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# Synthesis of spherical $Al_2O_3$ and AlN powder from C@$Al_2O_3$ composite powder

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**Abstract** A novel approach has been taken to produce (1) spherical $Al_2O_3$ particles by decarbonisation and (2) spherical AlN particles by nitridation and subsequent decarbonisation of C@$Al_2O_3$ composite particles. C@$Al_2O_3$ composite particles have been prepared by heterogeneous nucleation and crystallisation of $Al(NO_3)_3$ on surfactant encapsulated carbon nano particles followed by evaporative decomposition of the nitrate. Overpressure (0.4 MPa) of nitrogen and a temperature range (1723–1873 K) have been used for nitridation. Whiskers as well as spherical particles of AlN have been observed in the final product. The final product has been characterised by X-Ray Diffraction, Scanning Electron Microscope and Carbon–Hydrogen–Nitrogen content analysis by Elemental Analyser and the mechanism of the nitridation reaction has been analysed. The average size of the spherical AlN particles consisting of crystallites in nano-dimensions (30–50 nm) could be varied from 100 nm to 8 μm by changing the composition of the sol.

## Introduction

Aluminum nitride (AlN) powders are of interest for the manufacture of ceramic components for use in electronics, refractory etc. since it is a very good heat conductor and at the same time a good electrical insulator. AlN has excellent oxidation and thermal shock resistance and it can be made optically transparent and translucent if it is of high purity and density [1]. It has attracted much attention as a high thermal conductivity ceramic substrate. Its thermal conductivity is affected with the purity of the starting powder. Oxygen has especially marked influence on thermal conductivity [2, 3]. The presence of oxygen as impurity in crystal lattices deteriorates the thermal conductivity of the dense material. The development of high purity powder is, therefore, very important for achieving better properties. Several methods have been tried for synthesizing AlN powder. These are carbothermal nitridation of $Al_2O_3$ [4–9]; direct nitridation of aluminum [10]; fluoride decomposition [11]; reaction between high purity aluminum and nitrogen gas under a DC arc [12]; decomposition of poly(isopropyliminoalane) under Ar and $NH_3/N_2$ atmosphere [13]; melting metallic aluminum and $AlCl_3(NH_3)$ together in Ar atmosphere at low temperature followed by reaction in presence of hydrogen and then introduction of ammonia at much higher temperature [14] and reaction of different $Al_2O_3$ precursors with $NH_3$ [15]. Advantages of carbothermal reaction are the cost effective production of comparatively pure powder with fine particles. Fineness of the particles is a requisite for its good sinterability. Carbothermal reaction of $Al_2O_3$ to form AlN involves intimate mixing of aluminum oxide with carbon. Several methods such as sol–gel process of mixing carbon source material consisting of organic carbon source and carbon powder to the sol of boehmite [16]; decomposition of sucrose coated on several aluminum oxides ($\alpha$-$Al_2O_3$, $\theta$-$Al_2O_3$ & AlOOH) [17]; etc., have been tried for homogenisation. The overall carbothermal reaction is given by the reaction,

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g) \qquad (1)$$

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Although the stoichiometric ratio of C: $Al_2O_3$ in this reaction is 3:1, higher ratios (25.5:1) are necessary for full conversion of $Al_2O_3$ to AlN [4–9]. It is believed that the need for excess carbon for full conversion of $Al_2O_3$ to AlN arises out of agglomeration of the precursor powder during processing and resulting in an imperfect mixing. Excess carbon is usually eliminated by burning at 873–1073 K in dry air after the carbothermal reaction [4–9]. Still there is a chance of unconverted $Al_2O_3$ being present in the final product, which will ultimately increase the oxygen content of the material. Increase in Oxygen content can also be due to some oxidation occurring during burning out of Carbon. Therefore, Carbon particles coated with $Al_2O_3$ should be better alternative for synthesis of AlN particles than the vice versa.

Porous and hollow oxide particles like $Al_2O_3$ and $TiO_2$ have wide applications as catalyst media because of their high surface area. Many studies [18–20] have been made to produce spherical oxide particles such as $Al_2O_3$, $TiO_2$, $SiO_2$ particles coated with CdS, etc. by stabilisation of colloid particles precipitated from their precursors in aqueous or non-aqueous media or using oil/water emulsion template. Stabilisation of the particles has been achieved by electrostatic or steric means. Hollow spheres of $TiO_2$ have been produced [18] from composite particles of polystyrene coated with $TiO_2$. $SiO_2$ particles coated with CdS have been synthesised [19] by heterocoagulation technique. Hollow spheres of $Al_2O_3$ has been produced [20] by heterogeneous precipitation of $Al(OH)_3$ on enzyme catalysed hydrolysis of Al-salt. Considering the importance of these spherical powders efforts have been made in the present study to prepare them at a reduced cost using water as the dispersion media. In the rest of the article the composite particles or powders having a core shell configuration where the shell is $Al_2O_3$ and the core is Carbon is designated as C@$Al_2O_3$ following a terminology earlier used [19] to represent a composite core shell structure by C1@C2 where C1 is the core material and C2 is the shell.

