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Novel synthesis of Al_2O_3 nano-particles by flame spray pyrolysis

A.I.Y. Tok *, F.Y.C. Boey, X.L Zhao

School of Materials Science & Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

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Abstract

This paper reports on a novel, inexpensive, flame spray pyrolysis method to synthesize agglomerate-free nano-sized Al_2O_3 particles with a size range of 5–30 nm. The precursors and the resultant oxide powders were characterized by chemical analysis, X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis and transmission electron microscopy (TEM). The novel flame spray pyrolysis method successfully synthesized nano-sized Al_2O_3 of about 5–30 nm (α-phase + γ-phase), and 80–100 nm (α-phase, calcined) from $AlCl_3$ vapour.

Keywords: Al_2O_3; Synthesis; Nano-particles; Calcination

1. Introduction

Aluminium oxide (alumina, Al_2O_3) is currently one of the most useful oxide ceramics, as it has been used in many fields of engineering such as coatings, heat-resistant materials, abrasive grains, cutting materials and advanced ceramics. This is because alumina is hard, highly resistant towards bases and acids, allows very high temperature applications and has excellent wear resistance [1–2]. Annual demand for alumina has been growing steadily. From an annual production of 38 million tonnes in 1995, its demand is expected to reach 667 million tonnes by the year 2005 [3–4].

Nanotechnology has become a key area in the development of science and engineering [5]. Nanotechnology basically involves the production or application of materials that have unit sizes of about 10–100 nm. Comparing micron-sized and nano-sized alumina particles, nano-alumina has many advantages. A smaller particle size would provide a much larger surface area for molecular collisions and therefore increase the rate of reaction, making it a better catalyst and reactant. Finer abrasive grains would enable finer polishing, and this would also give rise to new applications areas like nano-machining and nano-probes. In terms of coatings, the use of nano-sized alumina particles would significantly increase the quality and reproducibility of these coatings [6].

There are several methods to synthesize nano-alumina [7–10], and these are categorized into physical and chemical methods. Physical methods include mechanical milling, laser ablation, flame spray and thermal decomposition in plasma. Chemical methods include sol–gel processing, solution combustion decomposition and vapour deposition. Most of the chemical methods have resulted in extremely low yield rates, and thus cannot be adapted to mass manufacturing. Physical methods like mechanical milling are not efficient as the size of the nano-particles cannot be easily controlled, and these methods are only limited to certain materials. Other methods such as laser ablation, vapour deposition and sol–gel are very costly as they require specialized equipment such as vacuum systems, high power lasers as well as expensive precursor chemicals. Finally, most systems are only possible for a specific range of materials.

This papers reports on a novel flame spray pyrolysis method to produce nano-sized alumina particles using gas and aqueous precursors. This method has many advantages over the other methods as it is low-cost, easy to control particle size, simple processing, high production yield, and ease of conversion to mass manufacturing [11]. In this process, a high temperature flame is used to heat the feedstock material as well as spray it into a condensation chamber, where it will condense as nano-sized particles.

2. Experimental procedure

2.1. Precursor synthesis

A commercial anhydrous $AlCl_3$ powder (purity 99.6%) from Mark, Germany was used as the starting material. Fig. 1 presents a schematic illustration of the

* Corresponding author. Tel.: +65 67 904 935; fax: +65 67 904 935.
E-mail address: miytok@ntu.edu.sg (A.I.Y. Tok).

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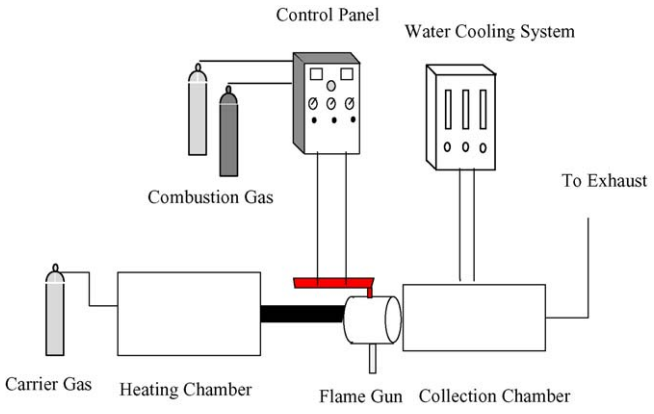

Fig. 1. Schematic diagram of the flame spray pyrolysis apparatus.

