparticles as well. ZnO 79, 80 and MgO 79 were prepared by direct evaporation and condensation of high vapour pressure ceramics. Due to the simplicity of the process, this technique became popular and some other oxide ceramics such as Al₂O₃ 79 were also prepared using this method.

Techniques that have been scaled-up for the commercial production of nanopowders include gas condensation, combustion synthesis, thermochemical synthesis, chemical precipitation and sol-gel processing. These methods are the main reason that a large number of nanopowders are available now 1, though as will be seen below, many are not of sufficient quality to be formed successfully into nanostructured ceramics.

### 2.5.1.2. Controlling Agglomeration in Nanocrystalline Powders

Nanocrystalline powders are often very heavily agglomerated, Figure 2-22 1. Therefore the true particle size in most powders is the agglomerate. Hard agglomerates delay the progress of eliminating pores, prevent dissimilar nanoparticles from mixing uniformly and can subsequently densify into large grains 1.
Non-agglomerated powders just have one peak in the pore size distribution, which indicates the presence of only small intra-agglomerate pores in the powder. In the case of agglomeration, the presence of both intra-agglomerate and inter-agglomerate pores in the agglomerated powder, Figure 2-23, will lead to two separate peaks in the pore size distribution curve; one related to the small intra-agglomerate pores and the other to the inter-agglomerate pores, Figure 2-23(b). A poorly agglomerated powder might have several overlapping peaks, as a result of possessing different degrees of agglomeration present in the powder, Figure 2-23(a) and finally an ideal powder, Figure 2-23(c), in which just small intra-agglomerate pores are present, has only one distribution peak.

Figure 2-23 Pore size distribution of a) a heavily agglomerated nanocrystalline TiO₂ powder, b) another TiO₂ powder with dual peak showing agglomeration and c) schematic distribution peak for an ideal powder with no agglomeration, in which just small, intra-agglomerate pores are present.
Pressureless sintering is very sensitive to the agglomeration of nanoparticles since the driving force, shrinkage and its rate inside the agglomerates are different from those in between the agglomerates. This causes internal stresses resulting in the appearance and stabilisation of large pores or microcracks, the size of which can be determined by the density, strength and size of the agglomerates. Therefore the presence of agglomerates is extremely damaging for the sintering of nanocrystalline particles to a nanostructured ceramic with mean grain sizes <100 nm.

As can be seen in Figure 2-24, which displays the sintering behaviour of nanocrystallite TiO$_2$ with three different agglomerate sizes, the larger the size of the agglomerate, the higher the sintering temperature will be$^{82,84}$. The latter is a result of the need to eliminate the large inter-agglomerate pores during densification. In the sintering process of an agglomerated powder, the small intra-agglomerate pores present initially disappear, partway through the sintering process. At this point the widely spaced large inter-agglomerate pores are the only pores present to pin the grain boundaries and control the grain growth, hence the grain size can easily grow to the size of the agglomerate.

![Figure 2-24](image_url)

**Figure 2-24** Relative density of nanocrystalline TiO$_2$ (anatase crystal structure) as a function of sintering temperature for three different sizes of agglomerates: non-agglomerated powder (N/A)$^{83}$ and powders with 80 and 340 nm agglomerate sizes$^{82,84}$. 

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2.5.2. Green Forming

The first step in the manufacture of a fully dense ceramic using a nanocrystalline powder is to form the latter into a cohesive compact termed as a 'green body'. As decades of study on conventional ceramic processing have revealed, the uniformity and homogeneity of particle packing in the green body has a great affect on the densification process and final density of ceramic compact. However the small size of particles in nanocrystalline powders causes the disadvantage of being relatively susceptible to the formation of inter-particle London-Van der Waals bonds, which occurs both in wet or dry states. Even if there is no bond formed during the synthesis process, the Van der Waals attraction can cause the powder particles to bond together to form agglomerates during the handling, drying, or storage stages. The consequences of forming agglomerates were discussed in section 2.5.1.2.

Generally green forming techniques used for consolidation of ceramic powders and producing the required shapes are divided into three major categories: (i) wet forming, (ii) dry forming and (iii) plastic forming, of which the first two methods have been used in this work and are explained below:

2.5.2.1. Wet Forming

2.5.2.1.1. Colloidal Processing of Ceramics

The most important steps in colloidal processing are preparing the suspension, forming it into the desired component shape and finally removing the solvent phase. Colloidal processing has been shown to produce more uniform microstructures and fewer defects from submicrometer ceramic powders. The major advantage of this method compared to the common powder processing (pressing) is that in colloidal processing the particle packing can be controlled by the particle size and not by the granule size (such as in pressing) and hence it can produce more dense green bodies.

Colloidal stability is governed by the total interparticle potential energy, $V_{\text{total}}$, which can be expressed as:

$$V_{\text{total}} = V_{\text{vdw}} + V_{\text{elect}} + V_{\text{steric}} + V_{\text{structural}}$$

Eq. 2-5
Where $V_{vdw}$ is the attractive potential energy due to long range van der Waals interactions between particles, $V_{elect}$ is the repulsive potential energy resulting from electrostatic interactions between like charged particle surfaces, $V_{steric}$ is the repulsive potential energy resulting from steric interactions between particle surfaces coated with adsorbed polymeric species, and $V_{structural}$ is the potential energy resulting from the presence of non-adsorbed species in solution that may either increase or decrease suspension stability. The various types of stabilisation are schematically illustrated in Figure 2-25.

![Figure 2-25](image)

**Figure 2-25** Schematic illustration of the interaction potential energy and relevant length scales for a) electrostatic, b) steric, and c) structural contributions, where $k^{-1}$ is the effective double-layer thickness, $\delta$ the adlayer thickness, and $\sigma$ the characteristic size of species resulting in ordering within the interparticle gap.

Ceramic aqueous suspensions have to fulfil several requirements. The ceramic particles should be able to remain in suspension and not settle rapidly under the effect of gravity, as otherwise segregation happens, which can result in density inhomogeneities in the green bodies. In addition, the suspensions need to be easily
reproduced and not be sensitive to minor variations in solids content, chemical composition and storage time. They have to be of high solids content as well to achieve reasonable casting rates and to decrease energy consumption in the subsequent drying stage, as there is lower moisture content to be removed \(^88, 89\). A recent trend in the ceramic industry is to develop very fine particles in order to increase the sintering rates as well as decreasing the size scale for mixing uniformity in powder blends. This combination of high solids loading and fine particles results in very high viscosity due to enhanced particle-particle interactions, which results in difficulties with handling the ceramic suspensions \(^90\).

As mentioned earlier, fine powders have the tendency to agglomerate because of the attractive inter-particle Van der Waals forces. Adding appropriate dispersants can eliminate this tendency by changing the powder surface properties so that repulsive forces become stronger than the attractive ones and the particles do not agglomerate in the ceramic suspension. This occurs either because of the electrostatic repulsion as a result of the overlapping of electrical double layers or due to steric hindrance resulting from absorption of large molecules \(^91\). Dispersant addition can dramatically reduce the viscosity of slurries with very high solids content, thus the ceramic industry has a constant demand for effective dispersants or deflocculants such as polyacrylates \(^92-94\).

Polyelectrolytes are polymers possessing a charge that is present along the length of the polymer chain, rather than having a charged species at one end of the molecule only as in other polymers. Polyelectrolytes that are derived from weak acid groups such as carboxylic acids and are consequently affected by the pH of the suspension are called weak polyacrylates. In contrast, strong polyelectrolytes have a tendency to stay relatively unaffected by pH changes \(^94\).

Various dispersants are used for the stabilization of oxide powder suspensions such as alumina, titania and zirconia, however polyacrylate salts, generally referred to by their commercial names, such as Dispex, Darvan and Dolapix, are most often employed. For these weak polyelectrolytes, such as ammonium polyacrylate in Figure 2-26, under certain conditions one mechanism dominates. In solutions with low electrolyte concentration and a pH above the dissociation point of the acid group, the charged polyelectrolyte stretches because of electrostatic repulsions along the polymer length \(^95, 96\). Therefore it will be adsorbed onto the powder surface in a thin, flat train...
configuration, with the formation of loops suppressed, Figure 2-27. Here the steric barrier is not of sufficient thickness to contribute to the overall dispersion of the powder; so it is mainly achieved by electrostatic repulsion. Steric repulsion will dominate, when the polyelectrolyte is associated or the electrostatic repulsions are suppressed by the presence of high concentrations of electrolyte. Under these conditions the polymer is coiled in solution and powder dispersion will be obtained only if the adsorbed layer is thick enough for the loops and tails to extend beyond the reach of van der Waals forces.  

![Chemical structure of ammonium polyacrylate](image)

Figure 2-26 Chemical structure of ammonium polyacrylate.

There is an assumption of the presence of a constant charge on the substrate onto which the polymer adsorbs, in the above treatment of polymer configuration. However adsorption onto a ceramic oxide powder becomes more complicated by the pH dependent behaviour of the surface layers. Dispersion of highly concentrated alumina suspensions using sodium polymethacrylate over a wide range of pH was comprehensively studied by Cesarano et al. It was reported that at lower pHs than the point of zero charge (PZC) alumina is positively charged and at higher pH, negatively charged and that the quantity of polymethacrylate required for covering the particles with a monolayer of polymer and, as a result complete electrosteric dispersion, reduced with increasing pH. This is associated with the domination of a loop and tail configuration at low pH, whereas at pH values up to the PZC, the presence of a train configuration of stretched negatively charged polymer adsorbed onto positively charged surface sites was considered to exist. At higher pHs, electrostatic repulsions between the negative powder and negative polymer caused the linear polyelectrolyte to dangle into the solution, adsorbing to the surface only at the few minor regions of positive surface charge. This model has been supported by Tjipangandjara et al., who studied the configuration of adsorbed polyacrylic acid
(20 ppm, molecular weight 88,000) on alumina from suspensions of fixed and varying pH using fluorescence spectroscopy techniques.

There are a number of methods existing for the preparation of ceramic green bodies from a colloidal suspension, which can be divided into different groups, including: (1) removal of the fluid such as pressure filtration, slip casting, osmotic consolidation, screen printing and tape casting, (2) particle flow such as sedimentation, centrifugation and electrophoretic deposition, and (3) gelation including aqueous injection moulding, gel casting and direct coagulation casting. As aqueous slips using electrostatic repulsion are generally used for slip casting, of all the techniques mentioned above just slip casting route will be discussed in detail below.

2.5.2.1.2. Slip casting

The slip casting technique is composed of several steps, including slip preparation by mixing the ingredients such as the powder, binders and required additives, then casting the slip into a mould with controlled porosity, the latter commonly being made of plaster. This porosity draws the water out of the slip via capillary forces during slip casting as shown in Figure 2-28. The amount of porosity in the mould can be controlled by the amount of water added during the manufacture of the plaster mould.46
Figure 2-28 Liquid removal during slip casting.  

Slip casting is a slow process since the casting rate decreases parabolically with the thickness of the cast layer. The setting time can differ from a few minutes to form a thin wall to several hours for producing a thick part.

There are two main issues to be considered during slip casting. First is the preparation of the slip. To obtain ceramic parts with the required properties in a reproducible way by slip casting, an appropriate choice of the particle size and shape, and controlling the particle surface chemistry is required. The particle size distribution is an important factor as well since it affects the packing of the particles during the consolidation. A good dispersion of particles is nevertheless required to achieve a homogeneous microstructure, a high green density and low pore volume. Ultrasonication has been found to improve the particles’ dispersion and consequently the quality of the green body.

The second issue in slip casting is the production of casting moulds. The absorption process of the liquid in the suspension is related to the capillary suction caused by the porosity existing in the mould. Therefore the porous network of the mould is of great importance for the setting rate and the properties of the green body.

There are different options for slip casting, which depend mainly on the complexity of the ceramic part. However drain and solid casting are the most common methods as shown in Figure 2-29. In drain casting, the slip is left in the mould until a wall with the required thickness is built, after which the excess slip is drained from the mould. Solid casting is similar to drain casting, but slip is constantly added to the mould until a solid body has been achieved.
The main disadvantage of slip casting is the long time required to cast components in the mould and subsequent drying of them, which results in requiring a huge amount of inventory of moulds, high labour force, and a large working space. However, the ability to achieve a better particle packing and pore size distribution compensates some of these drawbacks.

2.5.2.2. Dry Forming

For the preparation of nanostructured ceramics, achieving green bodies with high density and uniform density distribution is essential, as this uniformity and homogeneity influences the densification and grain growth as described above. Mostly, the poor compaction behaviour of nanocrystalline powders can be related to the level of agglomeration existing in the powder.

One of the forming approaches that can be considered is pressing, which is carried out by placing the powder in to an appropriate die and applying pressure to achieve compaction. There are two common categories of pressing including uniaxial and isostatic pressing.

2.5.2.2.1. Uniaxial Pressing

In this method the powder confined in a die is compacted by a pressure applied along a single axial direction, as displayed in Figure 2-30. However, uniaxial pressing results in density variations, which can cause cracking and distortion during the sintering.
Figure 2-30 Schematic illustrating uniaxial pressing.\(^{46}\)

During the pressing of spray-dried powder the sequence of steps occurring is as following, Figure 2-34:

- Step I: rearrangement of the granules
- Step II: deformation of the granules, followed by elimination of the macro-porosity between them
- Step III: elimination of the micro-porosity existing inside the granules\(^{102}\)

Figure 2-31 Three steps of compression.\(^{103}\)
2.5.2.2. Isostatic Pressing

Isostatic pressing is generally used for producing parts with elongated or complicated forms. In this technique the powder is formed at a low pressure (normally by uniaxial pressing), then encapsulated in a deformable, leak proof membrane (rubber, latex or polymer), and immersed in a liquid that is subsequently pressurised. The liquid distributes the stress along all the surfaces of the powder compact in uniform manner. Therefore density gradients will be lower compared to uniaxial pressing and a better particle packing can be achieved, which results in a high and uniform green density.

2.5.2.3. Green Forming of Alumina Nanoceramics

The effect of forming method on the particle packing and its consequent effects on the phase transformations and hence the sintering behaviour of a transition alumina powder in nanostructured transition alumina have been investigated by M. Azar et al. They prepared green compacts with densities of 62 ±1% of the true density of 3.49 g/cm³, by slip casting using a transition alumina powder with the average particle size of 47 nm and crystal phase ratio of 70:30; δ:γ.

The slip cast bodies were formed from alumina suspensions of 22 vol% solid loading. Hydrochloric acid was used to adjust the pH to 4.5 at which electrostatic dispersion was achieved. After stirring the slurry for 24 h they were cast into porous alumina moulds in order to avoid any contamination of the green bodies by diffusion of impurities. The alumina bodies were studied using scanning electron microscopy after being removed from the mould, both after 24 hrs and after spending another 24 hrs in a dessicator.

Figure 2-32 represents the SEM micrographs of the green bodies showing that colloidal suspensions can result in fairly uniform green microstructures with low level of agglomeration and a uniform inter-particle pore distribution, which improves the packing uniformity.
In the work by M. Azar, pressed samples were formed by uniaxial pressing of 56 MPa of the as-received powder, which was followed by cold isostatic pressing of 350 MPa in order to achieve the same green density as slip cast samples (62% of true density). However this green density was the maximum value that could be obtained using these two methods. As can be observed in SEM micrographs of pressed green bodies, Figure 2-33, this forming method leads to heterogeneous microstructures with large-sized agglomerates and pores. The agglomeration originated from the initial powder and after being formed by dry pressing the agglomerates present in the green body resulted in two types of pores: inter-agglomerate pores as well as smaller inter-crystallite (intra-agglomerate) pores.

The difference between the initial packing of slip cast and pressed green bodies, for the same number of particles per unit volume, is schematically illustrated in Figure 2-34.
J. Li, et al. 105 have studied the relative density of the green compacts prepared from α-alumina nanocrystalline powders as a function of the uniaxial compaction pressure on the green compacts 105. Figure 2-35 demonstrates the values of the relative density of the green bodies as a function of compaction pressure. As can be seen, the green compacts of a relative density of 56% could be achieved at a compaction pressure of 1420 MPa in this work; this pressure is well above the working range of ceramic industries.

In the work done by Rajendran 26, green compacts were prepared by isostatic pressing and their pore size distribution was then measured. The most frequent pores diameters were at 130 and 26 nm for unseeded and nitrated/seeded samples with green densities of 46 and 47% of theoretical density, respectively. The smaller average pore size of...
nitrated/seeded sample is due to the fact that it compacted uniformly with a narrow pore size distribution, as this powder contained soft agglomerates of ultrafine particles.

The nano $\alpha$-alumina powder synthesised by Li and Sun was milled using pure alumina balls, with either anhydrous alcohol or deionised water as milling fluid in order to observe the effect of milling media on the strength of the agglomerates. Both of the milled powders were pressed uniaxially at 30 MPa into pellets 10 mm in diameter and bars of $6 \times 35$ mm$^3$ in size followed by cold isostatic pressing at 200 MPa. Figure 2-36 shows the ball-milled powders and their agglomerates with diameters in the range of less than 0.1 $\mu$m to around 7 $\mu$m. The strength of these agglomerates significantly affected the homogeneity of the microstructure in the green compacts.

![Figure 2-36](image)

**Figure 2-36** FEG-SEM micrographs of the $\alpha$-alumina powder after milling in: a) anhydrous alcohol and b) deionised water$^{26}$.

The green bodies made of the powder milled in anhydrous alcohol were fairly homogeneous, Figure 2-37(a), which means that the final compaction pressure, 200 MPa, has been more than the strength of existing agglomerates for this powder. Therefore these agglomerates could be crushed and the powder can be considered as being soft agglomerated. However, the agglomerates present in the powder milled in deionised water, were not crushed, so this powder is considered as having hard agglomerates. Green bodies prepared by using the hard agglomerated powder were not as homogeneous as the soft agglomerated powder, Figure 2-37(b).
Relative green densities of all the compacts were measured to be 36.6 and 28.9\%, for soft- and hard-agglomerated powders, respectively. The green density versus compaction pressure curves for these powders are both composed of two straight lines with different slopes, Figure 2-38, which can be due to the strength of the agglomerates. By this assumption, the strength of the agglomeration for the powders milled in anhydrous alcohol and in deionised water was determined as 76 and 234 MPa, respectively.

Sintering, a technical term for the densification of a powder body, generally involves the removal of the pores from between the initial particles resulting in a high amount of shrinkage, followed by grain growth and strong bonding between nearby particles.
There are two main issues required for sintering to occur: a) a transport mechanism for the material, which is primarily either diffusion or viscous flow, and b) a source of energy to activate and sustain this mechanism, such as heat\(^\text{46}\).

### 2.6.1. Sintering Stages

The stages of the sintering and physical changes occurring at every stage are listed below: The first stage includes rearrangement of the particles and initial necking between adjacent particles as a result of high surface energy and material transport. Figure 2-39(a-c) shows the changes occurring during the initial sintering stage; it contains primarily of necking between the particles.

In the next stage, Figure 2-39(d-f), the necking process continues and the porosity decreases, which results in a noticeable volume shrinkage. The grain boundaries start to shift allowing more neck growth and porosity removal to occur. This intermediate step occurs as long as pore channels are interconnected and terminates when these pores become isolated.

The final stage consists of final removal of the porosity by vacancy diffusion along grain boundaries, assisted by grain boundary movement and controlled grain growth. However, if the grain growth rate is too high, the boundaries move faster than the pores, leaving them isolated inside the grains with less chance of being removed. Therefore grain growth needs to be controlled in order to achieve maximum porosity removal. The final distribution of grains and pores is termed the microstructure. Figure 2-39(g-e) displays the changes that happen during the last stage of sintering.

### 2.6.2. Different Sintering Mechanisms

Sintering mechanisms can be generally divided into four categories, as summarized in Table 2-3\(^\text{46}\). Each of these processes can work on its own or be accompanied by other mechanisms to improve the densification process.
Figure 2-39 Stages of the sintering process and physical changes occurring at each different stage.

Table 2-3 Different sintering mechanisms.

<table>
<thead>
<tr>
<th>Type of sintering</th>
<th>Material transport mechanism</th>
<th>Driving energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour-phase</td>
<td>Evaporation-condensation</td>
<td>Differences in vapour pressure</td>
</tr>
<tr>
<td>Solid-state</td>
<td>Diffusion</td>
<td>Differences in free energy or chemical potential</td>
</tr>
<tr>
<td>Liquid-phase</td>
<td>Viscous flow, diffusion</td>
<td>Capillary pressure, surface tension</td>
</tr>
<tr>
<td>Reactive liquid</td>
<td>Viscous flow, solution-precipitation</td>
<td>Capillary pressure, surface tension</td>
</tr>
</tbody>
</table>

2.6.2.1. Vapour-phase Sintering

In this mechanism, which is important only in small number of materials systems, the driving force is the variation in vapour pressure as a function of surface curvature. The material is carried from the surface of the particles with a positive curvature radius and a relatively high vapour pressure to the contact area between particles with a
negative radius of curvature and much lower vapour pressure, as shown in Figure 2-40. Particles with smaller sizes and greater positive surface curvature result in higher driving forces for vapour-deposition transport. This mechanism changes the shape of the pores and produces bonding between neighbouring particles, which increases the strength of the material and decreases its permeability due to open porosity, but it does not lead to shrinkage and cannot result in densification by itself.

![Figure 2-40](image)

*Figure 2-40* Schematic of vapour-phase sintering, showing the transport of material during the process.  

### 2.6.2.2. Solid-state Sintering

The main feature of solid state sintering is the entire absence of any liquid phase. Transport of material in solid-state sintering is carried out by volume diffusion as illustrated in Figure 2-41. Diffusion can involve transporting atoms or vacancies along a surface or grain boundary or through the volume of the material. The driving force in this mechanism is the difference in free energy or chemical potential between the free surfaces of particles and the points of contact between neighbouring particles.

### 2.6.2.3. Liquid-phase Sintering

Liquid-phase sintering, which is the initial densification mechanism in silicate and many other systems, consists of the presence of a viscous liquid at the sintering temperature. The rate of this mechanism is controlled by three factors: a) particle size, b) viscosity, and c) surface tension. The last two factors are influenced strongly by the composition of the material and temperature.
This type of sintering generally occurs at the sintering temperature when liquid formed at the sintering temperature wets the solid particles, which results in creating capillary forces in the narrow channels between the particles. This capillary pressure helps the densification by rearranging the particles to achieve a better packing, enhancing the contact pressure between adjacent particles, which increases the transfer rate of materials by solution and precipitation, creep and plastic deformation, and grain growth.

Various microstructures can be achieved due to liquid-phase sintering, which could be affected by particle size, the amount of liquid present at sintering temperature, or the cooling cycle. In Figure 2-42, a schematic of a range of different microstructure is presented; (a) shows what might result from the sintering of glass particles, where there is no grain or grain boundary other than a few residual spherical pores. Figure 2-42b illustrates the result of densification of a composition having a large amount of liquid, which solidifies as a glass on cooling, whilst (c) and (d) display similar situations but with less liquid present and hence less resulting glass. Figure 2-42(e) demonstrates a material after liquid phase sintering, where the liquid crystallized during cooling or by a following heat treatment; this mechanism is termed as reactive liquid sintering. In the reactive liquid mechanism, similar to liquid-phase sintering, a liquid is present during sintering which yields the same driving energies as discussed in the above section. However, in this mechanism the liquid changes its composition...
or disappears during or after the sintering process. This removal of the liquid in the reaction improves the high-temperature properties of the material, allowing the material to be used even at temperatures above the sintering temperature.

