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Synthesis of nano α-alumina powders using hydrothermal and precipitation routes: a comparative study

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Abstract

Two different synthesis methods, viz. precipitation and hydrothermal treatment, were used to synthesise ultra-fine α-alumina powders from aluminium chloride, ammonia solution and TEAH (tetraethyl ammonium hydroxide). XRD, BET surface area analysis, TEM and FEG-SEM were used to characterise the powders produced. The presence of industrial α-alumina powder as seed particles did not affect the transformation to α-alumina phase during the hydrothermal treatment at 220 °C, either in basic or acidic environments. The results obtained from the precipitation route, however, showed that the combined effect of adding α-alumina seeds and surfactants to the precursor solution could lower the transformation temperature of α-alumina from about 1200 °C for unseeded samples to about 800 °C, as well as reducing the level of agglomeration in the alumina powders. The difference in transformation temperature mainly results from the nucleation process caused by the α-alumina seeds, which enhanced the $\theta \rightarrow \alpha$ transformation kinetics. The lower level of agglomeration present in the final powders could be due to a surface modifying role of the surfactants, preventing the particles from coalescing during the synthesis process.

Keywords: Nanoparticle; Al_2O_3; Hydrothermal; Precipitation

1. Introduction

Alumina ceramics have found various technological applications as high-strength materials and in electronics and catalysts because of their distinctive combination of physico-chemical properties including hardness, resistance to aggressive media, refractoriness and electrical and thermal insulation [1,2]. In recent years, increasing attention has been focused on the development of alumina powders with particle sizes at the nanoscale for advanced engineering applications such as transparent armours for ballistic performance [3,4].

Reducing the dimensions of a particulate material from microscale to nanoscale leads to considerable changes, both in the physical properties, such as electronic conductivity and optical absorption, and the mechanical properties since a much greater fraction of the atoms are located on the surfaces of the particles [5]. Nano-sized powders have an extremely high surface area, resulting in changes in both surface energy and surface morphology. These parameters then alter the basic properties and the chemical reactivity of the nanomaterials [6]. For instance, some nanocrystalline ceramics have demonstrated superplastic behaviour at elevated temperatures, enabling these ceramics to undergo up to 300% elongation before failure [6]. They have also been used as solid state bonding agents for joining large-grained commercial ceramics together at moderate temperatures because of having many short-circuit diffusion paths as a result of the high fraction of grain boundaries [7]. There are indications that nanoceramics could have extremely low thermal conductivity due to phonon scattering caused by the grain boundaries [8,9].

The formation of α-alumina occurs at temperatures as high as 1200 °C after a series of polymorphic transformations, including γ-alumina → δ-alumina → θ-alumina → α-alumina, upon heating. The α-nuclei form within the θ-alumina matrix at low temperatures and then grow rapidly to produce α-alumina colonies in the form of a porous network. The $\gamma \rightarrow \delta \rightarrow \theta$ transformations are both displacive [10,11] and have

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fairly low activation energies. However θ→α is a reconstructive transformation with high activation energy and proceeds through a nucleation and growth process [12]. Most of the activation energy for this transformation is required for the nucleation part of the process; hence temperatures up to 1200 °C are required [12]. This inevitably leads to a considerable degree of particle coarsening. The resulting, heavily aggregated, α-alumina powders then need to be mechanically milled and sintered at temperatures as high as 1600 °C in order to achieve densities near to theoretical [13,14], which results in further coarsening and grain growth. Therefore, achieving a reduction in the θ→α transformation temperature is a key requirement of forming nanostructured α-alumina powder.

Powders of α-alumina can be synthesised by several well-established synthesis methods, such as the Bayer process, sol–gel, precipitation and hydrothermal treatment [5]. However, as indicated above, with most of these methods temperatures above 1200 °C are required to produce the final crystalline α-alumina phase. The exceptions require calcinations in specific atmospheres such as hydrogen halide [15], which raises costs. A number of researchers have attempted to use seeding to increase the kinetics of the θ→α transformation and, hence, to control the development of the α-phase [13,16–19]. Kumagai and Messing [17,20] reported that by introducing α-alumina seed to boehmite gels, both the kinetics of the transformation and the microstructure of the final product could be improved. These seeded gels could be sintered to almost full density at only 1200 °C. Dynys and Halloran [12] studied the effects of introducing metal oxides such as MgO, Cr_2O_3 and Fe_2O_3 via water-soluble salts to boehmite. The results illustrated that addition of Fe_2O_3 increased the kinetics of the phase transformation to α-alumina, whereas the other oxides had no effect. Li and Sun [13] investigated the effect of the presence of ammonium nitrate (a by-product of the precipitation of aluminium nitrate and ammonia solution) and α-alumina seeding on the transformation temperature to the α-phase. It was shown that addition of 5 wt% α-alumina seeds and 44 wt% ammonium nitrate could lower the temperature of the transition from around 1200 °C to 900 °C and the final α-alumina powder had a mean particle size of ~10 nm, though it also contained the much larger seeds.