flame spray pyrolysis (FSP) apparatus used to prepare the Al_2O_3 nano-particles. The apparatus consists of an in-house manufactured heating chamber, a flame gun (PG-550, Praxair Surface Technologies, USA), an in-house manufactured powder combustion and collection reactor with water cooling system and an exhaust gas system. The PG-550 spray gun, which is mounted at the front of a collection reactor, was operated with acetylene (65 PSI) and oxygen (70 PSI). The anhydrous $AlCl_3$ powders were injected into the flame gun using the heating chamber at 300 °C by means of nitrogen gas and were directly sprayed into the collection chamber. Combustion occurred at less than 2000 °C. In order to remove residual water and obtain fully crystallized particles with small particle size, the as-sprayed Al_2O_3 nano-particles were calcined at 1100 °C for 2 h using a heating rate of 10 °C min^{-1}. Cooling rate was set to 50 °C min^{-1} to reduce the possibility of agglomeration of nano-alumina powders.

2.2. Characterization

The flame-sprayed and calcined nano-particles were characterized using various methods.

2.2.1. Gas sorption

Measurement of specific surface area was conducted using a sorption analyzer (Model ASAP 2000, Norcross, GA) at 196 °C with nitrogen as the adsorbed gas. The samples were degassed at 110 °C for 4 h, and the temperature was then increased to 400 °C until the outgas rate was less than 5 mm Hg min^{-1}. Specific surface area was calculated using Brunauer–Emmett–Teller (BET) method.

$$D_{\mathrm{BET}} = \frac{6 \times 103}{d_{\mathrm{th}} S_{\mathrm{BET}}} \quad (1)$$

where D_{BET} is the average diameter of the particles, d_{th} the theoretical density of the material and S_{BET} is the surface area measured in $m^2\ g^{-1}$.

2.2.2. Differential thermal analysis

A Netzsch Model DSC 404 differential scanning calorimeter (DSC) was used to determine the nano-particle reaction behaviour. The measurements (about 50 mg $AlCl_3$) were performed using Al_2O_3 crucibles in flowing air, with a heating rate of 10 °C min^{-1} used to heat the samples to 1300 °C.

2.2.3. X-ray diffraction

Phase composition of the flame-sprayed nano-particles and calcined nano-particles were determined using X-ray diffraction (Rigaku 6000, Tokyo, Japan), using Cu Kα radiation at 50 kV and 20 mA. Scans were measured over a 2θ range from 20° to 80° at a scan rate of 4° min^{-1} using increments of 0.05° 2θ. The peak positions and relatively intensities of the powder pattern were identified by comparison with powder diffraction file (PDF) data. Calculation on the diameter of particles was based on Scherrer's equation:

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos\theta} \quad (2)$$

where D_{hkl} is the size of the particles, λ the wavelength of the X-ray and β_{hkl} is the width of the base of diffraction line at half its maximum intensity.

In Eq. (2), we assumed that the particles were perfectly spherical. The two highest peaks (1 0 0) and (4 0 0) in the XRD patterns were chosen to calculate the size of the nano-particles.

2.2.4. Transmission electron microscopy

TEM studies were performed using a JEOL (JEM-2010F, Tokyo, Japan) TEM (accelerating voltage 200 kV) equipped with a parallel electron energy loss spectrometer (PEELS Model 666, Gatan, Pleasanton, CA) and a double tilt specimen holder cooled with liquid nitrogen (Model 636, Gatan). Samples were prepared for TEM analysis by dipping a porous coated carbon copper grid from an ultrasonic dispersion of the as-processed powders mixed with alcohol.

3. Results and discussion

There are three important aspects to flame spray pyrolysis: aerosol production, combustion and powder collection. Although it seems that these processes are independent, they are actually inter-related. For example, incomplete combustion occurs when large droplets are injected into the combustion zone, resulting in porous particles akin to those produced via spray pyrolysis [12].

Fig. 2 shows the DSC curve of the anhydrous $AlCl_3$ powders. It can be seen that there was a broad endothermic peak at about 183 °C, measuring 306.3 J g^{-1}. This represents the boiling point of the anhydrous $AlCl_3$ powders. Therefore, in order to obtain the $AlCl_3$ vapour in this experiment, anhydrous $AlCl_3$ was directly heated up to 300 °C before it was carried out into the flame gun with nitrogen. In addition, a small exothermic peak was also observed at 760 °C, measuring 107.6 J g^{-1}. This represents the phase transformation of γ-Al_2O_3 to α-Al_2O_3. In order to fully convert the γ-Al_2O_3 to α-Al_2O_3, the as-sprayed nano-particles had to be calcined at above 1000 °C

XRD studies were also conducted to trace the conversion of γ-Al_2O_3 to α-Al_2O_3. Fig. 3 shows the XRD pattern of the flame-sprayed nano-particles, while Fig. 4 shows the XRD pattern of the calcined nano-particles. It can be seen from Fig. 3 that both α-phase and γ-phase Al_2O_3 were found in the as-sprayed nano-particles. In order to obtain the stable α-phase with non-agglomerated powders, calcination was performed at different temperature with different holding time. The results showed that complete phase transformation to α-phase alumina was obtained after calcination at 1100 °C for 2 h.