To achieve reactive liquid sintering, the main approach is to select starting powders or additive that will go through a series of chemical reactions with one or more liquid intermediate compounds formed before the final solid compound results. 46.

![Schematic of different microstructures resulted from liquid-phase sintering](image)

**Figure 2-42** Schematic of a range of different microstructures resulted from liquid-phase sintering; see text for explanation.

### 2.6.3. Grain Growth

The average size of the grains enlarges in the final stages of sintering in polycrystalline materials. A grain boundary is a region with a complex structure with thickness in the range of 0.5 to 1.0 nm between the grains. The atoms in a grain boundary have a higher energy than those in the bulk of the grains, therefore reduction in the grain boundary area and, as a result in the energy associated with these boundaries, can be a driving force for grain growth. Over the years considerable research has been performed to study recrystallisation and grain growth, from which a number of rules about the grain growth phenomena have been made. These rules include 106:

(i) Grain growth occurs by grain boundary migration and not by the coalescence of neighbouring grains as in water droplets;

(ii) Grain boundary migration is discontinuous and its direction may suddenly change;

(iii) One grain may grow into a nearby grain on one side while it is being consumed from a different side;
(iv) The rate of consumption of grains increases as the grain is about to disappear;

(v) A curved grain boundary usually migrates towards its centre of curvature;

(vi) If the grain boundaries in a single phase meet at angles other than 120 degrees, the grain having a sharper angle will be consumed with the intention that the angles come close to 120 degrees.

The above points have been used as the foundation of a number of theories, which attempt to express grain growth in terms of more fundamental characteristics such as driving forces and mechanisms of grain boundary migration.

2.6.4. Minimising Grain Growth and Maximising Densification During Sintering of Ultra-fine Particles

As explained previously, the final stage of sintering is constantly accompanied by grain growth, which is a major challenge in the processing of nanostructured ceramics. Investigations into nanopowder consolidation have resulted in similar densification phenomena as in conventional powders\textsuperscript{107}. The particular aspects of sintering ultra-fine powders are affected by their high tendency to be agglomerated, significant interparticle friction, high reactivity and associated contamination. Densification of nanocrystalline powders is performed at temperatures lower (up to several hundred degrees) than conventional powders with larger particles. The onset of sintering in nanopowders may be as low as \~0.2 Tm compared to about 0.5 Tm for the powders of a higher particle size\textsuperscript{108}. There are quite a few approaches to control grain growth during densification of nanocrystalline powders including\textsuperscript{109}:

2.6.4.1. The Addition of Solutes or Second Phase Particles

Adding solutes or second phase particles decreases the grain boundary mobilities or pins them. However this process is limited to additives that do not have negative effect on the desired properties of the final product and can therefore be a major difficulty for many ceramic systems.
2.6.4.2. Very Rapid Firing

The limitation of this process is that it requires firstly highly homogeneous green bodies, as local variety of green density results in regions of the same compact being at various locations on the sintering curve, and secondly, physically small-sized components to avoid excessive thermal gradients.

2.6.4.3. Pressure-assisted Techniques

So far, all the sintering techniques discussed are termed as “Conventional” or pressureless sintering, where no external pressure is applied during the densification. Pressure-assisted techniques including hot pressing, hot isostatic pressing, sinter forging and the spark plasma sintering have been used for the production of nanostructured ceramics very successfully. These techniques bring some disadvantages of higher processing costs with them, as well as limited component shape capability. However, they can be very effective at enhancing the densification and reducing grain growth by the application of pressure at the sintering temperature, which accelerates the kinetics of densification. This occurs by increasing the contact stress between particles and by rearranging particle positions to improve the packing. The energy available for densification is increased by applying pressure during sintering; this can reduce the sintering temperature, usually resulting in less grain growth than would occur with pressureless sintering.

- **Hot Pressing**

Hot uniaxial pressing has been used to consolidate nanocrystalline ceramics. Here pressure and temperature are applied simultaneously to a sample contained typically in a graphite die uniaxially pressed between two graphite punches in vacuum or inert gas. The heat is transferred by the graphite heating elements surrounding the pressing tool, via radiation/convection. The pressures used are typically in the range of 25 MPa to 50 MPa. The application of pressure at the sintering temperature accelerates the kinetics of densification by increasing the contact stress between particles and by rearranging particle positions to improve packing. The energy available for densification is increased by a factor of about 20 by application of pressure during sintering; this can reduce the sintering temperature, usually resulting in less grain growth.
growth than would occur with pressureless sintering. This technique can only be used for samples with simple shapes and has been reported for the sintering of metals, intermetallic compounds \(108\) and nanoceramics \(110\).

- **Hot Isostatic Pressing (HIP)**

In hot isostatic pressing, pressure is applied simultaneously from multiple directions whilst heating, resulting in a more uniform pressure distribution in the sample. Hipping is utilized in a wide range of industries; some of its applications include densification of pre-sintered bodies for achieving full density and preventing excessive grain growth in \(\text{Al}_2\text{O}_3\), \(\text{Zr}_2\text{O}_3\), \(\text{Si}_3\text{N}_4\) and other ceramics and consolidation of encapsulated powders for the similar aim in ceramic superconductors and ceramic-ceramic composites \(111\). HIP densification involves relatively long times and grain growth is more likely to occur than in hot pressing, however grain sizes <100 nm have been reported using this method \(108\). This is achieved by sintering the samples under very high pressure (2 to 5 GPa) for a relatively shorter period of time (30 min) \(112\), therefore the equipment cost is very high for this technique. Typical hipping pressures and temperatures for various ceramics are shown in Table 2-4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point / °C</th>
<th>Hipping temperature / °C</th>
<th>Hipping pressure / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite</td>
<td>-</td>
<td>1100</td>
<td>200</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>2050</td>
<td>1500</td>
<td>100</td>
</tr>
<tr>
<td>SiC</td>
<td>2837</td>
<td>1850</td>
<td>200</td>
</tr>
<tr>
<td>(\text{B}_4\text{C})</td>
<td>-</td>
<td>2000</td>
<td>200</td>
</tr>
</tbody>
</table>

- **Sinter Forging**

The most attractive benefit of sinter forging is its ability to densify green compacts with large inter-agglomerate pores. In sinter forging a uniaxial pressure is applied, but unlike hot pressing or HIPing the sample is not confined by the die walls. Hence the sample is free to move in the lateral direction \(113\). This shear deformation can lead to the elimination of large pores as shown in Figure 2-43. The stress levels required for sinter forging are also lower than in hot pressing or HIPing. This method has been
used extensively to achieve nanoceramic particle consolidation for ceramics such as ZrO$_2$, Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ toughened Al$_2$O$_3$.

![Figure 2-43 Schematic showing how shear deformation can lead to the elimination of large pores](image)

- **Ultra-high Pressure Sintering**
  Here the pressures applied during sintering are very high; values up to 5-7 GPa have been achieved using belt-type and piston-anvil devices and cubic anvil cells. This high pressure, in combination with lower sintering temperatures, can be used to sinter nanoceramics. This technique has been reported for the sintering of 200 nm grain size SiC ceramics by applying 980 MPa pressure at 1600°C for 1 h.

- **Shock Compaction**
  In shock compaction high velocity compressive waves are used to compact and sinter ceramic powders simultaneously. The shock wave induces high pressure and at the same time causes localised heating of the particle surfaces due to friction caused by rubbing between adjacent particles. As a result of their small size, nanocrystalline particles allow this surface heating to be transferred quickly to the core of the particles, thereby allowing the entire particle to be at elevated temperature before the shock wave has completely passed through the particle.

- **Field-assisted Sintering Techniques**
  FAST techniques utilise the effect of an electric field on the particle surface and the resulting enhanced mass transport. Spark plasma sintering (SPS) or pulse electro-
discharge consolidation, where a powder compact is subjected to one or more arc discharges before or during pressure assisted sintering can significantly reduce sintering temperature and time\textsuperscript{108}. In comparison to hot pressing, the closest technique to FAST, the sample is also uniaxially pressed in a graphite die between two graphite/binderless tungsten carbide (WC) punches and heated to the desired temperature in vacuum/inert gas. However in the case of FAST the heating method is different from HP. Here, an electrical current flows through the graphite die and punches with the purpose of the pressing tool acting as the heating element by the Joule effect\textsuperscript{117}.

The key characteristics of SPS are:

1. The generation of local electric discharge and its effect on heat and mass transport;
2. The combined effect of external fields such as force and electric field on the densification and phase formation in a particulate system;
3. Influence of electric current in the near surface layers of conductors and semiconductors as well as insulators;
4. Rapid and uniform heating/cooling throughout the sample which gives the possibility to avoid thermal gradients.

Alumina ceramics fabricated by SPS have a grain size and density comparable to those densified by HIPing due to the advantage of high heating rate\textsuperscript{118}. For example, fully dense alumina bodies with mean grain size of 0.5 μm were obtained at 1200°C with dwelling times of 3-10 minutes by SPS\textsuperscript{119}. This short heating time suppresses the grain growth considerably. Dobedoe et al.\textsuperscript{120} achieved transparent alumina ceramics using SPS at 1200°C. By using SPS, Salvatore, et al. fabricated highly transparent pure alumina bodies with a fine mean grain size\textsuperscript{121-123}. The commercial alumina powder was sintered at temperatures as low as 1000°C under high pressures, Figure \textbf{2-44}. The application of the latter allowed fully dense alumina to be obtained with an in-line transmission of about 64% for a wavelength of 645 nm at low temperatures with no significant grain growth\textsuperscript{122}. 
2.6.4.4. Two-stage Sintering

Two-stage sintering technique was initially used by Lin et al. \(^{124}\) to improve the microstructure of alumina ceramics. The \(\text{Al}_2\text{O}_3\) powder compacts were heated up to 800\(^\circ\)C for 50 hours for a pre-coarsening step and then the temperature was increased to 1450\(^\circ\)C for the final densification step. After comparing the results with samples sintered without the pre-coarsening step, it was observed that the microstructures of the samples sintered using two-stage sintering method were more uniform with lower amounts of closed porosity for the same density. Moreover, applying the two-step method resulted in a noticeable higher sintered density, a smaller grain size and a narrower grain size distribution. This microstructural improvement was described as a result of a decrease in the effects of differential densification and the resulting delay of the pore channel pinch-off at higher density.

A similar method was applied to sinter silicon nitride ceramics, where the first step suppressed the densification as the \(\alpha\)-to-\(\beta\) phase transformation occurred, and in the second step, densification and grain growth were both promoted at higher temperatures \(^{125}\). The theory of two-step sintering changed completely after Chen et al. \(^{126,127}\) worked on the sintering of nanostructured \(\text{Y}_2\text{O}_3\) ceramics using a new route in which the green compacts were heated to a high temperature (e.g. 1250 or 1310\(^\circ\)C), known as \(T_1\), for a very short time and were then cooled down rapidly to a lower temperature (e.g. 1150\(^\circ\)C), \(T_2\), where they were held until they were fully dense, on average about 20 hours. The main aspect of the process was that there was no grain

**Figure 2-44** FEG-SEM micrographs of (a) as-received commercial alumina powder and (b) fracture surface of sintered sample at 1000\(^\circ\)C under 500 MPa \(^{122}\).
growth reported during the second step. As can be seen in Figure 2-45 an adequately high-density, e.g. >70% for the nano-yttria, was required in the first step \(^{126}\). Having a ‘frozen microstructure’ or simply no grain growth during the second step whilst the densification process was still occurring was explained as being related to a grain boundary network pinned by triple-point junctions with a higher activation energy for migrating than the grain boundaries. Therefore the fact of having a densification without grain growth was thought to be dependent on the suppression of grain-boundary migration although the grain-boundary diffusion was still active.

![Figure 2-45](image.png)

**Figure 2-45** Grain size as a function of density for yttria sintered via two-step approach \(^{126}\).

It was also suggested by the authors that there was a kinetic window for the second stage, which covered a wider temperature range with increasing grain size, Figure 2-46 \(^{128}\). At temperatures above this kinetic window, grain growth took place and the driving force diminished with grain size enhancement. At temperatures under the kinetic window, sintering was exhausted before full density was achieved. Nevertheless, fully dense bodies did not resist grain growth at \(T_2\), so an increase in the grain size was reported after a long enough ‘incubation period’. The effect of adding dopants on the second stage of sintering was also reported to be in agreement with observations made during single-stage sintering of yttria, for instance adding magnesium enhanced the kinetics whilst using niobium decreased them.
Further work by Chen et al. 127 was carried out on the two-step sintering of 10 nm BaTiO$_3$ and Ni–Cu–Zn ferrite powders, where green compacts were formed by die pressing followed by isostatic pressing. For both materials, the two-step sintering approach diminished the grain growth; however no more than one of the BaTiO$_3$ samples reached high density, 98% of theoretical density, whereas all the ferrite ceramics reached an average grain size greater than 100 nm. Subsequently a different BaTiO$_3$ nanopowder was sintered using the two-step route by other authors 129, where the average grain size of the fully dense compacts was reported to be about 1 μm after the second sintering stage.

2.6.5. Sintering Alumina Nanostructured Ceramics

In the work of Li and Ye 105, the synthesised $\alpha$-Al$_2$O$_3$ nanopowders with a wide range of average particle size were sintered using both conventional and two-step sintering routes. It was found that the relative density increased with increasing compaction pressure for the green compacts, Figure 2-47(a), and decreasing mean particle size of the starting $\alpha$-alumina nanocrystalline powders, Figure 2-47 (b).
Figure 2-47 Relative density of the alumina nanoceramics a) from the starting nanopowders of 48 nm sintered at 1500°C for 5 h vs the compaction pressure, b) pressed at 1120 MPa, which is well above the industrial pressure range, and sintered at different temperatures for 5 h vs mean particle size of the starting $\alpha$-alumina nanopowders $^{105}$.

This study showed that the densification of the alumina nanoceramics occurs mainly within a sintering temperature range of 1300°C and 1450°C, but fast grain growth occurs at temperatures above 1450°C. This suggests that the densification kinetics of the alumina green compacts differs from the grain growth kinetics. As these two processes take place in different temperature ranges, there is a possibility of increasing the density of nanoceramics without promoting grain growth. In order to obtain alumina nanoceramics with a high relative density and fine grains, a two-step sintering method was used, Figure 2-48, which resulted in an average grain size of 70 nm and a relative density of 95%. The high-quality densification was achieved by slower grain-boundary diffusion without encouraging the grain growth in the second step of sintering.

Figure 2-49 represents the density and densification rate versus temperature after sintering both slip cast and dry pressed compacts prepared by Azar, et al. $^{104}$. For both types of samples, the densification curve consists of two main stages (denoted I and II hereafter). The first stage of the densification (up to 1160°C for slip cast specimens and 1200°C for pressed bodies) occurs along with the transformation of transition alumina to $\alpha$-alumina. The second stage is related to the densification of the formed $\alpha$-alumina.
Figure 2-48  The average grain size of the alumina ceramics from the $\alpha$-Al$_2$O$_3$ nanopowders with a mean particle size of 10 nm pressed at 1120 MPa vs. the relative density using both single- (with the sintering time of 1 hr) and two-step sintering methods $^{105}$.

Figure 2-49  Density and densification rate versus temperature for slip cast (SC) and pressed (P) samples $^{104}$.

By comparing the densification curves of SC and P compacts, it was noticed that:

(a) Stage I is shifted towards lower temperatures for SC specimens and is accompanied by a higher amount of shrinkage.

(b) Stage II (densification of $\alpha$-alumina) results in more dense final bodies with SC samples. For instance the density of a slip cast compact after being sintered at 1700°C
was 98% of theoretical density (3.987 g cm\(^{-3}\)), while this value was only 79% for a dry pressed compact sintered at the same temperature.

Bulk density is demonstrated as the percentage of theoretical density in Figure 2-50 for the compacts prepared by Rajendran and sintered at temperatures in the range of 1200-1600°C for 2 hours \(^{26}\). Unseeded samples commenced to sinter only at 1300°C and to reach to the relative density of about 98%, they needed to be sintered to 1600°C. In contrast, sintering started from 1000°C for the nitrated/seeded samples and they could achieve 99% of TD after being sintered at 1450°C. Whereas the samples including only seed or nitrate sintered to higher densities compared to unseeded one; both achieved ~97% of TD after being sintered at 1500°C.

![Figure 2-50 Relative density of different samples as a function of sintering temperature \(^{26}\).](image)

An SEM micrograph of an un-seeded compact sintered at 1450°C for 2 h with a density of 88.0% TD, Figure 2-51(a), shows discontinuous and uneven grain growth with areas of different grain sizes and densities with average grain size of 1.8 μm, calculated by the linear intercept method. As shown in Figure 2-51(b), the sintered nitrated/seeded body under the same conditions had a density of 98.7% TD and displayed a narrow grain size distribution, with an average size of 0.94 μm. The kinetics of densification and grain growth are closely linked, as in the early stages of sintering grains almost grow linearly with densification. However, the grain growth becomes very fast as soon as the density of the ceramic body reaches about 95% TD. The amount of grain growth needed for full densification also depends on the pore
coordination number, \( n \): pore surrounded by number of grains. If this number is less than the critical coordination number, then the grain growth required to achieve full density is small. The average pore size of the nitrated/seeded sample was measured as 26 nm, which is about 5 times smaller than un-seeded compact, so more grain growth is needed for the latter to reach the full density.

![SEM images of un-seeded samples after sintering at different temperatures](image)

**Figure 2-51** SEM images of un-seeded samples after sintering at a) 1450°C and b) 1500°C, c) seeded sample after sintering at 1500°C and d) nitrated/seeded sample after sintering at 1450°C for 2 h $^{26}$.

The main focus of the present work was to synthesise nanosized alumina powders via precipitation and hydrothermal treatment and moreover to characterise the powders using different characterisation techniques. The nanopowders were used to prepare highly dense green bodies via both wet and dry forming methods. Densification of the green bodies was carried out by pressureless sintering, followed by measuring the density and grain size of the compacts. The resulting sintered compacts were compared to the submicron alumina products prepared using the commercial submicron-sized alumina suspension.
3. Experimental

3.1. Overall Methodology

This chapter demonstrates the experimental procedure involved in this project. Figure 3-1 and Figure 3-2 describe the overall work flow and the techniques involved.

![Flow chart of overall experimental work on nano α-alumina.](image-url)
Nanocrystalline $\alpha$-alumina powders were initially synthesized using two different synthesis methods viz. hydrothermal and precipitation routes. The hydrothermal treatment was carried out in both acidic and basic environments. The powders produced were characterised by using XRD, TEM and FEG-SEM.

The synthesised $\alpha$-alumina powders were then used to prepare colloidal suspensions of nanoalumina. After analysing the isoelectric and rheological behaviour of the prepared suspensions, different forming techniques including both dry and wet forming were applied to prepare nanoalumina green bodies. Spray freeze drying technique was used to produce granulated powders suitable for dry forming. After binder removal, sintering experiments were performed using both conventional single- and two-step heating. All the alumina compacts were characterised before and after being sintered using different characterisation techniques.

![Flow chart of overall experimental work on sub-micron $\alpha$-alumina.](image)

In order to compare the nanostructured alumina bodies to sub-micron sized compacts, a sub-micron alumina suspension received from Baikowski (Table 3-10) was processed similar to the nanoalumina suspension. The as-received suspension was characterised via using XRD, TEM and FEG-SEM. The isoelectric and rheological behaviour of this suspension was also analysed.
The alumina suspension was used to prepare granulated powder suitable for dry pressing via spray-freeze drying. Similar to the processing, sub-micron alumina bodies were formed using both slip casting and dry pressing. After binder removal of the green compacts, they were sintered using conventional single-step and two-step sintering methods. Both forming and sintering stages were followed by characterisation of the resultant alumina bodies.

3.2. Synthesis of Nanoalumina Powders

3.2.1. Synthesis Methodology

Synthesis of nano α-alumina was carried out by two different chemical routes: hydrothermal treatment and precipitation method. Figure 3-3 gives the detailed process flow chart for the synthesis of nanoalumina powder.

![Flow chart of synthesis experiments](image)

**Figure 3-3** Flow chart of synthesis experiments; AH: Acidic Hydrothermal treatment, BH: Basic Hydrothermal treatment and P: precipitation route.

Aluminium salts were dissolved in deionised water and stirred for 1 h before adding required amounts of surfactant and/or seed and further stirring. For hydrothermal
treatment two different sets of conditions were used: acidic and basic. Subsequently ammonia solution (for the basic route) or Tetraethylammonium hydroxide (for the acidic route) was added to the stirring suspension to form a gelatinous precipitate. The prepared precipitates were then transferred into autoclaves and placed in an oven for the hydrothermal treatment. Afterwards, the resulting powders were washed, desiccated in an oven and ground. The seeded samples were kept in 20% acetic acid solution for 30 min between washing and drying with the aim of removing any remaining aluminium hydroxide.

For the precipitation route, the precipitates prepared by using ammonia solution were filtered and desiccated in an oven followed by grinding. The ground powders were then heat treated in a conventional box furnace.

### 3.2.2. Raw Materials

The chemicals used for the synthesis of nanoalumina powders using both chemical methods are listed in Table 3-1:

### 3.2.3. Hydrothermal Synthesis

Aluminium salts such as aluminium chloride, aluminium nitrate and aluminium sulphate were used as the starting materials. A precursor solution was initially prepared by dissolving the aluminium salt in deionised water and stirring for 1 h at room temperature. Two different sets of conditions were used for the hydrothermal treatment, acidic and basic. For the former, no surfactant was used similar to the study by Yang, et al. 60, whilst for the latter a mixture of 2 surfactants, as studied before by Sharma, et al. 20, was added to the precursor solution: an amphoteric surfactant, viz. β-alanine and a non-ionic surfactant chosen from Tween-80, PEG or Dioctyl. The amount of 10 wt% (50 wt% β-alanine / 50 wt% non-ionic surfactant) with respect to the Al₂O₃ content was added separately to the precursor solution for some of the samples, with further stirring for 1 h.
### Table 3-1  List of chemicals used in this project.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Source</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium chloride hexahydrate</td>
<td>AlCl$_3$.6H$_2$O</td>
<td>99+%</td>
<td>Fisher Scientific, UK</td>
<td>Precursor</td>
</tr>
<tr>
<td>Aluminium nitrate nonahydrate</td>
<td>Al(NO$_3$)$_3$.9H$_2$O</td>
<td>98+%</td>
<td>Fisher Scientific, UK</td>
<td>Precursor</td>
</tr>
<tr>
<td>Aluminium sulphate</td>
<td>Al$_2$(SO$_4$)$_3$.16H$_2$O</td>
<td>96+%</td>
<td>Fisher Scientific, UK</td>
<td>Precursor</td>
</tr>
<tr>
<td>β-alanine</td>
<td>β-amino acid</td>
<td>98%</td>
<td>Sigma-Aldrich, UK</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Tween-80</td>
<td>Polyoxyethylene sorbitate</td>
<td>98%</td>
<td>Sigma-Aldrich, UK</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Dioctyl</td>
<td>Dioctyl sulfosuccinate</td>
<td>96%</td>
<td>Fisher Scientific, UK</td>
<td>Surfactant</td>
</tr>
<tr>
<td>PEG 3400</td>
<td>Polyethylene glycol</td>
<td>95+%</td>
<td>Sigma-Aldrich, UK</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>NH$_4$OH</td>
<td>35%</td>
<td>Fisher Scientific, UK</td>
<td>Precipitator</td>
</tr>
<tr>
<td>Tetraethylammonium hydroxide (TEAH)</td>
<td>(H$_2$C$_2$)$_4$NOH</td>
<td>25%</td>
<td>Merck, Germany</td>
<td>Precipitator</td>
</tr>
<tr>
<td>Alumina powder BMA15</td>
<td>α-Al$_2$O$_3$ (mean particle size of 150 nm)</td>
<td>99+%</td>
<td>Baikowski, France</td>
<td>Seed</td>
</tr>
<tr>
<td>Alumina powder SMA6</td>
<td>α-Al$_2$O$_3$ (mean particle size of 330 nm)</td>
<td>99+%</td>
<td>Baikowski, France</td>
<td>Seed</td>
</tr>
<tr>
<td>Alumina powder MR70</td>
<td>α-Al$_2$O$_3$ (mean particle size of 500 nm)</td>
<td>99+%</td>
<td>Albemarle, USA</td>
<td>Seed</td>
</tr>
<tr>
<td>Butanol</td>
<td>CH$_3$.,(CH$_2$)$_3$.OH</td>
<td>99+%</td>
<td>Fisher Scientific, UK</td>
<td>Milling aid</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>99%</td>
<td>Fisher Scientific, UK</td>
<td>Washing aid</td>
</tr>
</tbody>
</table>
Subsequently for the basic route, 4 wt% of one of the α-alumina powders with different particle sizes (BMA15, SMA6 and MR70 with mean particle size of 150 nm, 330 nm and 500 nm) was gradually mixed into the solutions to act as seeds for the seeded samples. Then 35% ammonia solution (Fisher Scientific, Loughborough, UK) was gradually added under continuous stirring until the suspension was converted to a gelatinous precipitate with a final pH of 10.0±0.1.