Hydrothermal synthesis is an attractive environmental friendly alternative to the approaches mentioned earlier, with the advantage of being a single-step, low energy consumption process with no need for high-temperature calcination and extensive milling [21]. Further advantages include high chemical and phase purity, low aggregation level and narrow crystallite size distribution for the resulting material, in addition to excellent control of particle morphology [1]. It is possible to produce a wide range of particle shapes, both equiaxed, such as cubes, spheres, diamonds and bipyramids, and elongated morphologies, such as fibres, whiskers, nanorods, nanotubes and also platelets, nanoribbons, nanobelts, etc. The particle size can also range from a few nanometers to large single crystals [2,22–27].

The phase relationships in the Al_2O_3–H_2O system, which were established initially by Laubengayer and Weisz [28] and subsequently studied by several other investigators such as Ervin and Osborn [29] and Kennedy [30,31], Fig. 1, revealed the presence of four phases in the temperature range of 0–500 °C and pressure range of 1–100 MPa. These phases include gibbsite $Al(OH)_3$, boehmite γ-AlOOH, diaspore α-AlOOH and α-alumina. By increasing the temperature under hydrothermal conditions, boehmite transforms either directly into the α-alumina phase at 380 °C and pressures between 1–15 MPa or into the intermediate diaspore phase from 210 °C and then into α-alumina from 360 °C at higher pressures, without forming transition aluminas. The following reactions occur under hydrothermal conditions at pressures in the range of 1–15 MPa [1]:

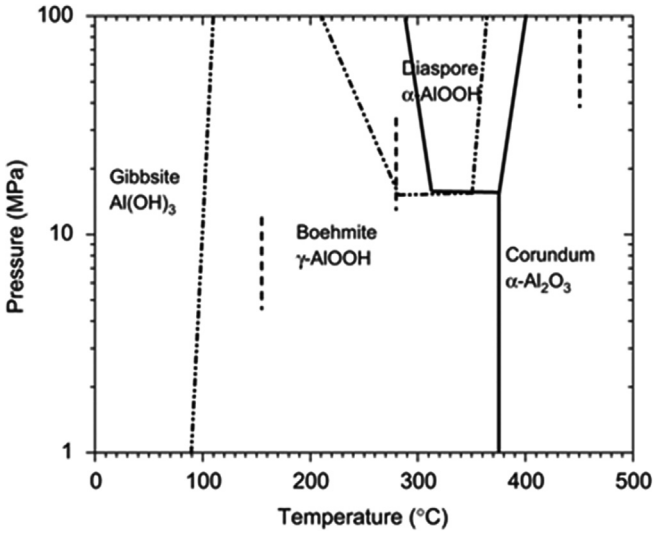

Fig. 1. Hydrothermal Al_2O_3–H_2O phase diagram from [1] with permission © 2009, The American Ceramic Society.

$$Al(OH)_3 \rightarrow \gamma\text{-}AlOOH + H_2O \text{ at } \sim 100\ ^\circ C \quad (1)$$

$$2\gamma\text{-}AlOOH \rightarrow \alpha\text{-}Al_2O_3 + H_2O \text{ at } \sim 380\ ^\circ C \quad (2)$$

A number of researchers have attempted to reduce the phase formation temperature of the α-alumina phase to < 380 °C by adding seeds to increase the kinetics of the α-alumina transformation and control the development of the desired α-phase [1,2,27]. Sharma and co-workers [2] reported the synthesis of α-alumina with a small amount of boehmite by using 4 wt% of seed with respect to the Al_2O_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 was also used during the precipitation of precursors in this work in order to reduce the surface free energy of the initial particles. Characterisation showed that the synthesised α-alumina particles were about 60 nm in size with a surface area of 245 $m^2\ g^{-1}$. Hydrothermal synthesis of fine α-alumina powders using seeds in an acidic environment at 200 °C was investigated by Yang et al. [27]. The results illustrated that α-alumina powders with a maximum crystallite size of 32 nm (calculated by the Scherrer formula) could be obtained by adding 4 wt% seed relative to the amount of the starting aluminium salt.