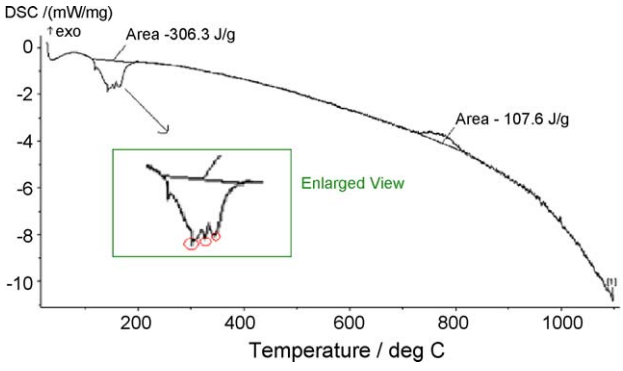

Fig. 2. DSC analysis of anhydrous $AlCl_3$ powder.

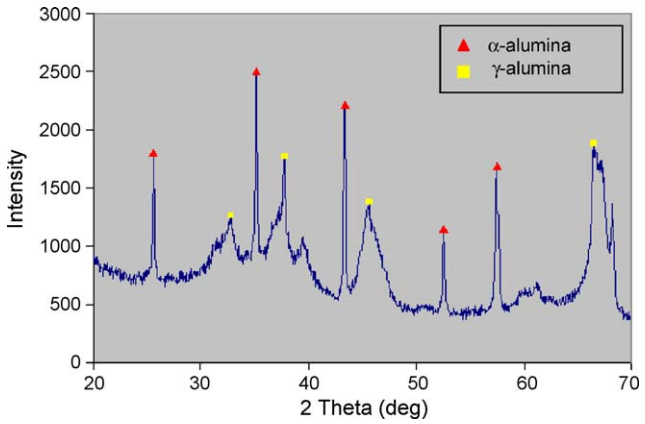

Fig. 3. XRD Pattern of as-sprayed alumina nano-particles.

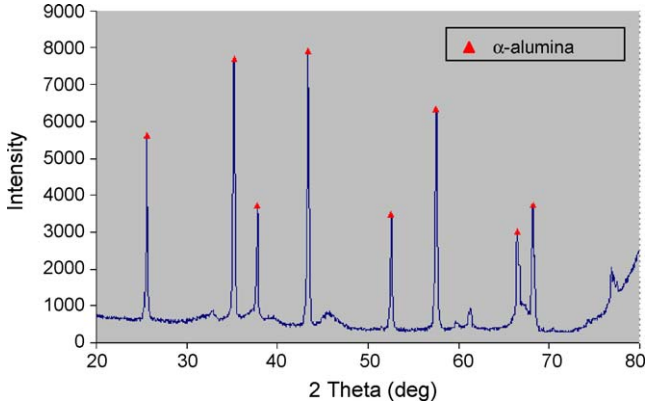

Fig. 4. XRD pattern of alumina nano-particles calcined at 1100 °C for 2 h.

Table 1 list the nano-particles size calcalated using Eq. (2) with XRD data. Calculations showed that the γ-phase Al_2O_3 had an average grain size of about 10 nm, and the α-phase Al_2O_3 had an average grain size of about 28 nm.

Figs. 5 and 6 show the TEM micrographs of the as-sprayed nano-particles and the calcined nano-particles respectively. It can be seen in Fig. 5 that the particle size of the as-sprayed nano-particles ranged from 10 to 30 nm. This result agrees well with BET measurements ($S_{BET} = 120\,m^2\,g^{-1}$, $d_{th} = 3.98\,g\,(cm^3)^{-1}$), as the average diameter calculated by Eq. (1) was 14.25 nm. It can also be observed that the nano-particles were generally spherical. Some agglomeration was present, and this was attributed to the large surface area of these nano-particles.