For the acidic route 0, 1, 2, 3 and 4 wt% seeds (BMA15) were used whilst the pH was subsequently changed; for the acidic route this involved gradually adding tetraethylammonium hydroxide, TEAH (Merck KGaA, Darmstadt, Germany), to obtain cloudy suspensions with a pH of 3.0±0.1.

In both cases, the precipitates were transferred into 150 ml stainless steel autoclaves lined with Teflon, which were placed in an oven held at different temperatures, starting from 190°C increasing to 220°C in intervals of 10°C, which was the safe working limit of the laboratory oven. The pressure that developed inside the autoclave was the autogenous water vapour pressure. Subsequently, the resulting powders were washed with deionised water and absolute ethanol then separated from the liquid phase by centrifuging at 3000 rpm, desiccated in an oven 80°C for 24 hours and ground using a pestle and mortar. The seeded samples were kept in 20% acetic acid solution for 30 min between washing and drying with the aim of removing any remaining aluminium hydroxide.

After characterising the hydrothermally-synthesised ground powders, they were heat treated in air in a box furnace at different temperatures from 800°C to 2100°C for several hours. The heating rate was kept constant at 5°Cmin⁻¹ for all the sintering experiments to minimise any possible thermal gradients within the samples. It also has to be mentioned that the furnaces were initially calibrated and their temperature was controlled during the sintering process at all times.
Table 3-2: Summary of the basic hydrothermal synthesis conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Salt</th>
<th>Seed</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB-C-0</td>
<td>Aluminium chloride</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HB-C-1</td>
<td>Aluminium chloride</td>
<td>BMA15 (150 nm)</td>
<td>-</td>
</tr>
<tr>
<td>HB-C-2</td>
<td>Aluminium chloride</td>
<td>BMA15 (150 nm)</td>
<td>B-alanine+ Tween 80</td>
</tr>
<tr>
<td>HB-C-3</td>
<td>Aluminium chloride</td>
<td>SMA6 (330 nm)</td>
<td>B-alanine+ Dioctyl</td>
</tr>
<tr>
<td>HB-C-4</td>
<td>Aluminium chloride</td>
<td>MR70 (500 nm)</td>
<td>B-alanine+ PEG</td>
</tr>
<tr>
<td>HB-S-0</td>
<td>Aluminium sulphate</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HB-S-1</td>
<td>Aluminium sulphate</td>
<td>BMA15 (150 nm)</td>
<td>-</td>
</tr>
<tr>
<td>HB-S-2</td>
<td>Aluminium sulphate</td>
<td>BMA15 (150 nm)</td>
<td>B-alanine+ Dioctyl</td>
</tr>
<tr>
<td>HB-S-3</td>
<td>Aluminium sulphate</td>
<td>SMA6 (330 nm)</td>
<td>B-alanine+ PEG</td>
</tr>
<tr>
<td>HB-S-4</td>
<td>Aluminium sulphate</td>
<td>MR70 (500 nm)</td>
<td>B-alanine+ Tween 80</td>
</tr>
<tr>
<td>HB-N-0</td>
<td>Aluminium nitrate</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HB-N-1</td>
<td>Aluminium nitrate</td>
<td>BMA15 (150 nm)</td>
<td>-</td>
</tr>
<tr>
<td>HB-N-2</td>
<td>Aluminium nitrate</td>
<td>BMA15 (150 nm)</td>
<td>B-alanine+ PEG</td>
</tr>
<tr>
<td>HB-N-3</td>
<td>Aluminium nitrate</td>
<td>SMA6 (330 nm)</td>
<td>B-alanine+ Tween 80</td>
</tr>
<tr>
<td>HB-N-4</td>
<td>Aluminium nitrate</td>
<td>MR70 (500 nm)</td>
<td>B-alanine+ Dioctyl</td>
</tr>
</tbody>
</table>
Table 3-3 Summary of the acidic hydrothermal synthesis conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Salt</th>
<th>Seed/wt% (BMA15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-C-0</td>
<td>Aluminium chloride</td>
<td>0</td>
</tr>
<tr>
<td>HA-C-1</td>
<td>Aluminium chloride</td>
<td>1</td>
</tr>
<tr>
<td>HA-C-2</td>
<td>Aluminium chloride</td>
<td>2</td>
</tr>
<tr>
<td>HA-C-3</td>
<td>Aluminium chloride</td>
<td>3</td>
</tr>
<tr>
<td>HA-C-4</td>
<td>Aluminium chloride</td>
<td>4</td>
</tr>
<tr>
<td>HA-S-0</td>
<td>Aluminium sulphate</td>
<td>0</td>
</tr>
<tr>
<td>HA-S-1</td>
<td>Aluminium sulphate</td>
<td>1</td>
</tr>
<tr>
<td>HA-S-2</td>
<td>Aluminium sulphate</td>
<td>2</td>
</tr>
<tr>
<td>HA-S-3</td>
<td>Aluminium sulphate</td>
<td>3</td>
</tr>
<tr>
<td>HA-S-4</td>
<td>Aluminium sulphate</td>
<td>4</td>
</tr>
<tr>
<td>HA-N-0</td>
<td>Aluminium nitrate</td>
<td>0</td>
</tr>
<tr>
<td>HA-N-1</td>
<td>Aluminium nitrate</td>
<td>1</td>
</tr>
<tr>
<td>HA-N-2</td>
<td>Aluminium nitrate</td>
<td>2</td>
</tr>
<tr>
<td>HA-N-3</td>
<td>Aluminium nitrate</td>
<td>3</td>
</tr>
<tr>
<td>HA-N-4</td>
<td>Aluminium nitrate</td>
<td>4</td>
</tr>
</tbody>
</table>

3.2.4. Precipitation Synthesis

For the precipitation method, the gelatinous precipitates prepared in section 3.2.3 were left at room temperature for 12 hours and then filtered using paper filters. Afterwards they were subjected to ultrasonic agitation produced by a SoniPrep ultrasound unit (MSE Ltd, London, UK, using 150 W at 15 kHz) and desiccated in an oven at temperatures in the range of 80-120°C for different durations and subsequently ground with a pestle and mortar.

To study the effects of adding surfactant and seed on the phase transformation of the precursor precipitates, samples with different compositions were prepared; for the first
group no α-alumina seed or surfactant was added; for the second group only α-alumina seed was introduced to the precursor gel, and for the third group a mixture of both surfactant (50 wt% β-alanine and 50 wt% Tween 80) and α-alumina seed were added. The ground powders were then treated in air in a box furnace using a heating rate of 5°C min\(^{-1}\) to temperatures ranging from 800°C to 1200°C with different dwelling times of 1 to 12 hours, as displayed in Table 3-4, with cooling rate of 10°C min\(^{-1}\).

For the two-step heat treatment route, a further high-temperature step (1200°C, 1175°C, 1150°C and 1100°C) was added to the low-temperature conventional heat treatment route (800°C) for a very short duration (1 minute) to the samples listed in Table 3-5.

### 3.2.5. Characterisation of Powders

The crystalline phase of the powders was determined using X-ray diffraction and Raman spectroscopy. The size of the particles was investigated by using transmission electron microscopy (TEM) and Mastersizer. The morphology of the synthesised powders was studied via Field emission gun scanning electron microscopy (FEG-SEM).

#### 3.2.5.1. X-ray Diffraction (XRD) Studies

The crystalline phase of the powders was determined using X-ray diffraction (Bruker D-8 Diffractometer, Bruker AXS GmbH, Karlsruhe, Germany) with a quarter-circle eul erian cradle, which is a non-destructive tool to analyse the crystalline phase and basic structure of the materials. Testing conditions were:

(i) CuK\(\text{α}\) radiation with a wave length of 1.5406 Å
(ii) All the samples were analyzed at a step size of 0.02° increment in 2\(\theta\) with a step time of 1 second
(iii) XRD patterns were recorded over the range of 20 from 20 to 60°
Table 3-4 Summary of the precipitation synthesis conditions used for the different powders (conventional heat treatment).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Surfactant wt% (β-alanine and Tween 80)</th>
<th>Salt</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-10-1</td>
<td>-</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/1 h</td>
</tr>
<tr>
<td>P-10-6</td>
<td>-</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
<tr>
<td>P-11-1</td>
<td>-</td>
<td>-</td>
<td>Cl</td>
<td>1100°C/1 h</td>
</tr>
<tr>
<td>P-11-3</td>
<td>-</td>
<td>-</td>
<td>Cl</td>
<td>1100°C/3 h</td>
</tr>
<tr>
<td>P-12-1</td>
<td>-</td>
<td>-</td>
<td>Cl</td>
<td>1200°C/1 h</td>
</tr>
<tr>
<td>P-S4-8-6</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>800°C/6 h</td>
</tr>
<tr>
<td>P-S4-8-12</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>800°C/12 h</td>
</tr>
<tr>
<td>P-S8-8-12</td>
<td>8</td>
<td>-</td>
<td>Cl</td>
<td>800°C/12 h</td>
</tr>
<tr>
<td>P-S4-10-1</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/1 h</td>
</tr>
<tr>
<td>P-S4-10-3</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/3 h</td>
</tr>
<tr>
<td>P-S2-10-6</td>
<td>2</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
<tr>
<td>P-S4-10-6</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
<tr>
<td>P-S8-10-6</td>
<td>8</td>
<td>-</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
<tr>
<td>P-S4-11-1</td>
<td>4</td>
<td>-</td>
<td>Cl</td>
<td>1100°C/1 h</td>
</tr>
<tr>
<td>P-S4S10-8-12</td>
<td>4</td>
<td>10</td>
<td>Cl</td>
<td>800°C/12 h</td>
</tr>
<tr>
<td>P-S8S10-8-12</td>
<td>8</td>
<td>10</td>
<td>Cl</td>
<td>800°C/12 h</td>
</tr>
<tr>
<td>P-S4S10-10-6</td>
<td>4</td>
<td>10</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
<tr>
<td>P-S8S10-10-6</td>
<td>8</td>
<td>10</td>
<td>Cl</td>
<td>1000°C/6 h</td>
</tr>
</tbody>
</table>
Table 3-5  Summary of the precipitation synthesis conditions used for the different powders (two-step heat treatment).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Surfactant wt% (β-alanine and Tween 80)</th>
<th>pH</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-TS-0</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>1200°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-1</td>
<td>4</td>
<td>-</td>
<td>10</td>
<td>1200°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-2</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1200°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-3</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>1100°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-4</td>
<td>4</td>
<td>-</td>
<td>10</td>
<td>1100°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-5</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1100°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-6</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1150°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-7</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1175°C/1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-8</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1200°C/1 min-800°C/6 h</td>
</tr>
<tr>
<td>P-TS-9</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-10</td>
<td>-</td>
<td>10 (Tween 80)</td>
<td>10</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-11</td>
<td>-</td>
<td>10 (β-alanine)</td>
<td>10</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-12</td>
<td>-</td>
<td>5 (β-alanine)</td>
<td>10</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-13</td>
<td>-</td>
<td>10 (β-alanine)</td>
<td>9</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
<tr>
<td>P-TS-14</td>
<td>-</td>
<td>10 (β-alanine)</td>
<td>8</td>
<td>1200°C/0.1 min-800°C/12 h</td>
</tr>
</tbody>
</table>
3.2.5.2. Transmission Electron Microscopy (TEM)

The particle size of the powders was determined using Transmission Electron Microscopy, TEM (JEOL JEM 2000FX, JEOL Ltd. Tokyo, Japan). The selected area electron diffraction (SAED) was performed using TEM. The samples were subjected to a parallel beam of high energy electrons. In that case, electrons were treated as wave-like, rather than particle-like. Because the wavelength of high-energy electrons was a fraction of a nanometer, and the spacing between atoms in a solid was only slightly larger, the atoms acted as a diffraction grating to the electrons. Some fraction of them were diffracted to particular angles, determined by the crystal structure of the sample, while others continued to pass through the sample without deflection. It resulted in ordered spots corresponding to the planes of that crystal structure. Hence this technique was used to confirm the crystallinity of the powders.

To prepare samples for Transmission Electron Microscopy, an ultrasonic agitator was used to suspend the prepared powders in ethanol as a solvent medium. After applying a small drop of the suspensions onto copper grids, they were left to dry in the sample box for 10-15 minutes before being studied on the TEM.

3.2.5.3. Mastersizer

The particle size distribution was measured using a particle size analyser (Mastersizer 2000, Malvern Instruments, Worcestershire, U.K). This facility is a fully-automated modular instrument designed for measuring the particle size distribution of wet and dry samples (from 0.02 to 2000 microns, depending on material properties) with the help of laser diffraction: the particle passing through the laser beam will scatter light at an angle that is inversely proportional to their size: large particles scatter at low angles and small particles scatter at higher angles. The map of scattering intensity versus angle is the primary source of information used to calculate the particle size. The scattering of particles will then be predicted by the Mastersizer 2000 software.

Sample preparation included making a dilute suspension by dispersing the powders in ethanol, ultrasonically the dilute suspensions for 3 minutes in order to break the soft agglomerates and finally circulating the suspensions into the cell. Seven measurements were taken for each sample.
3.2.5.4. **Field Emission Gun Scanning Electron Microscopy (FEG-SEM)**

The morphology of the alumina particles was studied by using a FEG-SEM (Leo 1530VP FEGSEM, LEO Elektronenskopie GmbH, Oberkochen, Germany) at different magnifications. The powders were dispersed in ethanol first, then sprayed on to a conducting carbon film mounted on aluminium stubs and left to dry for 10-15 minutes in the sample box. Subsequently each sample had to be sputter coated with gold before the analysis to make it conductive in order to prevent any possible charging. The SE2 detector was used to record the images at 5 kV accelerating voltage and a working distance of 10-15 mm.

3.2.5.5. **Thermal Analysis**

Thermal analysis of the crushed powders was carried out at 1200°C. This helped to analyse crystallization and the phase evolution of the alumina. This equipment recorded the Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry simultaneously (SDT 2960 Simultaneous TGA/DSC, TA instruments, U.K Ltd.) in argon. The results were used to determine the heat change associated with the decomposition and phase transformation of the material. In general, a sharp exothermic peak was an indicative of crystallization or fusion process whereas broad endothermic peaks in conjunction with weight loss signified dehydration or decomposition reactions.

3.3. **Processing of Nanostructured Alumina Ceramics**

3.3.1. **Raw Materials**

All chemicals used in the processing of nanostructured alumina ceramics are listed in Table 3-6:
### Table 3-6 List of chemicals used in this project.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Solids content</th>
<th>Source</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispex-A40</td>
<td>Ammonium polyacrylate</td>
<td>98+%</td>
<td>40%</td>
<td>BASF, Germany</td>
<td>Dispersant</td>
</tr>
<tr>
<td>Darvan-C</td>
<td>Ammonium polymethacrylate</td>
<td>99+%</td>
<td>20%</td>
<td>RT Vanderbilt, Germany</td>
<td>Dispersant</td>
</tr>
<tr>
<td>Dolapix CE-64</td>
<td>Ammonium salt of polymethacrylic acid</td>
<td>98+%</td>
<td>65%</td>
<td>Zschimmer &amp; Schwarz, Germany</td>
<td>Dispersant</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
<td>99+%</td>
<td>-</td>
<td>Fluka, UK</td>
<td>Binder</td>
</tr>
<tr>
<td>Freon 11</td>
<td>Trichlofluoromethane</td>
<td>99.5%</td>
<td>-</td>
<td>Spex CertiPrep. Inc, UK</td>
<td>Foaming agent</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>-</td>
<td>-</td>
<td>Fisher, UK</td>
<td>pH modifier</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>-</td>
<td>-</td>
<td>Fisher, UK</td>
<td>pH modifier</td>
</tr>
<tr>
<td>Epoxy resin and hardener</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Struers Ltd., UK</td>
<td>Mounting aid</td>
</tr>
<tr>
<td>Polishing suspensions</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Struers Ltd., UK</td>
<td>Polishing aid</td>
</tr>
</tbody>
</table>
3.3.2. **Suspension Preparation**

Appropriate quantities of deionised water and each dispersant were mixed and stirred for 1 h. The water associated with the dispersant solution was accounted for in the calculation. The nanoalumina powder, weighed to 0.001 g, was added and the mixture was ball-milled for 12 hours in order to achieve an homogeneous suspension. The slurries were then subjected to ultrasonic agitation, after which the beakers were sealed to prevent water evaporation and left for 1 h to cool and attain equilibrium. Finally, the samples were held at a reduced pressure of 60 mm mercury for 10 minutes to remove as many air bubbles as possible prior to the rheological testing.

3.3.3. **Characterisation of Prepared Suspensions**

The prepared alumina suspensions were characterised using a variety of techniques, which are described below.

3.3.3.1. **Determination of Solids Content**

A very small amount of each suspension was weighed into a petridish, which had been thoroughly dried in an oven. Subsequently the suspension was heated at 60ºC for 24 hours to remove the water and the weight lost after complete drying was noted. The dried alumina sample was then placed in a silica crucible and was further heated in a conventional furnace at a rate of 5ºCmin⁻¹ up to 700ºC and held at this temperature for 2 hours in order to burn off all the organics. Next the crucible was cooled down to room temperature and the percentage of solid content was calculated based on the initial weight of suspension taken for drying. The solids content of the suspension was calculated using Eq. 3-1.

\[
\text{Solids content (wt\%)} = \frac{\text{Weight of solids after heating}}{\text{Weight of initial suspension}} \times 100
\]

Eq. 3-1

3.3.3.2. **Measurement of Zeta Potential**

The electrokinetic behaviour of each alumina suspension was characterized using an AcoustoSizer II (Colloidal Dynamics Ltd., Sydney, Australia). This can measure a
wide range of parameters in a colloidal suspension, including zeta potential over a wide range of pH from 2 to 13 by using ultrasonic. This equipment consists of a Central Signal Processing Unit (CSPU) and various sensors, which are all controlled by a particular application software on the PC. The CSPU generates voltage pulses with frequencies between about 1 and 20 MHz, which are then applied to the Electrokinetic Sonic Amplitude and attenuation sensor, where they make ultrasonic signals. The resulting ultrasound pulses, which contain data about the particle size and charge, will subsequently be converted back to voltage pulses. After processing, the pulses are passed to the PC to be analyzed along with data from the pH, temperature and conductivity sensors PC for determination of particle size and zeta potential [105].

Dilute suspensions with solids content of around 5 wt% were used; pH modifying agents were dosed in small quantities to achieve pH values higher or lower than the intrinsic pH. 0.1 M NaOH and HCl solutions were used for increasing/decreasing the pH respectively. An equilibration time of 180 seconds was used to make sure that the pH modifier was mixed homogeneously within the system before each zeta potential measurement was made. As a general practice, the pH was initially measured in increments of 1 pH point to the nearest extreme and then back again to the other extreme pH, in steps of 1 pH point.

3.3.3.3. Investigation of Rheological Behaviour

The rheological behaviour of the prepared suspensions was measured using an Anton Paar RheolabQC rotational rheometer (Anton Paar, Österreich, Austria). This equipment is a controlled speed device that measures shear stress and viscosity as a function of shear rate ranging from 0.1 s⁻¹ to 1000 s⁻¹. All the measurements were carried out at room temperature. Three trials were carried out for each prepared suspension.

3.3.4. Green Body Preparation

Green bodies were prepared by both wet (slip casting) and dry (die pressing) forming routes.
3.3.4.1. Slip Casting

As an initial green forming step, it was decided to prepare bodies using slip casting. Wet processing is a relatively simple process for preparing green bodies using conventional ceramic powder suspensions; however because of the high surface area and hence surface energy of nanopowders, this could be different for the nanoalumina suspensions. Using nanopowders could also clog the pores present in the Plaster of Paris (PoP) mould after a few casting cycles. The use of slip casting required the optimisation of a large number of parameters including the solid content of the suspension. Therefore three batches of suspensions with different solids contents of 50, 60 and 70 wt% were prepared.

Prior to slip casting, the suspensions were exposed to ultrasound for 3 minutes to crush the possible agglomerates present in the suspension, whilst keeping it in a cold water bath in order to prevent unwanted heating during the process. Casting was performed into PoP moulds, which were produced using a plaster-to-water ratio of 60:40. The preparation used for the moulds was found to be critical after the initial experiments. Initially, circular cavities of different sizes were simply machined into the cast moulds, however the resultant surface finish was not good enough and lead to cracking of the cast samples during drying. To improve the surface finish, a 6 mm thick plate of acrylic sheet was drilled to yield an array of nine 15 mm diameter holes. This was clamped to a flat plate of PoP and the suspension was cast into the holes after applying some lubricant to the walls of the holes in the acrylic sheet, the latter to ease the release of the cast alumina discs. This approach allowed up to 9 samples to be cast simultaneously, the dewatering process occurring into the plaster plate beneath the acrylic sheet. The slurries were subjected to ultrasonic agitation prior to casting produced by a Kerry ultrasound unit (Kerry Ultrasonics Ltd, Hitchin, UK) using 150 W at 20 kHz, after which the beakers were sealed to prevent water evaporation and left for 1 h to cool and attain equilibrium. The optimum duration of the ultrasonic dispersion was experimentally pre-determined by monitoring the time required to produce the minimum viscosity.

Drying was carried out under ambient conditions of about 20ºC and 50% humidity for 72 hours before samples were removed from the acrylic sheet with great care. Following this preliminary drying, all the samples were placed on a Teflon sheet for
further drying; the Teflon sheet assisted with sample shrinkage by providing minimal resistance. The solid content of the suspension, its viscosity and the amount of organics used were all found to affect the quality of the slip cast bodies.

3.3.4.2. Granulation

Powders to be dry pressed were granulated by spray freeze drying the well-dispersed prepared alumina suspensions as outlined in the following sections.

3.3.4.2.1. Spray Freeze Drying

The granulated powder was prepared by spray freezing the suspensions into liquid nitrogen followed by drying the frozen granules in a freeze dryer. Before spraying the suspension, ultrasonication was applied to break up any existing agglomerates for 1 minute. The suspension was sprayed using a twin fluid atomiser (BÜCHI Labortechnik AG, Postfach, Switzerland) into a container that contained liquid nitrogen. The flow rate of the suspension sprayed into the liquid nitrogen could be controlled by changing the amount of compressed air flow from the VT 150 air compressor (Bambi Air Compressors Ltd, Birmingham, UK) using a flowmeter. Due to the high pressure of the suspension coming out of the atomiser, it was broken down into fine droplets. For this purpose, the flow rate of compressed air was set at 3.8 l min⁻¹ using a flowmeter. The distance between the tip of the atomizer and the liquid nitrogen was about 15-20 cm, which was found to be sufficient for the droplets to become spherical. The process of spray freezing is shown in Figure 3-4. The fine droplets were converted into frozen granules instantly on contact with the liquid nitrogen. Finally the excess nitrogen of the container was evaporated off and the frozen granules were freeze dried.
The freeze drying process was carried out in a Benchtop freeze drier, Virtis® Benchtop SLC, New York, USA (Figure 3-5). The frozen granules were placed in borosilicate glass flasks connected to the equipment. The condenser was cooled down to -50°C and evacuated to vacuum levels below 13.33 Pa (100 mTorr) before connecting the samples. As soon as the frozen sample was connected, vacuum was created in the flask. During the initial stages, frozen granules were observed to be a cohesive mass; however as drying proceeded, powder flowability was visible. The process of freeze drying took at least 48 hours, depending on the amount of sample required to be dried. As a last step sieving was undertaken to separate out the granules into different size fractions. The powder was sieved to extract the fraction between 125 and 250 μm to maximise the flowability.

**Figure 3-4** Schematic diagram of spraying suspension in to liquid nitrogen.

**Figure 3-5** Benchtop freeze drier with 4 ports.
3.3.4.2.2. Granule Morphology

The agglomerate morphology of the spray freeze dried (SFD) alumina granules was analysed using FEG-SEM at different magnifications. The SFD powders were applied on to conducting carbon films mounted on aluminium stubs and were then sputter coated with gold. The in-lens detector was used to record the images at 5 kV accelerating voltage and a working distance of 5 mm.

3.3.4.2.3. Flowability Measurements

The flowability of the powders was characterized by measuring the flow rate using a Hall Flowmeter (orifice diameter 2.5 and 5 mm). Firstly, the orifice was closed and a certain mass of the spray freeze dried granules was added into the funnel. Then, the orifice was opened releasing the powder by gravity, with the time required for the flow meter to empty being recorded. The flow rate was determined by:

\[
\text{Flowability} = \frac{\text{Mass of granules passing through the orifice}}{\text{Time for discharging granules}}
\]

Eq. 3-2

The bulk and tap densities of the samples were also calculated by measuring the volume of each powder sample after the flowability test and also after tapping it 200 times. To minimise the experimental error, the mass and the flow measurements were repeated 5 times for every sample in the same condition.

3.3.4.2.4. Granule Strength

After the initial electron microscopy analysis, it was found that the dry pressed alumina samples contained agglomerates that were difficult to break. Therefore, in the next step, 1-2 vol% Freon 11 was added to the each suspension before spray freeze drying to control the strength of the agglomerates and make them weaker. This idea had previously been studied for zirconia nanostructured ceramics with different foaming agents being added to the suspension at different addition levels in order to create defects in the granule structure and improve their crushability, whilst having negligible impact on their flowability. 2 vol% additions of Freon were found to yield excellent results. After spray freeze drying, the powders were heat treated at 70ºC for
1 hour to burn off the Freon and then sieved with different mesh sizes. The flowability and morphology of the granules were analysed as described above.

3.3.4.2.5. **Dry pressing**

Nanoalumina green bodies were dry pressed using a Lloyds mechanical testing machine (L10000 Tensometer, Lloyds Instruments, Fareham, UK) in a single-action, hardened steel die with a diameter of 10 mm. Prior to each pressing, the die and the punch wall were carefully cleaned, polished and washed with acetone. About 0.5 g of powder was used for every pellet. The ram speed was 1 mm.min\(^{-1}\) and was held at a different consolidation pressure in the range of 150-480 MPa for 1 minute. The pellets were slowly ejected from the die and used for further processing.

3.3.5. **Binder Removal**

In order to remove the organics and additives present in the samples, a slow heating cycle was applied to them. A binder removal cycle was designed based on the evaporation/combustion temperatures of all the agents added to the initial alumina suspensions. The samples were heated at a rate of 0.5 °Cmin\(^{-1}\) with dwells at 100°C, 200°C, 300°C and 400°C for 30 minutes each and finally at 700°C for 2 hours before being cooled down to room temperature at a rate of 0.5 °Cmin\(^{-1}\). After binder removal all the samples were visually inspected for the presence of any defects (e.g. cracks).

3.3.6. **Green Body Characterisation**

3.3.6.1. **Green Density Measurement**

The green density of slip cast bodies was measured after binder removal using the Archimedes principle and mercury. The green density was calculated from:

\[ \rho = \frac{M_2}{M_2 + M_1} \cdot \rho_H \]

Eq. 3-3

Where \( M_2 \) is the mass of the sample in air, \( M_1 \) is the mass of the sample in mercury and \( \rho_H \) is the density of mercury at the measurement temperature. The green densities of the dry pressed compacts were also calculated geometrically, using the mass of the
sample (measured to ±0.001 g) and the dimensions of the compact (measured to ±0.01 mm by a digital micrometer). The dimensions were measured in at least three different locations across each sample and their average was used for the calculations.

3.3.6.2. Fracture Surface Analysis

To investigate the uniformity of the green bodies, they were fractured into two pieces and FEG-SEM was used to image the fracture surfaces. In the case of the die pressed samples, this investigation was also used to assess the crushability of the granules of the SFD powders.

3.3.7. Densification

Densification experiments were carried out using a conventional box furnace (Carbolite Ltd, Hope Valley, UK) and the temperature was controlled by means of a Eurotherm 902 controller (Eurotherm UK Ltd., West Sussex, UK) connected to a thermocouple inside the chamber of the furnace.

3.3.7.1. Single-stage Sintering

The green samples were sintered at temperatures between 1400°C to 1550°C for different dwelling times, as displayed in Table 3-7. To avoid the effect of heating rate on density and grain growth, the conventional heating trials were conducted at a constant heating rate of 10°Cmin⁻¹.

Table 3-7 Summary of the conventional single-step sintering experiments using both SC and DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>t / hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC/NDP-1400-5</td>
<td>1400</td>
<td>5</td>
</tr>
<tr>
<td>NSC/NDP-1400-10</td>
<td>1400</td>
<td>10</td>
</tr>
<tr>
<td>NSC/NDP-1500-5</td>
<td>1500</td>
<td>5</td>
</tr>
<tr>
<td>NSC/NDP-1500-10</td>
<td>1500</td>
<td>10</td>
</tr>
<tr>
<td>NSC/NDP-1550-5</td>
<td>1550</td>
<td>5</td>
</tr>
</tbody>
</table>
3.3.7.2. Two-step Sintering

The samples were also sintered for 0.1 minute at temperatures shown in Table 3-8 (NSC-1600 and NDP-1600) in order to mimic the first stage heating, which was necessary to design an optimal two-step sintering schedule. For two-stage sintering experiments a range of sintering temperatures and sintering times were examined, as presented in Table 3-8 (NSC-1600-1500-10 and NDP-1600-1500-10). The first step temperature, known as $T_1$, was changed in the range of 1500-1600°C (heating rate of 5 °C min$^{-1}$) with a very short dwelling time of 0.1 minute. The second step temperature, $T_2$, was chosen in the range of values of about 100-200°C lower than $T_1$ for each experiment to achieve optimal densification.

![Figure 3-6 Schematic of the two-stage sintering schedule.](image)

3.3.8. Sintered Body Characterisation

3.3.8.1. Sintered Density Measurement

The density of the slip cast sintered bodies was measured using the Archimedes principle and distilled water using the equation below:

$$\rho = \frac{M_s}{M_s-M_1} \cdot \rho_l$$

Eq. 3-4

Where $M_s$ is the mass of sample in air, $M_1$ is the mass of sample in water, and $\rho_l$ is the density of the liquid at measuring temperature. The sintered densities of the dry pressed compacts were also calculated geometrically, as mentioned in section 3.3.6.1.
Table 3-8 Summary of the two-step sintering experiments using both SC and DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1 / °C</th>
<th>t / min</th>
<th>T2 / °C</th>
<th>t / hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC/NDP-1400</td>
<td>1400</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NSC/NDP-1500</td>
<td>1500</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NSC/NDP-1600</td>
<td>1600</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NSC/NDP-1600-1400-5</td>
<td>1600</td>
<td>0.1</td>
<td>1400</td>
<td>5</td>
</tr>
<tr>
<td>NSC/NDP-1600-1400-10</td>
<td>1600</td>
<td>0.1</td>
<td>1400</td>
<td>10</td>
</tr>
<tr>
<td>NSC/NDP-1600-1500-5</td>
<td>1600</td>
<td>0.1</td>
<td>1500</td>
<td>5</td>
</tr>
<tr>
<td>NSC/NDP-1600-1500-10</td>
<td>1600</td>
<td>0.1</td>
<td>1500</td>
<td>10</td>
</tr>
<tr>
<td>NSC/NDP-1600-1500-20</td>
<td>1600</td>
<td>0.1</td>
<td>1500</td>
<td>20</td>
</tr>
</tbody>
</table>

3.3.8.2. Mounting and Polishing of Sintered Bodies

For the polishing process, the sintered samples were initially mounted using a transparent epoxy resin and its hardener (Epofix kit, Struers Ltd., Solihull, UK) with a mixing ratio of 15:2. The mounted samples were left for at least 12 hours at room temperature and then polished using a semi-automatic polishing machine (TegraPol-25, Struers Ltd., Solihull, UK) with a rotating sample holder (TegraForce-5, Struers Ltd., Solihull, UK) and an automatic feeding system for the polishing media (TegraDoser-5, Struers Ltd., Solihull, UK).

As a typical polishing cycle, mounted samples were initially plain ground using grinding disc with a grit size of 220 (MD-Piano, Struers Ltd., Solihull, UK), followed by polishing discs of 600 and 1200 grit-sized discs (MD-Piano, Struers Ltd., Solihull, UK) and water as cooling media. Subsequent polishing continued using polishing cloths, MD-Plan and MD-Dac (Struers Ltd., Solihull, UK), and stable diamond suspension containing a unique mixture of high performance diamonds and cooling lubricants, DP-Plan and DP-Dac (Struers Ltd., Solihull, UK), consisting of particles of 9 μm and 3 μm in size, respectively. Between polishing steps, the mounted samples were removed from the specimen holder, cleaned with deionised water and dried with
a heat gun. When the final stage was completed, in order to get a clean surface without any contamination all the samples were separately subjected to ultrasound in deionised water, acetone and ethanol for 2 minutes each and dried using a heat gun. The samples were then taken out of epoxy resin by heating it in an air oven at 150°C for 15 minutes to soften the epoxy.

3.3.8.3. Thermal Etching

In order to reveal the microstructure of the sintered samples, they were thermally etched. This was carried out at temperature that was 100°C lower than that of the sintering temperature in the case of single-step sintering process and at the second step temperature for two-step sintered samples. To avoid any possible grain growth, the holding time in both cases was 10 minutes.

3.3.8.4. Field Emission Scanning Electron Microscopy (FEG-SEM)

The microstructure of the sintered alumina bodies was observed by FEG-SEM on polished and etched surfaces, after they were coated with a thin layer of gold via an ion sputter coater for 30 s. The grain size of the samples was calculated by the use of the linear intercept method (ASTM E 112-96). This technique measures the average grain size with the number of grains (intercepts) or grain boundaries (intersections) that intersect one or more lines of known length superimposed on a field of view or micrograph. A conversion factor of 1.56 \(^{131}\) was used to convert the two dimensional grain size to three dimensional. Using this method, three micrographs and at least 300 grains were evaluated to determine the mean grain size of each alumina compact. The average grain size was calculated using the following equation:

\[
D = \frac{L \times A_i}{M \times N}
\]  

Eq. 3-4

Where D is the equivalent average grain diameter, L is the length of the superimposed lines, A\(_i\) is the shape correction factor (1.56), M is the magnification and N is the quantity of intercepts or intersections.
3.3.9. **Spark Plasma Sintering (SPS)**

The synthesised nanoalumina powder was spark plasma sintered using an SPS facility (Dr. Sinter 1020, Sumitomo Coal Mining Co. Ltd., Tokyo, Japan). The device was composed of two (outer and inner) graphite dies and the nanoalumina powder was pressed between two WC punches, as shown in Figure 3-7. As the application of high pressure restricts the available sample size, two different sizes of dies with diameters of 10 (for 70 MPa) and 5 mm (for 500 MPa) were used.

![Figure 3-7](image.png)

**Figure 3-7** Schematic of the SPS facility; the temperature was measured by a pyrometer at the inner die surface.$^{122}$

The powder was sintered in vacuum with the heating rate of $100^\circ$C min$^{-1}$ for all the experiments. When the temperature reached $700^\circ$C, the pressure was applied; this pressure remained constant during the sintering process. Subsequently, the temperature was raised to the desired sintering temperature, as displayed in Table 3-9, followed by a dwell time of 30 minutes. An optical pyrometer was used to measure the temperature, which was focused on the half-through hole in the graphite die, where the variation of the total height of the graphite die assembly with the temperature was recorded. The applied pressure was removed when the dwell time was over followed by turning the power off immediately in order to allow the sample to cool down naturally in the furnace.

Based on the size of the graphite dies, the final dimensions of the sintered samples were ~5 and 10 mm diameter and 2.5 mm in thickness. To eliminate the layers affected by heavy carbon contamination, the surfaces of the sintered alumina bodies were removed ~1 mm in depth by grinding; the samples were then mirror polished on
both sides to a thickness of ~0.5 mm. The density of the sintered bodies was measured using the Archimedes principle and their microstructure was investigated using FEG-SEM after thermal etching the polished samples, as previously described.

Table 3-9 Summary of the SPS experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>Pressure / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-70-10</td>
<td>1000</td>
<td>70</td>
</tr>
<tr>
<td>S-70-12</td>
<td>1200</td>
<td>70</td>
</tr>
<tr>
<td>S-70-14</td>
<td>1400</td>
<td>70</td>
</tr>
<tr>
<td>S-500-10</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>S-500-12</td>
<td>1200</td>
<td>500</td>
</tr>
</tbody>
</table>

3.4. Processing of Sub-Micron Alumina Ceramics

3.4.1. Raw Materials

All the chemicals used in the processing of sub-micron alumina ceramics are listed in Table 3-10.
### Table 3-10 List of chemicals used in this project.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Solids content</th>
<th>Source</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina suspension</td>
<td>α-Al₂O₃</td>
<td>99+%</td>
<td>58.8%</td>
<td>Baikowski, France</td>
<td>Sub-micron alumina</td>
</tr>
<tr>
<td>BA15PS</td>
<td>(mean size of 150 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freon 11</td>
<td>Trichlofluoromethane</td>
<td>99.5%</td>
<td>-</td>
<td>Spex CertiPrep. Inc, UK</td>
<td>Foaming agent</td>
</tr>
<tr>
<td>Epoxy resin and hardener</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Struers Ltd., UK</td>
<td>Mounting aid</td>
</tr>
<tr>
<td>Polishing suspensions</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Struers Ltd., UK</td>
<td>Polishing aid</td>
</tr>
</tbody>
</table>
3.4.2. Characterization of the Alumina Suspension

A very small amount of the as-received BA15PS suspension was used to measure its solids content as outlined in section 3.3.3.1. The remaining powder was characterised by X-ray diffractometer to confirm the crystalline phase of $\alpha$-alumina. The morphology of the powder was investigated via Field Emission Gun Scanning Electron Microscopy (FEG-SEM) and its particle size was analyzed by using Transmission Electron Microscopy (TEM) and a mastersizer. Thermal analysis of the dried powder was also carried out as explained in section 3.2.5.6. In addition the electokinetic and rheological behaviour of the suspension was studied using Acoustozizer and Rheometer as described in sections 3.3.3.2 and 3.3.3.3, respectively.

3.4.3. Green Body Preparation

Slip casting was the initial route, which was applied to form the alumina green bodies using the as-received suspension (see section 3.3.4.1). However the spray freeze drying method (with/without adding Freon) was used afterwards to produce alumina granules for dry pressing process (see section 3.3.4.2). The resulting granulated powder was dry pressed as in section 3.3.4.3; following morphology and flowability analysis (see section 3.3.4.2).

3.4.4. Binder Removal and Densification

Although no binder was added to the suspension or powder during the preparation and forming processes, the binder removal cycle was applied to the green bodies in order to remove any existing organics (see section 3.3.5). Subsequently the binder-removed samples were investigated by FEG-SEM and their average density was measured using the Archimedes principle in mercury (Eq. 3-3).

Densification was carried out using both single- and two-step sintering methods in a conventional box furnace, as shown in Tables 3-11, 3-12 and 3-13, with the latter having $T_1$ in the range of 1350-1450°C and $T_2$ being 100-150°C lower than $T_1$ and the former having the temperature range of 1300-1400°C for different dwelling times.
Then the density and grain size of the sintered alumina bodies were measured as described in section 3.3.8.

**Table 3-11** Summary of the conventional single-step sintering experiments using both SC and DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>t / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC/SDP-1300-2</td>
<td>1300</td>
<td>2</td>
</tr>
<tr>
<td>SSC/SDP-1350-2</td>
<td>1350</td>
<td>2</td>
</tr>
<tr>
<td>SSC/SDP-1400-2</td>
<td>1400</td>
<td>2</td>
</tr>
</tbody>
</table>

**Table 3-12** Summary of the two-step sintering experiments using SC samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1 / °C</th>
<th>t / min</th>
<th>T2 / °C</th>
<th>t / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC-1300</td>
<td>1300</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SSC-1400</td>
<td>1400</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SSC-1450</td>
<td>1450</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SSC-1400-1150-5</td>
<td>1150</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1150-15</td>
<td>1150</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1250-2</td>
<td>1250</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1250-5</td>
<td>1250</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1250-10</td>
<td>1250</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1300-5</td>
<td>1300</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSC-1400-1300-10</td>
<td>1300</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3-13  Summary of the two-step sintering experiments using DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T₁ / °C</th>
<th>t / min</th>
<th>T₂ / °C</th>
<th>t / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDP-1300</td>
<td>1300</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDP-1400</td>
<td>1400</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDP-1450</td>
<td>1450</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDP-1400-1250-5</td>
<td>1400</td>
<td>0.1</td>
<td>1250</td>
<td>5</td>
</tr>
<tr>
<td>SDP-1450-1250-2</td>
<td>1450</td>
<td>0.1</td>
<td>1250</td>
<td>2</td>
</tr>
<tr>
<td>SDP-1450-1250-5</td>
<td>1450</td>
<td>0.1</td>
<td>1250</td>
<td>5</td>
</tr>
<tr>
<td>SDP-1450-1300-5</td>
<td>0.1</td>
<td>1300</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

In the following chapter, all the results of the experiments carried out in this project are presented along with the discussions.
4. Results and Discussion

4.1. Hydrothermal Synthesis

4.1.1. Basic Route

All the $\alpha$-alumina powders used in this work for seeding were characterised by X-ray diffraction; this confirmed they were all pure $\alpha$-alumina, as shown in Figure 4-1. All the diffraction peaks for each powder were indexed as $\alpha$-alumina phase (JCPDS 46-1212).

![Figure 4-1 XRD patterns of a) standard $\alpha$-alumina (JCPDS 46-1212) and the seeding powders b) BMA15 (150 nm), c) SMA6 (330 nm) and d) MR70 (500 nm).](image)

TEM analysis was conducted to analyze the $\alpha$-alumina seeding powders used. Figure 4-2 shows the representative TEM images of these powders. The samples consisted of sub-micron particles with an average size of ~150 nm, 350 nm and 500 nm for powders BMA15, SMA6 and MR70, respectively, which were comparable to the data sheets from providing companies, Baikowski and Albemarle.
For the powders synthesised via the basic route (Table 4-1), before the hydrothermal treatment, all the unseeded samples showed more or less amorphous behaviour with sharp peaks of crystalline ammonium salts including ammonium chloride $\text{NH}_4\text{Cl}$ (salammonia), ammonium nitrate $\text{NH}_4\text{NO}_3$ (nitrammite) or ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ (mascagnite), as displayed in Figures Figure 4-3, Figure 4-4 and Figure 4-5 for samples prepared using $\text{AlCl}_3$, $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al(NO}_3)_3$, respectively. However some weak broad peaks were observed as well; these coincide with boehmite ($\text{AlOOH}$, aluminium oxyhydroxide, JCPDS 88-2112). This showed that the pseudoboehmite phase was formed during the precipitation process; the formation of this phase at high pH was due to the excessive amount of hydroxyl groups coming from $\text{NH}_4\text{OH}$. Pseudoboehmite is a poorly crystallized boehmite and an XRD pattern of broad lines matching those of boehmite $^{132}$. 

Figure 4-2 TEM micrographs of the $\alpha$-alumina powders a) BMA15 (150 nm), b) SMA6 (330 nm) and c) MR70 (500 nm).
Table 4-1 Summary of the basic hydrothermal synthesis conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB-C-</td>
<td>AlCl₃</td>
</tr>
<tr>
<td>0</td>
<td>No seed</td>
</tr>
<tr>
<td>1</td>
<td>4 wt% BMA15</td>
</tr>
<tr>
<td>HB-N-</td>
<td>Al(NO₃)₃</td>
</tr>
<tr>
<td>0</td>
<td>No seed</td>
</tr>
<tr>
<td>1</td>
<td>4 wt% BMA15</td>
</tr>
<tr>
<td>HB-S-</td>
<td>Al₂(SO₄)₃</td>
</tr>
<tr>
<td>0</td>
<td>No seed</td>
</tr>
<tr>
<td>1</td>
<td>4 wt% BMA15</td>
</tr>
</tbody>
</table>

Figure 4-3 XRD patterns of samples prepared using aluminium chloride: sample HB-C-0 a) before and b) after hydrothermal treatment at 220°C for 24 h and sample HB-C-1 c) after the same hydrothermal treatment and d) after being heat treated at 1000°C.
Figure 4-4  XRD patterns of samples prepared using Aluminum sulphate: sample HB-S-0 a) before and b) after hydrothermal treatment at 220°C for 24 h and sample HB-S-1 c) after the same hydrothermal treatment and d) after being heat treated at 1000°C.