The appearance of the two phases γ-Al_2O_3 and α-Al_2O_3 in the XRD and TEM analyses may indicate that two particle formation mechanisms are present. γ-Al_2O_3 particles with size below 10 nm was formed by precursor evaporation and subsequent higher cooling rate solidification. α-Al_2O_3 particles with size above 25 nm was formed by precursor evaporation

Table 1
Particle size of flame-sprayed alumina nano-particles

Phase	2θ (°)	β_{hkl} (rad)	D_{hkl} (nm)
α-Alumina	43.35	0.306	27.94
γ-Alumina	45.65	0.871	9.89

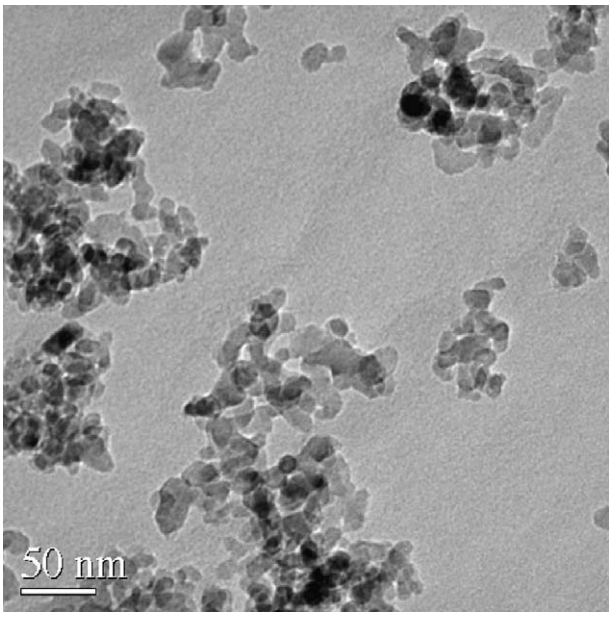

Fig. 5. TEM micrograph of as-sprayed alumina nano-particles.

and subsequent gas-phase reaction, alumina nucleation, surface growth, coagulation, and partial sintering. Therefore, the size of α-Al_2O_3 particles was smaller than that of the γ-phase Al_2O_3 in as-sprayed powders calculated in Table 1.

In addition, the calcined nano-particles in Fig. 6 show a particle size range of about 50–100 nm. Therefore, only three and four grains of as-sprayed powders were grown into one α-phase Al_2O_3 particle after calcination. This was also in good agreement with BET calculations, which showed a surface area of about $40\,m^2\,g^{-1}$. It can be seen in Fig. 6 that the nano-particles become more spherical after calcination. The structural advantage of the highly crystalline flame-sprayed alumina nano-particles may be due to it distinct primary α-Al_2O_3 particles, which account for

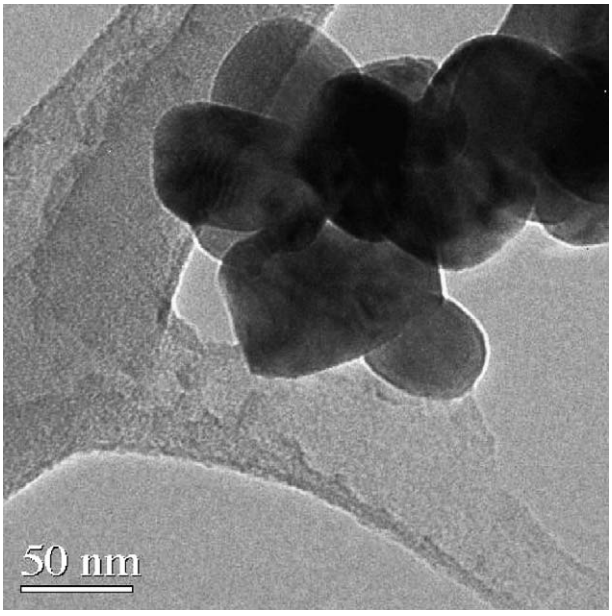

Fig. 6. TEM of alumina nano-particles calcined at 1100 °C for 2 h.

about 40 vol.% calculated from XRD results in Fig. 3, and grain growth only occurred at 1100 °C during the phase transformation from the smaller γ-Al_2O_3 phase powders as shown in Fig. 5.

Comparing the flame spray method to precipitation processing (production rate is about 50–60 kg month^{-1}) commonly used in research and industry [6,8,9], the flame spray method has shown superiority in allowing closely controlled characteristics, high specific surface areas, and a high production rate of up to 10 kg h^{-1}.

4. Conclusion

The novel flame spray pyrolysis method has successfully produced nano-sized Al_2O_3 of about 10–30 nm (α-phase + γ-phase), and 80–100 nm (α-phase, calcined) from $AlCl_3$ vapour. Based on XRD results, the as-sprayed nano-particles consisted of α-phase and γ-phase Al_2O_3, which can be converted to α-phase by calcination at 1100 °C for 2 h. The particle size of calcined powders was about 80–100 nm.

Although this work focused on the synthesis of Al_2O_3 nano-particles, it can be seen that this method has the flexibility of easily producing other nano-particles by flame spraying other metal chlorides that have a low boiling point.

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