Figure 4-5  XRD patterns of samples prepared using aluminium nitrate: sample HB-N-0 a) before and b) after hydrothermal treatment at 220°C for 24 h and sample HB-N-1 c) after the same hydrothermal treatment and d) after being heat treated at 1000°C.
After hydrothermal treatment, peaks matching the boehmite phase were observed for all the unseeded samples. Note that washing the post-hydrothermal powders with deionised water and absolute ethanol did not help to remove the anions present from the dissolution of the aluminium salts and a 30 min wash in acetic acid solution did not succeed in removing the residual boehmite phase.

Figure 4-6 displays TEM images of the powders synthesised using aluminium chloride via the basic route. TEM investigation showed that the major component of the non-seeded sample, HB-C-0, consisted of typical acicular (needle-like) boehmite particles as demonstrated in Figure 4-6(a). The morphology of the powder was changed with the addition of seeds, which led to the formation of a bimodal morphology consisting of both the acicular particles and their agglomerates and more equiaxed α-alumina particles, as shown in Figure 4-6(b). The appearance of the α-alumina particles was similar to those observed in the seeding powder BMA15, therefore it can be suggested that the alumina particles presented in the seeded samples after synthesis were actually mainly just the α-alumina powder added to the precursor solution as seeding powder.

Figure 4-6 TEM micrographs of powders prepared using aluminium chloride after hydrothermal treatment at 220°C for 24 h: a) HB-C-0 with no added seed, b) HB-C-1 with 4 wt% seed (BMA15).

Figure 4-7 shows the effect of temperature of the hydrothermal treatment process on the \( I_{(113, \ \alpha\text{-alumina})}/I_{(120, \ \text{boehmite})} \) values, which represent the integral intensity, after subtracting the background of the (113) peak of α-alumina and the (120) peak of boehmite, of the seeded samples HB-C-1, HB-S-1 and HB-N-1. When the temperature was increased from 190°C to 220°C in increments of 10°C, this value slightly
decreased for all the samples, suggesting that a slightly higher fraction of boehmite phase was formed at higher temperatures. With increasing time of the hydrothermal synthesis, as demonstrated in Figure 4-8, the value of $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ and as a result the conversion to boehmite phase was not affected noticeably.

**Figure 4-7** Comparison of the $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ values of the samples prepared using different salts and 4 wt% seed (BMA15) after hydrothermal treatment at different temperatures for 24 h.

**Figure 4-8** Comparison of the $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ values of the samples prepared using different salts and 4 wt% seed (BMA15) after hydrothermal treatment at 220°C for different times 1-24 h.
As shown in Figures 4-9, 4-10 and 4-11 for samples prepared by using the surfactants (Table 4-2), the addition of these agents to the precursor solution prior to seeding yielded similar results to the seeded samples with no surfactant. This meant adding the surfactants did not affect the phase transformation process during the hydrothermal treatment. It was expected that the presence of surfactants would reduce the degree of agglomeration of the $\alpha$-alumina seed particles, resulting in each of the seeds working as a nucleus for direct transformation to $\alpha$-alumina phase. However the addition of surfactants did help to lower the degree of agglomeration of final calcined powders, which will be discussed later.

Table 4-2 Summary of the basic hydrothermal synthesis conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Salt</th>
<th>Sample Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB-C-</td>
<td>2</td>
<td>4 wt% BMA15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4 wt% SMA6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4 wt% MR70</td>
</tr>
<tr>
<td>HB-N-</td>
<td>2</td>
<td>4 wt% BMA15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4 wt% SMA6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4 wt% MR70</td>
</tr>
<tr>
<td>HB-S-</td>
<td>2</td>
<td>4 wt% BMA15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4 wt% SMA6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4 wt% MR70</td>
</tr>
</tbody>
</table>
Figure 4-9  XRD patterns of samples prepared using aluminium chloride with added seeds and surfactants: a) HB-C-2, b) HB-C-3 and c) HB-C-4 after hydrothermal treatment at 220°C for 24 h.

Figure 4-10  XRD patterns of samples prepared using aluminium sulphate with added seeds and surfactants: a) HB-S-2, b) HB-S-3 and c) HB-S-4 after hydrothermal treatment at 220°C for 24 h
Figure 4-11 XRD patterns of samples prepared using aluminium nitrate with added seeds and surfactants: a) HB-N-2, b) HB-N-3 and c) HB-N-4 after hydrothermal treatment at 220°C for 24 h.

Table 4-3 Values of $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ of the powders synthesised by the basic hydrothermal route at 220°C for 24 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB-C-0</td>
<td>No $\alpha$-alumina</td>
</tr>
<tr>
<td>HB-C-1</td>
<td>0.12</td>
</tr>
<tr>
<td>HB-C-2</td>
<td>0.13</td>
</tr>
<tr>
<td>HB-C-3</td>
<td>0.15</td>
</tr>
<tr>
<td>HB-C-4</td>
<td>0.13</td>
</tr>
<tr>
<td>HB-S-0</td>
<td>No $\alpha$-alumina</td>
</tr>
<tr>
<td>HB-S-1</td>
<td>0.82</td>
</tr>
<tr>
<td>HB-S-2</td>
<td>0.88</td>
</tr>
<tr>
<td>HB-S-3</td>
<td>0.88</td>
</tr>
<tr>
<td>HB-S-4</td>
<td>0.89</td>
</tr>
<tr>
<td>HB-N-0</td>
<td>No $\alpha$-alumina</td>
</tr>
<tr>
<td>HB-N-1</td>
<td>0.35</td>
</tr>
<tr>
<td>HB-N-2</td>
<td>0.38</td>
</tr>
<tr>
<td>HB-N-3</td>
<td>0.37</td>
</tr>
<tr>
<td>HB-N-4</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Table 4-3 reports the values of $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ for samples prepared at 220°C for 24 h. It can be seen that this value was roughly constant for each group, showing that the amount of the $\alpha$-alumina phase present in the prepared samples was not affected by adding different types of surfactants within each group.

As can be observed in Figure 4-12, 4 wt% seeded samples synthesised using aluminium sulphate and nitrate also contained a bimodal morphology similar to previously discussed samples. This showed that using different salts of aluminium could not result in any change in the final powder and boehmite phase along with the $\alpha$-alumina seeds were found in the seeded samples.

![Figure 4-12 TEM micrographs of powders prepared using different salts with added seeds and surfactants after hydrothermal treatment at 220°C for 24h: a) HB-C-2, b) HB-S-2 and c) HB-N-2.](image)

In the basic hydrothermal route, changing process parameters such as the type of aluminium salt, seeding the precursor solution with $\alpha$-alumina powders of different particle size, adding different types of surfactants and increasing the process
temperature (190-220°C) and time (1-24 h) did not affect the hydrothermal process for conversion of the precipitate to pure α-alumina powder.

The XRD peaks indexed as boehmite in all the post-hydrothermal powders vanished after they were heat treated at 1000°C, as shown in Figures Figure 4-3, Figure 4-4 and Figure 4-5. Upon heating the boehmite phase goes through a series of polymorphic transformations including $\gamma \rightarrow \delta \rightarrow \theta$ at ~600°C and 800°C before reaching the stable $\alpha$-alumina form 25.

![Thermal analysis of hydrothermally-prepared samples with and without added seeds: HB-C-1 and HB-C-0, respectively.](image)

**Figure 4-13** Thermal analysis of hydrothermally-prepared samples with and without added seeds: HB-C-1 and HB-C-0, respectively.

Thermal analysis of samples HB-C-0 and HB-C-1, Figure 4-13, showed two endothermic peaks existing at 70.5°C and 188.8 °C for both samples. The former was due to the evaporation of absorbed water and the latter was caused by removal of the structural water existing in the oxyhydroxide phase 25. There was a noticeable endothermic peak at 328.5°C for both samples, which was compatible with the decomposition point of ammonium chloride and was associated with sublimation of this material present in the samples as the by-product of synthesis process 133. There were exothermic peaks at 975.5°C and 1157.7°C for HB-C-0 and H-B-1 samples,
respectively, which were caused by the $\theta$-alumina $\rightarrow$ $\alpha$-alumina phase transformation.

The crystallite size of the $\alpha$-alumina powders obtained by high temperature calcination was 68 nm, 90 nm and 61 nm respectively for samples HB-C-2, HB-S-2 and HB-N-2, calculated by using Scherrer equation and XRD results. The calculated crystallite size for each of these samples is comparable to the size of the ultra-fine particles of about 50 nm observed on TEM, as can be seen in Figure 4-14b for sample HB-C-2.

After heat treatment at 1000°C, the boehmite particles present in sample HB-C-1 transformed to nanosized $\alpha$-alumina particles; displayed in Figure 4-14a. The morphology of the post-hydrothermal samples changed markedly after calcination and the resulting powder was comprised of polycrystalline agglomerates with particle sizes of ~50 nm. Heat treatment of sample HB-C-2 at 1000°C, Figure 4-14b, resulted in less agglomerated $\alpha$-alumina particles with smaller particle size of <50 nm. This could be due to the presence of surfactant added to the initial precursor, which modified the surface of growing particles during the precipitation process to prevent the particles from growing together by reducing their surface free energy.

![Figure 4-14](image)

**Figure 4-14** TEM micrographs of powders prepared by using basic hydrothermal treatment after heat treatment at 1000°C/6 h: a) HB-C-1 and b) HB-C-2 with and without added surfactants, respectively.

From the particle size distribution analysis of samples HB-C-1 and HB-C-2 after being calcined at 1000°C, it was found out that sample HB-C-2 consisted of less agglomerates compared to the HB-C-1. The considerable shift towards smaller particle sizes in the graphs shown in Figure 4-15 was due to the addition of surfactant.
to the initial solution, which affected the level of agglomeration in the gelatinous precipitate.

![Particle Size Distribution](image)

**Figure 4-15** Effect of adding surfactant on the particle size distribution of powders prepared by using basic hydrothermal treatment after heat treatment at 1000°C/6 h: a) HB-C-1 and b) HB-C-2 with and without added surfactants, respectively.

### 4.1.2. Acidic Route

The XRD patterns of unseeded and 4 wt%-seeded samples prepared using AlCl$_3$ before hydrothermal treatment are shown in Figure 4-16, with the former sample being in an amorphous state and consisting of a broad curve without observable diffraction peaks. This indicates that amorphous aluminium hydroxide was formed by the precipitation. For the 4 wt%-seeded samples, however, the XRD results show the sharp peaks of the α-alumina seeds along with the amorphous phase.
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Figure 4-16  XRD patterns of a) unseeded (HA-C-0) and b) 4 wt%-seeded (HA-C-4) samples before hydrothermal treatment.

The pre-hydrothermal TEM micrographs of ground HA-C-4 and HB-C-1 (4 wt% seeded) samples are shown in Figure 4-17.

Figure 4-17  TEM micrographs of pre-hydrothermal samples a) HA-C-4 and b) HB-C-1.

The sample prepared via the basic route, contained a porous spongy structure of irregular shapes along with the added seeds. Electron diffraction patterns from such structures consisted of very weak diffused rings, which could be due to the existence of amorphous aluminium hydroxides as well as patterns related to the $\alpha$-alumina seeds. However TEM study of the pre-hydrothermal HA-C-4 sample could only identify the added seeds and there was no trace of the spongy phase found on the
prepared TEM grid. This is probably due to the very low amount of the amorphous hydroxide phase present in this sample.

Figure 4-18 shows the phases existing in the powders obtained by acidic hydrothermal treatment of sample prepared using aluminium chloride at 220°C for 24 h, characterised by X-ray diffraction. Sample HA-C-0 made without any seeds, consisted entirely of boehmite, whilst 1-4 wt% seeded samples showed decreasing amounts of boehmite compared to α-alumina as the amount of seeds added increased. Although the seeded post-hydrothermal powders were washed in acetic acid solution, traces of boehmite remained in all the samples, showing that aluminium oxyhydroxide could not be entirely washed away. For samples containing 4 wt% seed, the only phase detected was α-alumina.

![Figure 4-18 XRD patterns](image)

**Figure 4-18** XRD patterns of samples a) HA-C-0 (with no seed), b) HA-C-1 (with 1 wt% seed), c) HA-C-2 (with 2 wt% seed), d) HA-C-3 (with 3 wt% seed) and e) HA-C-4 (with 4 wt% seed) after hydrothermal treatment at 220°C for 24 h and f) HA-C-4 after being heat treated at 1000°C/6 h.

Table 4-4 provides the values of $I_{(133, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ for the samples prepared by the acidic route. As can be observed, the values enhanced as the α-alumina seed content increased and the highest value belonged to sample HA-C-4 with highest seed
content, which contained pure $\alpha$-alumina. However the temperature and time of hydrothermal process did not have any effect on the final powder.

**Table 4-4** Values of $I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$ of the powders synthesised by acidic hydrothermal route using aluminium chloride at 220°C /24 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{(113, \alpha\text{-alumina})}/I_{(120, \text{boehmite})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-C-0</td>
<td>No $\alpha$-alumina</td>
</tr>
<tr>
<td>HA-C-1</td>
<td>1.2</td>
</tr>
<tr>
<td>HA-C-2</td>
<td>2.3</td>
</tr>
<tr>
<td>HA-C-3</td>
<td>13.4</td>
</tr>
<tr>
<td>HA-C-4</td>
<td>Pure $\alpha$-alumina</td>
</tr>
</tbody>
</table>

The images in Figure 4-19 are very similar to Figures Figure 4-6 and Figure 4-12. For sample H-A-0, Figure 4-19(a), only the typical acicular boehmite particles may be seen, whilst as the amount of $\alpha$-alumina seeds increased the fraction of $\alpha$-alumina particles in the TEM micrographs also enhanced, Figure 4-19(b) and Figure 4-19(c), which is compatible with the XRD data. The boehmite structure transformed to mainly fine equiaxed $\alpha$-alumina particles with a particle size of $\leq 50$ nm with a small amount of larger particles representing the added seeds, as shown in Figure 4-19(d), after being heat treated at 1000°C, similar to Figure 4-14(a).

FEG-SEM investigation of sample HA-C-4 showed a few needle like particles of boehmite, hundreds of nanometers in length and $\sim 10$ nm in width, which are lightly agglomerated more or less covered the equiaxed $\alpha$-alumina particles, as displayed in Figure 4-20. This is further proof confirming the existence of boehmite in the 4 wt%-seeded samples, although no trace of the boehmite phase could be found in related XRD results.
Figure 4-19  TEM micrographs of powders a) HA-C-0 (with no seed), b) HA-C-1 (with 1 wt% seed) and c) HA-C-4 (with 4 wt% seed) samples after hydrothermal treatment at 220°C for 24 h and d) shows sample HA-C-4 after heat treatment at 1000°C.

Figure 4-20  FEG-SEM micrographs of powder HA-C-4 (with 4 wt% seed) after hydrothermal treatment at 220°C for 24 h: a) lower and b) higher magnification.

4.1.3. Comparison of Acidic and Basic Hydrothermal Synthesis Routes

Comparison of the above results reveals that when similar conditions of hydrothermal treatment and 4 wt% seed addition were used, the acidic route led to pure α-alumina
phase, at least to the limit of resolution of X-ray diffraction, whilst the basic route led to a powder that still retained significant quantities of boehmite and ammonium salts. However, the amounts of powder produced by the acidic route were considerably less than the powder made by the basic route. This might be because the basic aluminium salts are highly soluble and can be precipitated only at a high OH/Al ratio\textsuperscript{134}. Therefore, during the acidic route at pH~3 less precipitate was formed compared to the basic route. This resulted in less boehmite after the hydrothermal treatment, which could not be fully detected in the samples, particularly 4 wt%-seeded one due to the limited resolution of X-ray diffraction and the high fraction of $\alpha$-alumina seed used. This assumption, along with the fact that the morphology of the $\alpha$-alumina particles in the final powder is very similar to the seeding powder, suggests that, unlike the conclusions reported by Yang, et al.\textsuperscript{60} and Sharma, et al.\textsuperscript{20}, very low amount of $\alpha$-alumina was detected after the hydrothermal treatment and that the alumina particles present in the seeded samples after synthesis were actually mainly just the $\alpha$-alumina powder added to the precursor solution as seeding powder.

4.2. Precipitation Synthesis

4.2.1. Single-Step Heat Treatment

For each of the powders formed without using seed or surfactant (Table 4-5), the XRD patterns and the phases present are presented in Figure 4-21 and Table 4-6. It can be seen that heat treatment at higher temperatures and/or for longer times led to a greater fraction of $\alpha$-alumina phase in the final powder, as expected.

Table 4-5 Summary of the precipitation synthesis conditions with no added seeds/surfactants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-10-1</td>
<td>1000°C/1 h</td>
<td></td>
</tr>
<tr>
<td>P-10-6</td>
<td>1000°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-11-1</td>
<td>1100°C/1 h</td>
<td>Aluminium chloride</td>
</tr>
<tr>
<td>P-11-3</td>
<td>1100°C/3 h</td>
<td></td>
</tr>
<tr>
<td>P-12-1</td>
<td>1200°C/1 h</td>
<td></td>
</tr>
</tbody>
</table>
As for the unseeded samples either 3 h at 1100°C or 1 h at 1200°C were required to produce powder in which no θ phase could be detected by X-ray diffraction; similar results have been reported by other researchers 21, 25, 26.

![XRD patterns of powders prepared using aluminium chloride with no added seed/surfactant after heat treatment at different temperatures:](image)

**Figure 4-21** XRD patterns of powders prepared using aluminium chloride with no added seed/surfactant after heat treatment at different temperatures: a) P-10-1 (1000°C/1 h), b) P-10-6 (1000°C/6 h), c) P-11-1 (1100°C/1 h), d) P-11-3 (1100°C/3 h) and e) P-12-1 (1200°C/1 h).

**Table 4-6** Phases present in the powders synthesised by precipitation using aluminium chloride and no seed/surfactant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases detected by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-10-1</td>
<td>θ</td>
</tr>
<tr>
<td>P-10-6</td>
<td>α + ~50% θ</td>
</tr>
<tr>
<td>P-11-1</td>
<td>α + ~10% θ</td>
</tr>
<tr>
<td>P-11-3</td>
<td>α</td>
</tr>
<tr>
<td>P-12-1</td>
<td>α</td>
</tr>
</tbody>
</table>
TEM investigation of the unseeded samples revealed that calcination at 1000°C for 1 h yielded ≥20 nm particles of θ-alumina, Figure 4-22a. To obtain only α-alumina particles required calcination at temperatures as high as 1200°C was required, although these conditions yielded particles with a mean size of about 200 nm after undergoing the usual metastable phase changes during heat-treatment, which is significantly larger than that of the θ-alumina particles obtained at 1000°C, Figure 4-22. Similar enhancements in particle size accompanying the formation of α-alumina phase at high temperatures have been observed in other work on preparation of α-alumina.\textsuperscript{22, 26}

![Figure 4-22 TEM micrographs of unseeded powders after calcination: a) P-10-1 (1000°C/1 h) and b) P-12-1 (1200°C/1 h).](image)

The morphology of the unseeded sample after heat treatment at 1200°C, P-12-1, was studied by FEG-SEM, as shown in Figure 4-23(a). Irregular, large and strong-bonded agglomerates consisting of relatively large interconnected particles were observed, which were not breakable after many hours of wet milling. Necking of the α-alumina particles can be seen in Figure 4-23(b). As mentioned previously, a high transformation temperature to α phase always results in the coarsening of particles and formation of hard agglomerates in the powder.
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Figure 4-23 FEG-SEM micrographs of calcined sample P-12-1 (1200°C/1 h): a) low and b) high magnifications.

When 4 wt% of seeds were included (Table 4-7), either 1 h at 1100°C or 6 h at 1000°C was sufficient to avoid the theta-alumina phase; without seeds these conditions led to the θ phase being present, sometimes in significant proportions, Figure 4-24.

Table 4-7 Summary of the precipitation synthesis conditions with added seeds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Heat treatment</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-S4-8-6</td>
<td>4</td>
<td>800°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-S4-8-12</td>
<td>4</td>
<td>800°C/12 h</td>
<td></td>
</tr>
<tr>
<td>P-S8-8-12</td>
<td>8</td>
<td>800°C/12 h</td>
<td></td>
</tr>
<tr>
<td>P-S4-10-1</td>
<td>4</td>
<td>1000°C/1 h</td>
<td></td>
</tr>
<tr>
<td>P-S4-10-3</td>
<td>4</td>
<td>1000°C/3 h</td>
<td>Aluminium chloride</td>
</tr>
<tr>
<td>P-S2-10-6</td>
<td>2</td>
<td>1000°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-S4-10-6</td>
<td>4</td>
<td>1000°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-S8-10-6</td>
<td>8</td>
<td>1000°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-S4-11-1</td>
<td>4</td>
<td>1100°C/1 h</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-24  XRD patterns of powders prepared using aluminium chloride with added seeds after heat treatment at different temperatures: a) P-S4-8-12 (800°C/12 h), b) P-S4-8-6 (800°C/6 h), c) P-S4-10-6 (1000°C/6 h), d) P-S4-10-3 (1000°C/3 h), e) P-S4-10-1 (1000°C/1 h), f) P-S4-11-1 (1100°C/1 h) and g) P-S4-12-1 (1200°C/1 h).

Table 4-8 Phases present in the seeded powders synthesised by precipitation using aluminium chloride and added seeds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases detected by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-S4-8-6</td>
<td>θ</td>
</tr>
<tr>
<td>P-S4-8-12</td>
<td>α + ~50% θ</td>
</tr>
<tr>
<td>P-S4-10-1</td>
<td>α + ~20% θ</td>
</tr>
<tr>
<td>P-S4-10-3</td>
<td>α + ~10% θ</td>
</tr>
<tr>
<td>P-S4-10-6</td>
<td>α</td>
</tr>
<tr>
<td>P-S4-11-1</td>
<td>α</td>
</tr>
<tr>
<td>P-S4-12-1</td>
<td>α</td>
</tr>
</tbody>
</table>
As shown in Table 4-8, a temperature as low as 800°C, albeit for 12 h, could be used to achieve an approximately 50/50 mix of \( \alpha \) and \( \theta \)-alumina when the seeds were used; without the seeds, 1000°C for 6 h was required to achieve a similar result. This reduction in the formation temperature of \( \alpha \)-alumina is due to the effect of seeding, which can be described by heterogeneous nucleation theory. As each of the added seeds provided multiple nucleation sites for phase transformation to \( \alpha \)-alumina, the transformation kinetics increased considerably and as a result the transformation temperature was lowered \(^{25,135,136}\).

Figure 4-25 shows that by reducing the amount of \( \alpha \)-alumina seed to 2 wt\%, there was a slight decrease in the formation of \( \alpha \)-alumina after heat treatment at 1000°C for 6 h.

![XRD patterns of powders after heat treatment at 1000°C/6 h: a) P-S2-10-6 and b) P-S4-10-6 and c) P-S8-10-6 with 2, 4 and 8 wt% seed, respectively.](image)

However increasing the seed amount to 8 wt\%, as shown in Figure 4-26, did not affect the transformation kinetics at 800°C/12 h, as it led to a final powder with a higher fraction of ~5\% \( \alpha \)-alumina phase, which could be due to the existence of more seeding powder in the initial sample. Kumagai and Messing \(^{22}\) have reported the temperature for the \( \theta \rightarrow \alpha \) transformation as a function of the wt\% of \( \alpha \)-alumina seeds. They showed that for unseeded samples the transformation temperature is 1215°C, which was reduced to around 1075°C by adding 4 wt\% \( \alpha \)-
alumina. This temperature however, only decreased by a further 25°C after increasing the amount of the added seeds to 10 wt%. Clearly, the introduction of only a small amount of seeds is required to enhance the \( \theta \rightarrow \alpha \) transformation significantly.

**Figure 4-26** XRD patterns of powders after heat treatment at 800°C/12 h: a) P-S4-8-12 and b) P-S8-8-12 with 4 and 8 wt% seed, respectively.

TEM micrographs of the \( \alpha \)-alumina powders resulting from calcination of seeded precipitates at 1000°C for 6 h are presented in Figure 4-27, displaying the synthesised nanosized particles with a mean size of ~20 nm along with the added seeds for both 4 wt%- and 8 wt%-seeded samples.

**Figure 4-27** TEM micrographs of powders after heat treatment at 1000°C/6 h: a) P-S4-10-6 and b) P-S8-10-6 with 4 and 8 wt% seed, respectively.
The microstructures of both 4 wt%- and 8 wt%-seeded samples after heat treatment at 1000°C for 6 h, Figure 4-28 and Figure 4-29, appear the same and consist of added α-alumina seeds, highlighted with red signs, along with the aggregates of synthesised ultrafine particles of ~20 nm.

**Figure 4-28** FEG-SEM micrographs of powder with 4 wt% seed calcined at 1000°C/6 h (S4-10-6) at a) low and b) high magnifications showing the aggregates of synthesised nanoparticles and the seeds, highlighted in red.

**Figure 4-29** FEG-SEM micrographs of powder with 8 wt% seed calcined at 1000°C/6 h (S8-10-6) at a) low and b) high magnifications showing the aggregates of synthesised nanoparticles and the seeds, highlighted in red.

After being calcined, P-S4-8-12 and P-S8-8-12 samples contained highly agglomerated mixtures of ultra-fine particles of θ and α-alumina along with the seed particles, as Figure 4-30 displays. This showed that the transformation to α-alumina and also the morphology of the final powders were not affected by increasing the seed concentration.
The introduction of surfactant to the initial precursor solution (Table 4-9) had a noticeable effect on the amount of α-alumina phase observed in the final powders calcined at 800°C.

**Table 4-9** Summary of the precipitation synthesis conditions with added seeds and surfactants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Surfactant wt% (β-alanine and Tween-80)</th>
<th>Heat treatment</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-S4S10-10-6</td>
<td>4</td>
<td>10</td>
<td>1000°C/6 h</td>
<td>Aluminium chloride</td>
</tr>
<tr>
<td>P-S8S10-10-6</td>
<td>8</td>
<td>10</td>
<td>1000°C/6 h</td>
<td></td>
</tr>
<tr>
<td>P-S4S10-8-12</td>
<td>4</td>
<td>10</td>
<td>800°C/12 h</td>
<td></td>
</tr>
<tr>
<td>P-S8S10-8-12</td>
<td>8</td>
<td>10</td>
<td>800°C/12 h</td>
<td></td>
</tr>
</tbody>
</table>

As shown by the XRD results, Figure 4-31, and displayed in Tables 4-4 and 4-5, samples P-S4S10-8-12 and P-S8S10-8-12 each contained approximately 10% less θ-alumina, and hence 10% more α-alumina, than P-S4-8-12 and P-S8-8-12 respectively, the equivalent samples without any surfactant added.

Table 4-10 displays the phases present in several surfactant-added samples after heat treatment at 800°C and 1000°C.
Figure 4-31  XRD patterns of powders heat treated at 800°C/12 h: a) P-S4-8-12 and b) P-S4S10-8-12 both containing 4 wt% seeds without and with added surfactant, respectively and c) P-S8-8-12 and d) P-S8S10-8-12 both containing 8 wt% seeds without and with added surfactant, respectively.

Table 4-10  Phases present in the surfactant-added powders synthesised by precipitation method using aluminium chloride.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases detected by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-S4S10-10-6</td>
<td>α</td>
</tr>
<tr>
<td>P-S8S10-10-6</td>
<td>α</td>
</tr>
<tr>
<td>P-S4S10-8-12</td>
<td>α + ~ 40% θ</td>
</tr>
<tr>
<td>P-S8S10-8-12</td>
<td>α + ~ 35% θ</td>
</tr>
</tbody>
</table>

A TEM micrograph of sample P-S4S10-8-12 is displayed in Figure 4-32(a), where the top left inset presents the SADP of the agglomerated areas showing ring patterns consistent with those of both θ and α-alumina and the bottom right inset shows sharp diffraction spots corresponding to α-alumina, which could be due to the presence of
alumina seeds; Figure 4-32(b) displays sample P-S8S10-8-12. As can be observed in both figures, where the addition of surfactant did help was in uniform dispersing of the individual seed particles in the matrix and also uniform packing of the surrounding gelatinous precipitate matrix nearby those seed particles. The former could be due to the surfactant interaction with the particle surface in order to reduce the particle surface free energy, which resulted in softer and less-agglomerated powder with higher fraction of $\alpha$-alumina after heat treatment.

![Figure 4-32 TEM micrographs](image)

**Figure 4-32** TEM micrographs of samples containing added surfactants calcined at 800°C/12 h: a) P-S4S10-8-12 with 4 wt% added seeds showing the synthesised nanoparticles with the related SAED (top right inset) and the seeds with the related SAED (bottom left), both highlighted in red and b) P-S8S10-8-12 with 8 wt% added showing the seeds highlighted with arrows.

![Figure 4-33 FEG-SEM micrographs](image)

**Figure 4-33** FEG-SEM micrographs of powders containing added surfactants heat treated at 1000°C/6 h: a) P-S4S10-10-6 and b) P-S8S10-10-6 with 4 and 8 wt% added seeds, respectively.
The FEG-SEM study of surfactant-added powders, Figure 4-33, showed lower level of agglomeration after calcination at 1000°C for 6 h compared to powders without surfactant calcined with the same heating profile (Figures 4-28 and 29). The addition of surfactant offers the advantage of uniform packing of the initial precipitate, resulting in less agglomeration in the final powder after calcination.

4.2.2. Two-Step Heat Treatment

By introducing a further high-temperature step for a very short duration (1 minute) to the low-temperature conventional heat treatment route (800°C/12 h), both 4 wt% seed and 10 wt% surfactant-added samples, P-TS-1 and P-TS-2 respectively (Table 4-18), transformed completely into α-alumina phase, as shown in Figure 4-34. This short dwell time at a temperature as high as 1200°C could significantly improve the previously-presented results, even for the specimen with no seed/or surfactant (P-TS-0). However the mean particle size and the degree of agglomeration presented in the resultant powders were quite different in the samples depending on the existence of seed/or surfactant.

Table 4-11 Summary of the precipitation synthesis using two-step heat treatment method (1200°C/1 min - 800°C/12 h).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Surfactant wt% (β-alanine and Tween-80)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-TS-0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-TS-1</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>P-TS-2</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 4-34  XRD patterns of samples a) P-TS-0 (no added seed/surfactant), b) P-TS-1 (with 4 wt% added seeds) and c) P-TS-2 (with 10 wt% added surfactants).

The TEM micrographs of the three different samples calcined at 1200°C/1 min-800°C/12 h showed very dissimilar morphologies as can be seen in Figure 4-35. The presence of α-alumina seeds in the precipitate, sample P-TS-1, caused a significant decrease in the mean particle size compared to sample P-TS-0 without seeds. The latter consisted of a bimodal size distribution with particles in a range of 20-50 nm and also 2-3 μm, Figure 4-35(a), but the former had the particle size of 20-50 nm accompanied by added seeds Figure 4-35(b). Furthermore by introducing 10 wt% of surfactant (to create a mixture as discussed previously), the mean size of the particles remained almost the same as sample P-TS-1 and with fairly low agglomeration Figure 4-35(c). Due to the relatively low temperature of the second calcination step, exaggerated growth and hard agglomeration of transition alumina particles during the transformation to pure α-alumina could be eliminated. The newly-added step provides high activation energy for partially phase transformations to α-alumina, but at the same time the dwelling time is not long enough to cause any particle growth.

By decreasing the temperature of the first heat treatment step to 1100°C, none of the samples converted to pure α-alumina powder, as shown in Figure 4-36.
Figure 4-35 TEM micrographs of different powders after two-step heat treatment at 1200°C/1 min - 800°C/12 h; samples a) P-TS-0 (no added seed/surfactant), b) P-TS-1 (with 4 wt% added seed) and c) P-TS-2 (with 10 wt% added surfactants).

Table 4-12 Summary of the precipitation synthesis using two-step heat treatment method (1100°C/1 min - 800°C/12 h).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed wt% (BMA15)</th>
<th>Surfactant wt% (β-alanine and Tween-80)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-TS-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-TS-4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>P-TS-5</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

Despite raising the temperature from 1100°C to 1150°C and further to 1175°C for the sample with 10 wt% surfactant, only weak peaks of α-alumina were observed in the X-ray pattern of the former and traces of existing θ-alumina phase could also still be detected by X-ray diffraction in the latter, Figure 4-37. As demonstrated earlier in this work and also reported by Kumagai and Messing 22, the number of seeds is critical to
the successful control of transformation to $\alpha$ phase. This suggests that the minimum temperature of 1200°C is required for the first step for development of phase transformation to pure $\alpha$-alumina.

![Figure 4-36 XRD patterns of samples a) P-TS-3, b) P-TS-4 and c) P-TS-5 after two-step heat treatment at 1100°C/1 min-800°C/12 h.](image)

**Figure 4-36** XRD patterns of samples a) P-TS-3, b) P-TS-4 and c) P-TS-5 after two-step heat treatment at 1100°C/1 min-800°C/12 h.

![Figure 4-37 XRD patterns of samples a) P-TS-6 and b) P-TS-7 after two-step heat treatment at 1150°C/1 min-800°C/12 h and 1175°C/1 min-800°C/12 h, respectively.](image)

**Figure 4-37** XRD patterns of samples a) P-TS-6 and b) P-TS-7 after two-step heat treatment at 1150°C/1 min-800°C/12 h and 1175°C/1 min-800°C/12 h, respectively.
The transformation kinetics to $\alpha$ phase for samples with 10 wt\% surfactant that has been heat treated at 1200°C/1 min-800°C/6 h (P-TS-8) and 1200°C/0.1 min-800°C/12 h (P-TS-9) were compared to the P-TS-2 sample. As displayed in Figure 4-38, sample P-TS-8 is ~80% transformed to $\alpha$-alumina after 6 hours of heat treatment at 800°C and the other sample is ~90% transformed with quite a short first step dwelling time. As phase transformation is a time-dependant process, this suggested that pure $\alpha$-alumina could be achieved by using longer times for both heat treatment steps.

![XRD patterns](image)

**Figure 4-38** XRD patterns of samples a) P-TS-8 and b) P-TS-9 after two-step heat treatment at 1200°C/1 min-800°C/6 h and 1200°C/0.1 min-800°C/12 h, respectively.

TEM study of the ground dry precipitates before the heat treatment process showed that these powders consisted of a porous spongy structure of irregular shapes (Figure 4-39), which was less agglomerated in sample P-TS-2 due to the presence of the surfactant in the initial solution. Electron diffraction patterns from such structures contained some weak diffused rings matching the aluminium oxyhydroxide pattern as well as patterns related to $\alpha$-alumina in the seeded sample, as shown in Figure 4-39b.
Figure 4-39  TEM micrographs of dry precipitates of samples a) P-TS-0 (no added seed/surfactant), b) P-TS-1 (with 4 wt% added seeds) showing the synthesised nanoparticles and the seeds (highlighted with arrows) along with its SAEPs of the spongy structure (inset, top left and seed particles (inset, bottom right) and c) P-TS-2 (with 10 wt% added surfactants).

The samples were also characterized after the first heat treatment step at 1200°C/1min. Figure 4-40 shows the transmission electron micrographs of these powders, which were composed of two different structures: firstly, very fine agglomerated particles of α-alumina (including the seed particles in case of the seeded sample) and secondly an amorphous spongy structure, as demonstrated in Figure 4-40(a-c). The ultrafine alumina particles could be formed by the activation energy given to the system by the short dwelling at 1200°C, although this energy was obviously not enough to transform all the powder to α-alumina. Therefore, the first step of the new calcination route can be considered as an in-situ seeding, followed by a conventional nucleation and growth process.
Figure 4-40  TEM micrographs of samples after 1st step calcination:  a) P-TS-0 (no added seed/surfactant), b) P-TS-1 (with 4 wt% added seed) and c) P-TS-2 (with 10 wt% added surfactant); inset SAEPs of the spongy structure (top left) and fine particles (bottom right).

Figure 4-41  XRD patterns of samples a) P-TS-10 (with 10 wt% Tween-80) and b) P-TS-11 (with 10 wt% β-alanine) after two-step heat treatment at 1200°C/1 min-800°C/12 h.
To study the effect of adding each of the surfactants separately (not a mixture of them), new samples prepared by using 10 wt% of each of the surfactants were investigated by XRD and TEM. It can be seen from Figure 4-41 that, as expected, pure α-alumina powder was achieved after two-step calcination of both samples.

Figure 4-42 displays the TEM micrographs of samples with 10 wt% of β-alanine and Tween-85, P-TS-11 and P-TS-10 respectively. Introducing the former resulted in the formation of plate-like α-alumina particles of ≤20 nm in size with a lower level of agglomeration compared to when the latter was used. This led to slightly higher agglomerated α-alumina particles of irregular forms with a size of ≤50nm.

TEM investigation showed that, similar to the samples with 10 wt% mixture of both surfactants, the dry precipitates of samples P-TS-10 and PT-S-11 were composed of a porous spongy structure, Figure 4-43, with less agglomeration in sample P-TS-11, which was produced using β-alanine.

Figure 4-42 TEM micrographs of samples after calcination at 1200°C/0.1min-800°C/12h: a) P-TS-10 (with 10 wt% Tween-80), b) P-TS-11 (with 10 wt% β-alanine) and c) high magnification of the area highlighted in the previous one.
Since samples made using β-alanine showed a lower level of agglomeration compared to those containing Tween 80, only β-alanine was investigated. The α-alumina powder prepared by adding 5 wt% β-alanine appeared to be highly agglomerated compared to the one with double this amount, Figure 4-44. Therefore 10 wt% was chosen as the optimum value of added surfactant to avoid agglomeration of the resulting alumina powder using β-alanine.

The structural analysis of the powders derived from pH 8 and 9 was investigated by XRD and TEM and is shown in Figure 4-45 and Figure 4-46. One of the critical parameters in precipitation synthesis processing is pH, as it determines the phase, particle size and morphology of the final powder. Figure 4-45 shows the XRD
patterns of samples P-TS-13 and P-TS-14 after two-step heat treatment, showing both samples were highly crystalline $\alpha$-alumina powders.

![XRD patterns of samples prepared using 10 wt% $\beta$-alanine a) P-TS-13 and b) P-TS-14 with initial pHs of 9 and 8, respectively after two-step heat treatment at 1200 °C/1 min-800°C/12 h.](image)

**Figure 4-45** XRD patterns of samples prepared using 10 wt% $\beta$-alanine a) P-TS-13 and b) P-TS-14 with initial pHs of 9 and 8, respectively after two-step heat treatment at 1200 °C/1 min-800°C/12 h.

![TEM micrographs of samples prepared using 10 wt% $\beta$-alanine a) P-TS-13 and b) P-TS-14 with initial pHs of 9 and 8, respectively after two-step heat treatment at 1200 °C/1 min-800°C/12 h.](image)

**Figure 4-46** TEM micrographs of samples prepared using 10 wt% $\beta$-alanine a) P-TS-13 and b) P-TS-14 with initial pHs of 9 and 8, respectively after two-step heat treatment at 1200 °C/1 min-800°C/12 h.

However, decreasing the pH of the initial precipitate led to a change in the morphology of the plate-like particles to rod-like ones with dimensions of about 20 nm, as shown in **Figure 4-46(a)**. Particularly in the case of the powder made of the precipitate with pH~8, individual nanorods with lengths of 20-60 nm could be
distinguished, Figure 4-46(b). This could be due to the Zwitterionic nature of the β-alanine as an amino acid.

Figure 4-47 shows the thermal analysis (DTA and TG) behaviour of sample P-TS-11 prepared with 10 wt% β-alanine at pH 10. As can be observed, the DTA curve had two endothermic peaks existing at 72.7°C and 187.8°C, which could be linked to a gradual weight loss of about 5 wt% on the TG curve. The former was due to the evaporation of absorbed water and the latter was caused by removal of the structural water existing in the oxyhydroxide phase. There was a noticeable endothermic peak at 327.6°C, associated with about 64.7 wt% weight loss on the TG curve, which was compatible with the decomposition point of ammonium chloride present in the sample as the by-product of synthesis process. The decomposition of NH₄Cl consisted of 2 stages viz. melting and sublimation, occurring at 220°C and 338°C, respectively. There was also an exothermic peak at 1152.5°C without a corresponding weight loss on the TG curve, which was caused by the θ-alumina → α-alumina phase transformation.

Figure 4-47 Thermal analysis, DTA and TG, of a sample prepared using 10 wt% β-alanine, P-TS-11.
From the room temperature XRD pattern shown in Figure 4-48, as mentioned previously in section 4-1, it was observed that the dry precipitate consisted of NH₄Cl with sharp peaks along with an amorphous phase showing very weak broad peaks in the positions expected for boehmite (AlOOH). The XRD pattern of the sample heat treated at 200°C showed a similar trend to the non-treated sample. At 400°C, the NH₄Cl peaks disappeared and those corresponding to boehmite developed to stronger but still broad peaks indicating that the materials could still be amorphous 26. Material calcined at 600°C and 800°C gave diffraction peaks due to γ- and δ-alumina, whilst the peaks for θ-alumina occurred in the pattern of the 1000°C heat treated sample. After 1100°C α-alumina and minor amounts of θ-alumina were observed and by 1200°C only peaks corresponding to the α-alumina phase were detected. The peaks associated with the transition alumina phases were very broad compared to the α-alumina peaks, suggesting that they had much finer crystallite sizes 26.

![XRD patterns](image)

**Figure 4-48** High-temperature XRD patterns of a sample prepared using 10 wt% β-alanine, P-TS-11.
After washing the precipitates with 10 wt% β-alanine with ethanol, butanol and deionised water and centrifuging them, these samples were heat treated using the two-step calcinations route. TEM observation of the resulting pure α-alumina powders, Figure 4-49, showed that all of them were agglomerated with increased particle size compared to powder resulted from the unwashed precipitate. This could be due to the removal of the β-alanine after washing and centrifuging the gelatinous precipitate.

![TEM micrographs of α-alumina powder resulted by calcination of washed precipitate of sample P-TS-11 (prepared using 10 wt% β-alanine with a) ethanol b) butanol and water.](image)

**Figure 4-49** TEM micrographs of α-alumina powder resulted by calcination of washed precipitate of sample P-TS-11 (prepared using 10 wt% β-alanine with a) ethanol b) butanol and water.

In Figure 4-50 TEM micrographs of two-step heat treated powders using the precipitates ball milled in butanol is presented. It shows that the agglomerates existing in the initial precipitate could be broken using this mill fluid, which resulted in considerably softer powder both before and after the two-step heat treatment. This is due to the boiling point of butanol being higher than that of water. Therefore the water present in the precipitate, which causes hydrogen bonds in the system, vaporized prior to butanol during the dehydration of the precipitate. This made the resulting powder significantly softer compared to powders milled in deionised water.
or ethanol. When the dehydration process was finished, the residual butanol remaining in the dried precipitate could be further removed during the subsequent calcination process.

![Figure 4-50](image)

**Figure 4-50** TEM micrograph of ball milled precipitate of a sample prepared using 10 wt% β-alanine, P-TS-11 in butanol.

Figure 4-51 shows that milling in butanol greatly affected the level of agglomeration in the final α-alumina powder. It can be seen that the powder made from the non-milled precipitate consisted of agglomerates of about 1-4 μm, whilst the size of agglomerates was considerably smaller in the milled powder, which could also be compacted more easily. Consequently this powder could be considered as being soft agglomerated.

![Figure 4-51](image)

**Figure 4-51** FEG-SEM micrographs of the sample prepared using 10 wt% β-alanine, P-TS-11, after heat treatment: a) without and b) with ball milling the precipitate.
4.3. Industrial “Benchmark” Nanosized $\alpha$-alumina Powder

The XRD pattern of the PlasmaChem “benchmark” powder is compared with that of the Lboro-synthesised powder in Figure 4-52. It confirmed that the benchmark was 100% $\alpha$-alumina powder.

![XRD patterns of Lboro-synthesised and PlasmaChem (benchmark) powders.](image)

**Figure 4-52** XRD patterns of Lboro-synthesised and PlasmaChem (benchmark) powders.

The TEM images of the PlasmaChem powder are given in Figure 4-53; at low magnification it shows the agglomerates of the alumina particles with particle size of $\geq 50$ nm, as demonstrated in high-magnification image.

![TEM micrographs of PlasmaChem (benchmark) powder: a) low and b) high magnifications.](image)

**Figure 4-53** TEM micrographs of PlasmaChem (benchmark) powder: a) low and b) high magnifications.
Figure 4-54 shows the FEG-SEM images of Lboro and PlasmaChem \( \alpha \)-alumina nanopowders. It can be seen that the latter consisted of a range of particle sizes between 50-200 nm.

![FEG-SEM micrographs of a) Lboro and b) PlasmaChem (benchmark) powders.](image)

Considering the results mentioned above, it can be concluded that the PlasmaChem benchmark powder consisted of \( \alpha \)-alumina powders ranging between 50-200 nm, whereas the Lboro powder prepared by two-step calcination route led to \( \alpha \)-alumina particles of \( \sim \) 20 nm in size.

4.4. Processing of Alumina Ceramics

4.4.1. Suspension Preparation and Slip Casting

Figure 4-55 shows the effect of adding 1 wt% of different ammonium-based dispersants (Dispex-A40, Darvan-C and Dolapix-CE64) on the zeta potential values of the suspensions with 60 wt% solids content prepared using the \( \alpha \)-alumina nanopowder synthesised by two-stage heat treatment of ball-milled precipitate containing 10 wt% \( \beta \)-alanine (P-TS-11). It may be seen that the isoelectric point (IEP) of the nanoalumina suspension, at which the surface charge on the particles is zero and there is no repulsive force between them, decreases from about pH 8.4 for the suspension with no added dispersant to values of 3 - 4 by adding 1 wt% of each dispersant. The (negative) zeta potential values were all broadly similar, having values of -27, -34 and -30 mv, respectively for Dispex-A40, Darvan-C and Dolapix-CE64 additions at pH 7.
Chapter 4        Results and Discussion

**Figure 4-55**  Effect of adding 1 wt% different types of dispersants on the zeta potential of the 60 wt% nanoalumina suspensions.

Table 4-13 displays the maximum values of the zeta potential for all of the above suspensions; a value of ±40 mV is typically needed for the successful production of a suspension; it ensures that the particles will repel sufficiently so that the suspension will be dispersed. The data shows that Dolapix-CE64 was the best dispersant and the pH range of 6–10 in which the zeta potential was a maximum was very convenient, neither too acidic nor basic.

**Table 4-13**  The IEP and max. zeta potential values of the 60 wt% nanoalumina suspensions with different types of dispersants.

<table>
<thead>
<tr>
<th>Dispersant type</th>
<th>IEP</th>
<th>Max. ZP value / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>No dispersant</td>
<td>8.4</td>
<td>-16</td>
</tr>
<tr>
<td>Dispex-A40</td>
<td>4.0</td>
<td>-30.5</td>
</tr>
<tr>
<td>Darvan-C</td>
<td>3.0</td>
<td>-35.5</td>
</tr>
<tr>
<td>Dolapix-CE64</td>
<td>3.7</td>
<td>-38.1</td>
</tr>
</tbody>
</table>

The appearance of the suspensions of 60 wt% prepared using the as-calcined α-alumina nanopowder both without and with 1 wt% dispersant (Dispex-A40) is shown
in Figure 4-56. The former consisted of some powder floating on the surface, some settled at the bottom and water in between, whilst the latter formed a suspension.

![Image of 60 wt% nanoalumina suspension a) with no dispersant and b) with 1 wt% Dispex-A40.](image)

**Figure 4-56** Images of 60 wt% nanoalumina suspension a) with no dispersant and b) with 1 wt% Dispex-A40.

The mechanism of the interaction between the ammonium-based polyelectrolyte dispersants and the alumina powder is presented in Figure 4-57. As we know, ceramic oxide powder dispersed in water can adsorb water molecules and form a hydration layer. The surface chemical properties of the oxide particles are determined by the H⁺ and OH⁻ ions adsorbed on the particle surface. Therefore, the H⁺ and OH⁻ ions present in aqueous suspension determine the surface charge of the alumina particles. By using an anionic dispersant the negatively charged polymer group dissociated from the dispersant is adsorbed on the positive charged alumina surface, therefore the particles will have negative charge, as seen in this figure.

![Mechanism of absorption of dispersant on to the alumina powder surface.](image)

**Figure 4-57** Mechanism of absorption of dispersant on to the alumina powder surface.
The particle size distributions of the 60 wt% nanoalumina suspensions without and with 1 wt% of different dispersants are presented in Figure 4-58 in number%. It may be seen that unimodal distributions were obtained in each case, though given the fundamental particle size of ~20-50 nm. These curves show the size of the agglomerates present in the suspensions. It can be seen that whilst the Darvan-C had relatively little effect, both the Dispex-A40 and the Dolapix-CE64 reduced the mean agglomerate size significantly, with the Dolapix-CE-64 having the greatest effect. This is probably due to the larger zeta potential value of the nanosuspension.

It is possible to convert between the number (%) distributions and volume (%) distributions. Nevertheless, because of the errors involved in such a conversion, the resulting distributions should just be considered as an indicative of the particle size distribution of the suspension. Volume-based distribution is very sensitive to the existence of even a small number of particles with large volumes. Therefore the volume-based trends are generally used for detection of large agglomerates. Figure 4-59 demonstrates the distributions of the above nanoalumina suspensions in volume (%). The distributions show the presence of agglomerates in all the nanosuspensions with multimodal distribution for the suspension with no dispersant, monomodal distribution for the one with Dispex-A40 and bimodal distributions for the other two suspensions. It can be seen that unlike the number-based results, the Darvan-C was more effective compared to Dispex-A40, yet the Dolapix-CE64 had the greatest effect in lowering the level of agglomeration of the nanosuspension. As mentioned previously, the high zeta potential value of this suspension is the reason for this behaviour.
Figure 4-58  Effect of adding 1 wt% dispersant on the number (%) particle size distribution of the nanoalumina suspensions a) without dispersant and with 1 wt% of b) Dispex-A40, c) Darvan-C and d) Dolapix-CE64 at pH~9.5.
Figure 4-59  Effect of adding 1 wt% dispersant on the volume (%) particle size distribution of the nanoalumina suspensions a) without dispersant and with 1 wt% of b) Dispex-A40, c) Darvan-C and d) Dolapix-CE64 at pH~9.5.
Since the suspension with Dolapix-CE64 displayed the greatest degree of dispersion, this dispersant was chosen for further experiments. Figure 4-60 displays the zeta potential values as a function of pH for different addition levels of Dolapix-CE64. It is noteworthy that a linear effect is not seen with increasing the levels of dispersant, rather the 2 wt% addition level results in the greatest value of the zeta potential.

![Graph showing zeta potential vs pH for different Dolapix-CE64 addition levels]

**Figure 4-60** Effect of different amounts of Dolapix-CE64 on zeta potential of the nanoalumina suspensions.

When the nanosuspensions with different addition levels of Dolapix-CE64 were slip cast, more uniform green bodies were formed using the suspension with 2 wt% of the dispersant, Figure 4-61(b), compared to those formed from the suspension made with 1 wt%, Figure 4-61(a). The large agglomerates seen in the fracture surface of the green body produced by slip casting the suspension containing 3 wt% of Dolapix-CE64, Figure 4-61(c), shows that the amount of the dispersant in the suspension is too high. This resulted in the dispersant acting as a binder in the suspension, leading to a high level of agglomeration.
Figure 4-61  FEG-SEM micrographs of fracture surfaces of the slip cast green bodies of 60 wt% solids content with a) 1 wt%, b) 2 wt% and c) 3 wt% of Dolapix-CE64.

The relatively high value of zeta potential at pH ~9.9 for the nanosuspension containing 2 wt% of Dolapix-CE64 indicates that this pH created the greatest interaction between the dispersant and the oxide powder. Therefore two batches of suspension with pHs of ~9.4 (the intrinsic pH) and ~9.9 (modified with ammonia solution) were prepared. The viscosities of these suspensions were measured using a rheometer as a function of shear rate, Figure 4-62. It can be seen that the small change in pH significantly lowered the viscosity (due to the higher zeta potential and hence greater dispersion of the nanoparticles). This lower viscosity made subsequent processing easier.

Figure 4-63 shows the rheological flow curves for the suspensions with pHs of 9.4 and 9.9; pseudoplastic and thixotropic behaviour was seen in both of the samples.
As an initial green forming step, it was decided to prepare bodies using slip casting. The use of slip casting, as mentioned previously, required the optimisation of a large number of parameters including the solids content of the suspension. Therefore three batches of suspensions with different solids contents of 50, 60 and 70 wt% were
prepared. The measured viscosities of these suspensions are plotted as a function of shear rate in Figure 4-64. In these experiments the pH of the nanosuspensions was ~9.5, the inherent pH of the suspensions. It can be seen that decreasing the solids content to 50 wt% considerably lowered the viscosity, however the green density of the compacts formed by slip casting is another important factor, which was investigated subsequently.

Green bodies were slip cast with nanosuspensions of 3 different solids contents, 50, 60 and 70 wt%. The best green density was ~53.0±0.1% theoretical density (3.987 gcm$^{-3}$) obtained with the 60 wt% suspension, and hence this was used. Lower solid content (50 wt%) yielded green bodies with 45.0±0.3%. The suspension with 70 wt% solid content was found to be too thick and therefore unsuitable for slip casting.

![Figure 4-64](image)

**Figure 4-64** Effect of % solids content on the viscosity of nanoalumina suspensions containing 2 wt% Dolapix-CE64.

A few of the green bodies cracked and failed during drying or organic burn out of the bodies at 700°C for 2 hours. This could have been caused by too rapid or insufficient drying. To solve this problem the green bodies were left in a humidity chamber with 60-80% moisture content and a temperature of 25°C to dry after casting. This solution was successful, however it increased the drying time to about 10-14 days making the forming process very slow.
The effect of ultrasonic agitation time as a function of viscosity of the nanoalumina suspension with 2 wt% Dolapix-CE64 (pH~9.9) is demonstrated in Figure 4-65. It can be seen that the viscosity of the suspension after being subjected to 30 s of sonication did not change noticeably.

![Graph showing viscosity vs. shear rate](image)

**Figure 4-65** Effect of ultrasonic agitation time on the viscosity of 60 wt% nanoalumina suspension with 2 wt% Dolapix-CE64.

The nanostructures of the fracture surfaces of the green bodies produced with and without exposing the suspension to 30 s of ultrasonication before the casting process are illustrated in Figure 4-66; it can be seen that the microstructure was more homogeneous when ultrasonication was used. This could be due to improved dispersion of the nanopowder in the suspension via the breakup of the agglomerates.

![FEG-SEM micrographs of the slip cast green bodies](image)

**Figure 4-66** FEG-SEM micrographs of the slip cast green bodies of 60 wt% solids content a) without and b) with 30 s ultra-sonication.
4.4.2. Characterisation and Slip Casting of the As-received Submicron Alumina Suspension

The X-ray diffraction pattern of the as-received submicron alumina suspension (Table 3-10) is shown in Figure 4-67. This confirmed that the as-received suspension consisted of pure $\alpha$- alumina phase, as noted on the data sheet received from Baikowski Ltd.

![XRD pattern of the alumina powder prepared by desiccation of the as-received suspension.](image)

**Figure 4-67** XRD pattern of the alumina powder prepared by desiccation of the as-received suspension.

The solids content of the as-received suspension used in the following experiments was measured as 58.8±0.2 wt%, which was compatible with the materials data sheet. The zeta potential of the as-received suspension as a function of pH is shown in Figure 4-68. The isoelectric point (IEP) of the suspension was 9.6; since the inherent pH of the as-received suspension was ~3.6, no agent was required to be added in order to improve the dispersion.
Figure 4-68 Zeta potential of the as-received alumina suspension.

The measured viscosity values of the as-received suspension versus shear rate are plotted in Figure 4-69. As can be seen the viscosity of the as-received submicron suspension was as low as the 50 wt% nanoalumina suspension. This is because the colloidally stable nanosuspensions are known to have a considerably lower volume loading at the same viscosity in comparison with the suspensions with particle sizes over 100 nm \(^{139, 140}\).

Figure 4-69 Viscosity of the as-received sub-micron alumina suspension as a function of shear rate.
The thermogravimetric analysis of the as-received alumina suspension is shown in Figure 4-70. From the figure it can be observed that ~0.4% of the weight loss for the suspension occurred below 100°C, which is due to the evaporation of physical water. The weight loss between 100°C and 250°C, ~0.5%, is presumably due to dehydration of more strongly chemisorbed water present in the sample. Finally the loss in the range of 250°C and 475°C could be caused by the evaporation of the other additives used in preparing the suspension such as polymer dispersants.

![Figure 4-70 TGA of the as-received suspension.](image)

Figure 4-71 displays the volume% particle size distribution of the as-received alumina suspension measured using the Mastersizer. The average size of the particles present in the alumina suspension was measured as 132 nm, which was compatible with the data received from the company. It is also noteworthy that the particle size distribution is very narrow.

FEG-SEM and TEM analysis was conducted to depict the characteristics of the submicron suspension. Figure 4-72 shows the representative FEG-SEM and TEM images of this suspension. The sample consisted of sub-micron particles with average size of ~150 nm, as shown on the material data sheet and also by the previous particle size distribution result.
Chapter 4

Results and Discussion

Figure 4-71  Particle size distribution of the as-received submicron suspension.

Figure 4-72  Micrographs of the $\alpha$-alumina particles of dried powder using the as-received suspension using a) FEG-SEM and b) TEM.

The as-received alumina suspension was slip cast into green bodies; this resulted in achieving homogenous and uniform compacts as can be seen in Figure 4-73. The green density of the slip cast samples was measured in mercury after binder removal and was found to be $53.5 \pm 0.5\%$ of theoretical density.

Figure 4-73  FEG-SEM micrograph of slip cast green bodies using the as-received submicron suspension.
4.4.3. Granulation of Nanoalumina Suspensions and Dry Pressing

In previous work by Binner, et al.,\textsuperscript{109} it was shown that if the solid content of a nanosuspension is too low (about 30 wt%) the resulting spray freeze dried powder will have very good crushability but poor flowability. However if the solid content is too high e.g. 70 wt%, the spray freeze dried granules will show good flowability but low crushability as they are very strong and cannot be crushed easily during die pressing procedure. Hence, a solid content of ~60 wt% was chosen in order to achieve both optimum crushability and flowability in the spray freeze dried powders.

Figure 4-74 shows the granule structure produced by spray freeze drying of the nanoalumina suspension with 2 wt% Dolapix-CE64 and pH of ~10 at different levels of magnification. As can be seen the particles were not properly held together after the drying process, resulting in granules with rough surfaces.

![Figure 4-74](image)

**Figure 4-74** FEG-SEM micrographs of SFD powder using 60 wt% suspension with 2 wt% Dolapix-CE64.

The addition of 0.5 wt% PVA as a binder led to denser packing of the particles together, Figure 4-75, as role of the binder is to create a mesh that holds the particles together. The resulting nanoalumina granules were compatible with the nanozirconia granules prepared by Binner, et al\textsuperscript{109}. However, denser packing can decrease the granule crushability, which is the key factor to production of nanostructured green bodies with high density by die pressing\textsuperscript{130}. 
To reduce the strength of the agglomerates, Freon was added to the suspension before spray freeze drying as a foaming agent to create defects in the structure of the granules and make them more crushable with insignificant effect on their flowability. Previously a variety of different foaming agents have been investigated by Annapoorani et al., and the best was found to be adding 1–2 vol% of Freon \textsuperscript{130}. Figure 4-76 shows the granules produced by spray freeze drying using 60 wt% nanosuspension with the use of 1 and 2 vol% Freon. It can be clearly seen that while the size and shape of the granules, and hence the flowability, is not considerably affected, the surface of the granules contained more defects compared to the ones prepared without using Freon (Figure 4-77b).

Figure 4-77 shows the fracture surface of the granules, fractured into halves, produced by spray freeze drying of the nanoalumina suspension without and with 2 vol% of Freon. As can be seen in Figure 4-78b, there were more defects in the interior
structure of the granules when Freon was used; this directly affected the strength of the granules and made them more crushable.

![FEG-SEM micrographs of the fracture surface of granules containing 0.5 wt% PVA and a) without and b) with 2 vol% Freon.](image)

The flow rate values of the spray freeze dried powders were measured at least 5 times using a Hall flow meter with orifices of 2.5 and 5 mm in diameter and the results are displayed in Table 4-6. As expected, the SFD granules produced without PVA additions did not flow and hence the fill and tap densities of these granules could not be measured. Adding the binder improved the flowability of the SFD powder as expected. The tap density values of the granules, as can be seen, were higher than the fill density values; this is due to the rearranging of the granules after being tapped and elimination of the large voids between them. It can also be seen that the flow rate values of the powders produced using 1-2 vol% of Freon was no different from the results when Freon was not used.

**Table 4-14** Volumetric flow rate for different spray freeze dried powders.

<table>
<thead>
<tr>
<th>Orifice size / mm</th>
<th>Flow rate/gs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 mm</td>
<td>0.27 1.59</td>
</tr>
<tr>
<td>5 mm</td>
<td>0.31 1.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orifice size / mm</th>
<th>Flow rate/gs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 mm</td>
<td>0.27 1.59</td>
</tr>
<tr>
<td>5 mm</td>
<td>0.31 1.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orifice size / mm</th>
<th>Flow rate/gs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 mm</td>
<td>0.31 1.60</td>
</tr>
<tr>
<td>5 mm</td>
<td>0.31 1.61</td>
</tr>
</tbody>
</table>
Table 4-15  Density values of different spray freeze dried powders.

<table>
<thead>
<tr>
<th></th>
<th>Fill density/gcm$^3$</th>
<th>Tapped density/gcm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No PVA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% PVA</td>
<td>0.51</td>
<td>0.64</td>
</tr>
<tr>
<td>0.5 wt% PVA + 1 vol% Freon</td>
<td>0.52</td>
<td>0.65</td>
</tr>
<tr>
<td>0.5 wt% PVA + 2 vol% Freon</td>
<td>0.53</td>
<td>0.65</td>
</tr>
</tbody>
</table>

After die pressing, the green density of the pellets as a function of compaction pressure in the range of 160-480 MPa are plotted in Figure 4-78. The ability of Freon-based granules to reach higher green densities at a given pressure directly results from the reduction in the strength of these granules. Whilst green densities of up to ~55% of the theoretical density could be achieved when using Freon, it required pressures as high as 480 MPa; this pressure is above that commonly being used in ceramic industry for preparing green bodies. However, achieving high densities after sintering is still possible by using green bodies with density values of ≥50% TD. This means that pressures as low as 250 MPa, which is inside the working range of most producers, can be used when Freon is used.

Figure 4-79 shows the fracture surfaces of green bodies pressed from granulated powders with and without the use of Freon at 480 MPa. It can clearly be seen that even at this high pressure some of the granules did not crush when the Freon was not used, whilst there was no evidence of un-crushed granules for the sample formed by using the Freon-based granulated powder. In addition, while die pressing the Freon-based granules, there was no tendency of sticking to the die leading to obtain green compacts with no delamination or capping defects.
4.4.4. Granulation of Submicron Suspension and Dry Pressing

As mentioned previously, to achieve both optimum crushability and flowability in the spray freeze dried powders suspensions a solid content of ~60 wt% was chosen for the suspension. Therefore there was no need to alter the inherent solid content of the as-received suspension for the spray freeze drying process.

Figure 4-80 shows the granules produced by spray freeze drying the submicron alumina suspension without and with using 2 vol% of Freon. Similar to spray freeze dried powders produced by nanosuspensions, although the size and shape of the
granules, and also their flowability were not considerably affected by the addition of Freon, it still can be noticed that the surface of the granules have more defects after using the Freon. The presence of these defects leads to a weakening of the granules making them more crushable.

![FEG-SEM micrographs of spray freeze dried alumina powders](image)

**Figure 4-80** FEG-SEM micrographs of spray freeze dried alumina powders a) without and b) with 2 vol% Freon.

The flowability of both spray freeze dried powders without and with 2 vol% Freon was measured at least 5 times using the same Hall flow meter as described previously. The calculated flow rate, tapped and fill density values are displayed in Table 4-16 and Table 4-17. As can be seen, the results are compatible with the values obtained for the nanoalumina granulated powders; the flowability and densities of the powders did not change noticeably, when Freon was used.

**Table 4-16** Volumetric flow rate for different spray freeze dried powders.

<table>
<thead>
<tr>
<th>Orifice size/mm</th>
<th>Flow rate / gs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
</tr>
<tr>
<td>2 vol% Freon</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>1.79</td>
</tr>
</tbody>
</table>
Table 4-17  Density values of different spray freeze dried powders.

<table>
<thead>
<tr>
<th></th>
<th>Fill density / g cm(^{-3})</th>
<th>Tapped density / g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Freon</td>
<td>0.59</td>
<td>0.67</td>
</tr>
<tr>
<td>2 vol% Freon</td>
<td>0.58</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The spray freeze dried powders (without and with 2 vol% Freon) were dry pressed at a pressure range of 160-480 MPa. As shown in Figure 4-81, similar to the nanoalumina granules, the ability of submicron alumina Freon-based granules to achieve higher densities after being pressed at a given pressure is a result of the higher crushability and lower granule strength.

Figure 4-81  Compaction characteristics of spray freeze dried powders containing additions of Freon.

Figure 4-82 displays the FEG-SEM micrographs of submicron alumina slip cast and die pressed green bodies. These results show that a very uniform and homogeneous green body of a relatively high density could be achieved using the slip cast method, whilst dry pressing resulted in less homogeneity and uniformity in the green bodies; this was significantly improved by the addition of Freon. The reason for this, as
explained previously, is the increase in the crushability of the spray freeze dried granules, which has also been previously studied and proven in zirconia ceramics. 

Figure 4-82 FEG-SEM micrographs of the fracture surface of green bodies: a) slip cast and die pressed with b) no Freon and c) 2 vol% Freon pressed at 480 MPa.

4.4.5. Sintering of Nanostructured Alumina Bodies
Pressureless sintering experiments were performed on both dry and wet processed green compacts using conventional single-step and two-step sintering cycles. The final density of the samples after the various single step heating experiments were measured and are summarised in Table 4-18 and Table 4-19. It can be observed that during the conventional single-step sintering, density increased with temperature with the maximum at 1550°C.
Table 4-18 Summary of the conventional single step sintering experiments using slip cast (SC) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC-1400-5</td>
<td>1400</td>
<td>5</td>
<td>89.8±0.3</td>
</tr>
<tr>
<td>NSC-1400-10</td>
<td>1400</td>
<td>10</td>
<td>94.6±0.1</td>
</tr>
<tr>
<td>NSC-1500-5</td>
<td>1500</td>
<td>5</td>
<td>96.5±0.5</td>
</tr>
<tr>
<td>NSC-1500-10</td>
<td>1500</td>
<td>10</td>
<td>97.4±0.1</td>
</tr>
<tr>
<td>NSC-1550-5</td>
<td>1550</td>
<td>5</td>
<td>99.0±0.2</td>
</tr>
</tbody>
</table>

Table 4-19 Summary of the conventional single step sintering experiments using die pressed (DP) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDP-1400-5</td>
<td>1400</td>
<td>5</td>
<td>88.2±0.2</td>
</tr>
<tr>
<td>NDP-1400-10</td>
<td>1400</td>
<td>10</td>
<td>91.7±0.3</td>
</tr>
<tr>
<td>NDP-1500-5</td>
<td>1500</td>
<td>5</td>
<td>95.2±0.3</td>
</tr>
<tr>
<td>NDP-1500-10</td>
<td>1500</td>
<td>10</td>
<td>96.6±0.6</td>
</tr>
<tr>
<td>NDP-1550-5</td>
<td>1550</td>
<td>5</td>
<td>97.8±0.2</td>
</tr>
</tbody>
</table>

Figure 4-83 shows a comparison between the relative densities of slip cast and die pressed bodies after being sintered at different temperatures for 5/10 h as a function of temperature. The slip cast green compacts reached ~99% relative density after being held at 1550°C for 5 h, whilst under the same condition, the die pressed compacts could only reach 97.8% relative density. The difference between sintered slip cast and die pressed bodies was associated with the fact that the latter had lower green density and coarser nanostructure compared to the former.
Figure 4-83 Relative density of sintered slip cast and die pressed samples as a function of sintering temperature sintered for 5 h.

Figure 4-84 a) Image of the translucent slip cast alumina compact sintered using single-step sintering at 1550°C /5h and FEG-SEM micrograph of b) the same sample and c) DP sample after similar sintering process.

A representative microstructure of the translucent compact, Figure 4-85(a), achieved after single-step sintering of the slip cast samples at 1550°C/5h is presented in Figure
Due to the high sintering temperature used to achieve full density, enormous grain growth occurred in both slip cast and die pressed samples during the sintering process yielding a mean grain size of 1.84±0.05 and 2.13±0.11 μm, respectively. The need for using high temperatures could be attributed to the fact that there were hard agglomerates existing in the powder, which led to differential sintering within the alumina compacts. Since the agglomerates had relatively higher density compared to the surrounding particles, preferential sintering started in those areas at temperatures lower than the initial stage sintering temperature. Hence, the densification process was controlled by the sintering between the already densified areas, which required longer diffusion distances and higher activation energy; this was provided by sintering at elevated temperatures e.g. 1500°C.

As mentioned in literature review, considerably higher final density and smaller average grain size have been achieved by using the two-step sintering technique. Therefore both slip cast and die pressed green bodies were heated up to a high initial temperature in the 1400-1600°C range held at this temperature for a very short period of time (0.1 min); the density of these samples were measured and are summarised in Table 4-20.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1</th>
<th>Relative density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC-1400</td>
<td>1400</td>
<td>89.9</td>
</tr>
<tr>
<td>NSC-1500</td>
<td>1500</td>
<td>91.5</td>
</tr>
<tr>
<td>NSC-1600</td>
<td>1600</td>
<td>94.6</td>
</tr>
<tr>
<td>NDP-1400</td>
<td>1400</td>
<td>87.2</td>
</tr>
<tr>
<td>NDP-1500</td>
<td>1500</td>
<td>90.6</td>
</tr>
<tr>
<td>NDP-1600</td>
<td>1600</td>
<td>93.8</td>
</tr>
</tbody>
</table>

It may be observed that after the first step, the density reached around 95% of theoretical at 1600°C for 0.1 min., resulting in 1600°C being selected as T1. As a result T2 was varied from 1400°C to 1500°C to obtain samples with different
densities. The results of the various two-step sintering experiments are summarised in Table 4-21. It can be seen that the slip cast green compacts reached ~99% relative density after being sintered at 1600°C/0.1 min-1500°C /10,20 h, similar to the sample sintered conventionally at 1550°C /10 h, but with slightly finer mean grain size of 1.78±0.05 μm. The die pressed compacts could only reach 96.7% relative density under the same sintering condition, due to the differences between green compacts, which was discussed previously.

Table 4-21 Summary of the two-step sintering experiments using both SC and DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1 / °C</th>
<th>T2 / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC-1600-1400-5</td>
<td>1600</td>
<td>1400</td>
<td>5</td>
<td>94.8±0.3</td>
</tr>
<tr>
<td>NSC-1600-1400-10</td>
<td>1600</td>
<td>1400</td>
<td>10</td>
<td>95.1±0.5</td>
</tr>
<tr>
<td>NSC-1600-1500-5</td>
<td>1600</td>
<td>1500</td>
<td>5</td>
<td>96.2±0.3</td>
</tr>
<tr>
<td>NSC-1600-1500-10</td>
<td>1600</td>
<td>1500</td>
<td>10</td>
<td>98.7±0.2</td>
</tr>
<tr>
<td>NSC-1600-1500-20</td>
<td>1600</td>
<td>1500</td>
<td>20</td>
<td>98.5±0.4</td>
</tr>
<tr>
<td>NDP-1600-1400-5</td>
<td>1600</td>
<td>1400</td>
<td>5</td>
<td>94.0±0.5</td>
</tr>
<tr>
<td>NDP-1600-1400-10</td>
<td>1600</td>
<td>1400</td>
<td>10</td>
<td>94.2±0.2</td>
</tr>
<tr>
<td>NDP-1600-1500-5</td>
<td>1600</td>
<td>1500</td>
<td>5</td>
<td>95.3±0.4</td>
</tr>
<tr>
<td>NDP-1600-1500-10</td>
<td>1600</td>
<td>1500</td>
<td>10</td>
<td>96.7±0.1</td>
</tr>
<tr>
<td>NDP-1600-1500-20</td>
<td>1600</td>
<td>1500</td>
<td>20</td>
<td>97.2±0.3</td>
</tr>
</tbody>
</table>

The aim of the two-step sintering method, as explained previously, is to produce a uniform pore microstructure while minimising grain growth. The grain growth behaviour during the second stage of sintering can be described with kinetic growth equations of the general form:

$$G^n - G_0^n = kt$$  \hspace{1cm} Eq. 4.2
Where \( n \) is a constant characteristic for a given grain growth mechanism, \( G_0 \) and \( G \) are the starting and final grain size for a certain grain growth stage, respectively, \( k \) is a kinetic constant and \( t \) the time. Hence the grain size after the first stage of sintering, \( G_0 \), is a critical factor affecting the final grain size at the end of the sintering process. \( G_0 \) should be kept as low as possible to prepare samples with a lower final grain size. As a result further grain size reduction can be achieved by increasing the density of the green compacts and also by decreasing the level of agglomeration present in them. This can enable the first stage of the two-step sintering process to be carried out at lower temperatures leading to finer grain sizes.

### 4.4.6. Sintering of Submicron Alumina Bodies

The sintering experiments are divided into two sections; in the first group the results of the conventional single-step sintering experiments of the slip cast and die pressed samples are discussed and in the second the results of two-step sintering experiments are considered.

The density values of the samples after the various single-step sintering experiments were measured and are summarised in Table 4-22. It can be observed that the submicron samples reached higher relative densities after conventional single-step sintering at lower temperatures compared to the nanoalumina bodies.

**Table 4-22** Summary of the single-step sintering experiments using both SC and DP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC-1300-2</td>
<td>1300</td>
<td>2</td>
<td>97.5</td>
</tr>
<tr>
<td>SSC-1400-2</td>
<td>1400</td>
<td>2</td>
<td>99.4</td>
</tr>
<tr>
<td>SDP-1300-2</td>
<td>1300</td>
<td>2</td>
<td>88.1</td>
</tr>
<tr>
<td>SDP-1400-2</td>
<td>1400</td>
<td>2</td>
<td>98.2</td>
</tr>
</tbody>
</table>

The microstructures of the slip cast samples after the conventional single-step sintering experiments at two different temperatures of 1300°C and 1400°C are shown in Figure 4-85. The mean grain size of the SSC-1400-2 sample was measured to be 1.18±0.05, finer than the average grain size of sample NSC-1550-5 (1.84±0.05).
Figure 4-85  FEG-SEM micrographs of the microstructure of slip cast samples after single-step sintering at a) 1300°C and b) 1400°C.

Table 4-23 displays the density values of both slip cast and die pressed samples sintered for 0.1 minute at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T / °C</th>
<th>Relative Density / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC-1300</td>
<td>1300</td>
<td>86.2</td>
</tr>
<tr>
<td>SSC-1400</td>
<td>1400</td>
<td>94.7</td>
</tr>
<tr>
<td>SSC-1450</td>
<td>1450</td>
<td>96.2</td>
</tr>
<tr>
<td>SDP-1300</td>
<td>1300</td>
<td>85.1</td>
</tr>
<tr>
<td>SDP-1400</td>
<td>1400</td>
<td>89.7</td>
</tr>
<tr>
<td>SDP-1450</td>
<td>1450</td>
<td>90.2</td>
</tr>
</tbody>
</table>

For the two-step sintering process T_1 was selected using the above results and T_2 was then varied from 1150°C to 1300°C in order to obtain samples with different densities and mean grain sizes. The dwelling time at the second step was also varied trying to find the optimum densification profile with maximum density and minimum grain growth. Figure 4-86 displays the microstructure of sintered samples using conventional two-step sintering. The results of all the two-step sintering experiments for both slip cast and die pressed bodies are summarised in Table 4-24 and Table 4-25.
Table 4-24  Density and grain size of SC samples after two-step sintering using conventional furnace.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; / °C</th>
<th>T&lt;sub&gt;2&lt;/sub&gt; / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
<th>Grain size / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC-1400-1150-5</td>
<td></td>
<td>1150</td>
<td>5</td>
<td>94.9</td>
<td>0.55±0.07</td>
</tr>
<tr>
<td>SSC-1400-1150-15</td>
<td></td>
<td></td>
<td>15</td>
<td>96.0</td>
<td>0.73±0.01</td>
</tr>
<tr>
<td>SSC-1400-1250-2</td>
<td></td>
<td></td>
<td>2</td>
<td>96.3</td>
<td>0.53±0.04</td>
</tr>
<tr>
<td>SSC-1400-1250-5</td>
<td>1400</td>
<td>1250</td>
<td>5</td>
<td>97.4</td>
<td>0.56±0.05</td>
</tr>
<tr>
<td>SSC-1400-1250-10</td>
<td></td>
<td></td>
<td>10</td>
<td>98.3</td>
<td>0.68±0.02</td>
</tr>
<tr>
<td>SSC-1400-1300-5</td>
<td></td>
<td>1300</td>
<td>5</td>
<td>97.8</td>
<td>0.59±0.02</td>
</tr>
<tr>
<td>SSC-1400-1300-10</td>
<td></td>
<td></td>
<td>10</td>
<td>98.7</td>
<td>0.73±0.04</td>
</tr>
</tbody>
</table>

Table 4-25  Density and grain size of DP samples after two-step sintering using conventional furnace.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; / °C</th>
<th>T&lt;sub&gt;2&lt;/sub&gt; / °C</th>
<th>t / h</th>
<th>Relative density / %</th>
<th>Grain size / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDP-1400-1250-5</td>
<td>1400</td>
<td>1250</td>
<td>5</td>
<td>94.9</td>
<td>0.50±0.02</td>
</tr>
<tr>
<td>SDP-1450-1250-2</td>
<td></td>
<td>1250</td>
<td>2</td>
<td>97.2</td>
<td>0.61±0.08</td>
</tr>
<tr>
<td>SDP-1450-1250-5</td>
<td>1450</td>
<td>1250</td>
<td>5</td>
<td>97.4</td>
<td>0.67±0.05</td>
</tr>
<tr>
<td>SDP-1450-1300-5</td>
<td>1300</td>
<td>5</td>
<td>97.8</td>
<td>0.69±0.06</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-86  Microstructures of SC samples after two-step sintering at T₁=1400°C and T₂=1250°C with dwelling times of a) 2 h, b) 5 h and c) 10 h.

Figure 4-87 compares the density and grain size values for some of the SC and DP samples after single step and two-stage sintering cycles. This graph illustrates that unlike the work of Chen and Wang\textsuperscript{126, 128}, in which the two-stage sintering was developed, the microstructure of the submicron alumina bodies did not remain frozen during sintering at T₂ and a relatively small amount of grain coarsening was observed. Mazaheri et al.\textsuperscript{141} and Bodisova et al.\textsuperscript{142} have reported similar results for the sintering of nanoZnO and submicron alumina, respectively; the data was also compatible with the results reported by Loughborough Advanced Ceramic research group for the two-step sintering of ZrO₂\textsuperscript{109, 143}.

A major difference in the sintering cycles between that reported by Chen et al.\textsuperscript{126, 128} for the sintering process of Y₂O₃ and the present work was the difference in the density required after the first sintering stage of sintering. The lower final density could be due to the acceptance of a lower density after the first stage of sintering. In the present study, an intermediate density of ~95% was required for the submicrometer alumina bodies to yield samples with ~99% density. This suggested that higher densities could be required for the second stage of sintering. Since the
mechanism of two-stage sintering method, as proposed by Binner, et al.\textsuperscript{109} could be similar to the conventional sintering but using the samples with much higher green densities as a result of the short first heating stage compared to samples normally being used for ceramic sintering. This can be achieved by using green compacts of higher densities than increasing the temperature of the first stage of sintering, which results in additional grain growth.

![Graph](image)

**Figure 4-87** Variation in grain size with density for submicron SC and DP samples.

As mentioned previously two processes occur at high temperatures, while heating a green compact in ambient atmosphere, i.e. pressureless sintering: densification and grain growth. Both of these processes are driven by diffusion, where no pressure is being applied and it is difficult to promote densification without having grain growth\textsuperscript{1,8}. Therefore, using pressure-assisted techniques such as sinter-forging, hot pressing, hot isostatic pressing or spark-plasma sintering can be the solution to produce nanosized alumina components as they have been used very successfully for other nanostructured ceramics.

### 4.4.7. Spark Plasma Sintering of Nanoalumina Powder

Table 4-19 displays the relative density and mean grain size values of the sintered bodies using SPS. As expected, by increasing the pressure up to 500 MPa higher relative density values with lower mean grain size were obtained at lower
temperatures compared to samples compacted at 70 MPa. It was also found that the mean grain size could be suppressed to be in the submicron range for the compacts consolidated at 500 MPa, even when the nanopowder was sintered at 1200°C. The use of 1400°C/70 MPa and 1200°C/500 MPa, as can be seen in the table, led to highly dense alumina bodies with densities of ~99.9% of theoretical density and the appearance of these compacts was a degree of transparency, as demonstrated in Figure 4-89. Unevenness in the compact colour, which is usually caused by heavy carbon contamination during spark plasma sintering, was observed for S-70-14.

Table 4-26  Density and average grain size values of SPS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative density / %</th>
<th>Grain size / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-70-10</td>
<td>93.9</td>
<td>0.7</td>
</tr>
<tr>
<td>S-70-12</td>
<td>99.1</td>
<td>4.2</td>
</tr>
<tr>
<td>S-70-14</td>
<td>99.9</td>
<td>6.2</td>
</tr>
<tr>
<td>S-500-10</td>
<td>99.4</td>
<td>0.4</td>
</tr>
<tr>
<td>S-500-12</td>
<td>99.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 4-88  Image of the transparent alumina compacts sintered using SPS: a) S-14-70 and S-12-500. Both samples are immediately on the text.

Sample S70-14 possessed a coarse-grained microstructure with an average grain size of ~6.2 μm. Furthermore large grains of about 10 μm could be frequently observed in this sample, as shown in Figure 4-90a. Sample S500-12 showed relatively fine-grained microstructures with average grain sizes of ~0.6 μm, Figure 4-90b. In comparison with sample S70-14, the mean grain size of S500-12 was reduced to about
one tenth due to the higher applied pressure during SPS process. However, non-uniformity and extremely large grains could still be observed in this sample.

![FEG-SEM micrographs of sintered samples](image)

**Figure 4-89** FEG-SEM micrographs of sintered samples a) S-14-10 and b) S-12-500. Note the different magnifications used.

The oversized final grain size and the exaggerated grain growth of these samples could be induced by the presence of agglomeration in the starting as-calcined powder. Lange found that in the presence of agglomerates shrinkage would begin within them during conventional sintering, resulting in an increase in the size and coordination number of the inter-agglomerate pores. These pores would be stable and shrink at high temperature, which could lead to excessive grain growth. Therefore the agglomeration present in the alumina nanopowder has to be removed to avoid differential shrinkage during SPS experiments. In addition, according to Lallemant, et al. packing of the particles has to be as uniform as possible, since it can support the prevention of differential shrinkage within the compact. The solution to this problem could be to use bodies formed by slip casting or dry pressing to a high green density and then pressureless sintered to ~95% of theoretical (before the porosity closes and grain growth begins) prior to use of SPS to complete densification.
5. Conclusions

The main processing stages involved in the fabrication of nanostructured alumina ceramics are:

(i) synthesis of nanosized $\alpha$-alumina powder,
(ii) suspension preparation,
(iii) forming of components using different methods and
(iv) sintering the green compacts.

In the first stage, different chemical routes including hydrothermal and precipitation methods were used to synthesize nanopowders of $\alpha$-alumina. The resultant powders were characterized using XRD, TEM and FEG-SEM for phase and morphology evaluation.

Hydrothermal treatment as a direct transformation route to obtain $\alpha$-alumina without the formation of transient alumina phases could not occur at temperatures $\leq 220^\circ$C in both basic and acidic atmospheres under a saturated water vapour pressure, even after the addition of seeds of $\alpha$-alumina to the initial precipitate.

Comparing the results from both basic and acidic hydrothermal routes revealed that by adding $\alpha$-alumina particles as seeds under similar conditions, crystalline boehmite was the only phase formed using the basic route along with traces of $\alpha$-alumina in the case of seeded samples, whilst pure $\alpha$-alumina phase could be observed via the acidic route by adding 4 wt% $\alpha$-alumina seeds. However it is believed that the resulting $\alpha$-alumina phase could be mainly just the $\alpha$-alumina powder added to the precursor solution as the seeding powder.

The precipitation method was also used to synthesize ultra-fine $\alpha$-alumina powders from aluminium chloride and ammonia solution. It was shown that by seeding the initial precipitate, the temperature of the $\theta$-$\alpha$ transformation could be lowered to $800^\circ$C. The presence of sufficient amount of seeds have been reported to lower the $\theta \rightarrow \alpha$ transformation temperature, as seeding decreases the activation energy of the nucleation process. The addition 10 wt% of a mixture of two surfactants to the precipitate led to less agglomeration and a higher fraction of $\alpha$ phase in the powders heat treated at temperatures as low as $800^\circ$C by modifying both the surface of the primary particles and also the seed particles added to the precipitate.
By introducing a very short high-temperature step to the conventional heat treatment process, both seeded and surfactant-added samples entirely transformed into $\alpha$-alumina powder with ultra-fine mean particle size. Based on the results presented, it was suggested that the newly developed calcinations route (1200°C-800°C/12 h) of an in-situ seeding step, followed by conventional nucleation and growth stage. It was also found that using only one of the previously used surfactants (Tween 80 and $\beta$-alanine) resulted in nanosized powder of $\alpha$-alumina with mean particle size of $\sim$20 nm and low level of agglomeration.

For the processing of nanostructured bodies, the experiments were started with preparing suspensions using the synthesised powder. As the suspensions prepared with no additives were not stable, three different anionic ammonium-based dispersants were investigated. The ammonium salt of polymethacrylic acid (PMMA-NH$_3$) was found to be an effective dispersant for nanoalumina, producing suspensions with an intrinsic pH of 9.4 (IEP of pH $\sim$3.7). The suspension containing Dolapix-CE64 was observed to be more stable with higher zeta potential value at the intrinsic pH of the suspension. It was also shown that by modifying the pH of the suspension to $\sim$9.9 using ammonia solution the rheology behaviour could be improved.

Slip casting parameters were optimised for the preparation of green bodies from high solid content, low viscosity alumina suspensions. The optimum solid content was found to be $\sim$60 wt%. The density of the green bodies was found to be $\sim$53% of theoretical density and it was found out that by ultra-sonicating the suspension prior to casting process, the green microstructure could become more uniform.

Spray freeze drying method was used to produce granules for dry pressing. As the granules prepared by using the previously optimised suspension did not show good flowability due to their rough surfaces, a binder (PVA) was added to the suspension before the spray freeze drying. It has also been found that combining the spray freeze drying method with the addition of a foaming agent can yield granulated powder with higher crushability, which led to more uniform green microstructure. The density of the green bodies achieved by compacting the Freon-added granulated powder at 380 MPa was $\sim$51.8 % theoretical density.

For the processing of submicron bodies, the experiments were started with characterizing the as-received suspension followed by spray freeze drying process to
obtain a suitable powder for dry pressing. Using two different forming methods, slip casting and dry pressing, green bodies with densities higher than 50% of theoretical were prepared. The density of the slip cast green compacts was found to be \(~53.5\)% of theoretical, which was higher than that of the samples prepared by dry pressing at \(~51.5\)%.

Both single and two-step sintering experiments were conducted to achieve highly dense alumina ceramics, while retaining a mean grain size of \(<100\) nm. Green bodies could be sintered to densities of \(~99\)% theoretical by single-step sintering at high temperatures as \(1550^\circ\)C, but with a huge amount of grain growth due to the existence of hard agglomerates.

Using the two-step sintering route led to roughly similar results as the single-step sintering cycles. To reduce the final grain size of the alumina compacts during the two-step sintering, green bodies of higher densities with low level of agglomeration are required, which results in further lowering the temperatures of the first stage of sintering. This can be achieved both by improving the suspension preparation process in order to decrease the level of agglomeration in the suspension and the forming process of the green bodies. Thus further grain size reduction can be achieved by increasing the green density. The increased green density will enable the first stage sintering to be carried out at lower temperatures leading to finer grain size.

In the case of submicron alumina, unlike the previous work by Chen and Wang \(^{126}\), mentioned in chapter 3, the two-stage method did not completely restrain the final-stage grain growth, although it still resulted in much smaller average grain size than in conventional route. Similar to the nanoalumina bodies, using green compacts of higher densities was suggested in the case of submicrometer alumina bodies, to affect the grain growth during the sintering process. So overall it was concluded that nanoalumina ceramics could not be sintered to high densities with restrained grain growth even by using two-step sintering method, unlike the sub-micrometer alumina ceramics; the microstructure of these samples was not completely frozen during the second stage of sintering. Therefore, using pressure-assisted sintering methods such as hot pressing, hot isostatic pressing or spark-plasma sintering was suggested, which can lead to dense nanostructured alumina ceramics by applying pressure at lower temperatures than pressureless sintering.
In order to obtain full dense alumina ceramics with ultrafine grain size, spark plasma sintering technique was used using the as-synthesised nanoalumina powder, which led to compacts with high relative density of ~99.9 at 1400°C/70 MPa and 1200°C/500 MPa. However due to the presence of agglomerates in the starting powder, excessive grain growth and large final grain size was observed in these samples, 6.2 μm and 0.6 μm, respectively for S70-14 and S500-12. Using alumina bodies prepared by both wet and dry routes and pre-sintered to relative density of ~95% to be further sintered by SPS or hot press can be a solution to this issue.
6. Future Work

6.1. Synthesis

From the hydrothermal synthesis experiments it was found that in order to obtain α-alumina powder via hydrothermal method at low pressures, treatments at temperatures as high as 380°C and over need to be investigated. The formation of α-alumina can also be studied by using a non-aqueous solution; this method is termed as solvothermal synthesis route and seems to show some new characteristics, because of the differences between the solvents. To our knowledge no studies on the solvothermal synthesis of α-alumina nanopowder have been reported.

The new two-step calcination process can be extended to other ceramic nanopowders such as yttria stabilized zirconia (YSZ), yttrium aluminium garnet (YAG) and possibly many more ceramic powders.

6.2. Processing

From the conventional single and two-step sintering studies it was found that these pressureless sintering routes could not lead to high densities whilst retaining the intrinsic nanostructure of the green bodies due to the requirement of elevated temperatures. However, further investigation can be carried out on production of green bodies with higher densities and lower amount of agglomerates by improving both suspension preparation process and forming methods. This can reduce the temperature of the first stage during the two-stage sintering process, which leads to finer final mean grain size.

To achieve densities close to the theoretical density of α-alumina along with nanostructures as fine as possible pressure-assisted techniques such as hot pressing or hot isostatic pressing and also Field assisted sintering techniques such as spark plasma sintering (SPS) can be used. Using the as-synthesised nanoalumina powder for SPS experiments led to oversized powder and exaggerated grain growth particularly under low pressures due to the existence of agglomerates in the nanopowder. Therefore alumina compacts formed and pre-sintered to densities of ~95% of relative density prior to SPS experiment can be used in the future to restrain the grain growth.
Mechanical properties of the future fully dense sintered compacts including hardness, toughness and strength can be measured and compared to the submicrometer alumina bodies; this will require the preparation and testing of a large number of samples.
References


32. Anonymous "Alumina crystal structures,"


46. D. Richerson, Modern ceramic engineering: properties, processing, and use in design; CRC, 2005.


Conferences Attended:

- **Summer 2010-2013** Departmental research day - Materials dept of Loughborough University, UK
- **March 2012** Research conference: Research that matters - Loughborough University, UK
- **June 2011** ECERS 12th conference of the European ceramic society - Stockholm, Sweden

List of Publication:

- Synthesis of nano $\alpha$-alumina powders using hydrothermal and precipitation routes: a comparative study
  
  *Published online, International Ceramics journal*

- Synthesis of $\alpha$-alumina nanopowders with controlled particle size
  
  *To be protected as a patent, currently in scale up progress*

- Colloidal processing of nanosized $\alpha$-alumina powders
  
  *Written, under review*