In the present study a novel approach has been taken to produce C@$Al_2O_3$ particles by coating polymer encapsulated carbon black particles/agglomerates with $Al(NO_3)_3$ in water and subsequent decomposition of the nitrate to produce $Al_2O_3$ after calcinations. These composite particles are produced to obtain AlN particles after nitridation. Characterisation of the particles has been made with Scanning Electron Micrograph (SEM), Particle Size Analyser by Light Scattering, Thermo Gravimetric Analysis and Differential Thermal Analysis, (TG/DTA) Carbon–Hydrogen–Nitrogen Elemental Analyser (CHN Analyser) and X-Ray Diffraction (XRD). Adsorption studies have been carried out to understand the mechanism of formation of the composite particles.

## Experimental procedure

The specifications of the raw materials used are presented in Table 1. The detailed process has also been described in an earlier patent [21].

### Synthesis of C@$Al_2O_3$ composite particles

A stable carbon sol has been prepared by adding fixed amount of carbon particles in an aqueous solution of non-ionic surfactant and then adding slowly an aqueous solution of $Al(NO_3)_3$ (2.8 M $L^{-1}$). Polyoxyethylene (20)sorbitanmonooleate (Tween 80) has been chosen as the nonionic surfactant for the purpose. The quantity of $Al(NO_3)_3$ in the sol and the total volume of the sol have been kept constant (200 mL) in all the cases. The sol was sonicated with an ultrasonic probe (20 kHz) for 5 min. The carbon sol was first dried with magnetic stirring on a hot plate and the dried mass was then taken in a siliminite boat and inserted in a SiC heated furnace under ambient

**Table 1** Specifications of raw materials as per manufacturers' data

| Name of raw materials (Manufacturers) | Impurity content | Surface area $m^2$ $g^{-1}$ | Particle size |
|---|---|---|---|
| C-black (N-110 Garde, Phillips Carbon Black Industries, India) | – | 142 | 11 nm |
| $Al(NO_3)_3{\cdot}9H_2O$ (SQ Grade, Qualigen Fine Chemicals, India) | Chloride (Cl) 0.01%, Sulphate ($SO_4$) 0.01%, Iron (Fe) 0.02%, Potassium (K) 0.025% and Sodium (Na) 0.025% | – | – |
| $Al_2O_3$ (HP Grade, ACC, India) | $SiO_2$ 200 ppm, $Fe_2O_3$ 100 ppm, $Na_2O$ 700 ppm, CaO 800 ppm, LOI 0.51 | 12.4 | 0.61 $\mu$ |
| $H_2O$ (Eco Still Mark 1500 SQD, Qualigens Fine Chemicals, India) | Conductivity-1 $\mu$ Siemens $cm^{-1}$ | – | – |
| $N_2$ (XL Grade, BOC India) | Oxygen-10 ppm, Argon-2 ppm | – | – |
| Tween 80 (Aldrich Chemicals, USA) | N/A | – | – |

atmosphere. The temperature was increased slowly from room temperature to 673 K (1 K $min^{-1}$) and kept for 1 h at the same temperature. The decomposition temperature (673 K) was determined from the TG/DTA analysis. The exhaust gas was passed through water for absorption of $NO_x$ gas before venting out in atmosphere.

### Synthesis of spherical $Al_2O_3$ powder

Decarbonisation of the C@$Al_2O_3$ composite powder has been carried out by calcinations at 973 K in ambient atmosphere for 2 h for 1 g of starting composite powder taken in an $Al_2O_3$ boat. A white residue has been obtained. The residue has been characterised by X-ray Diffraction and Scanning Electron microscope. Weight loss of the powder has also been checked to see the amount of decarbonisation of the powder.

### Synthesis of AlN powder

Nitridation of the composite C@$Al_2O_3$ powder has been carried out in a graphite heated furnace (Thermal Technology, USA) in presence of flowing nitrogen at three different temperatures (1723, 1773, and 1873 K) under an overpressure of 0.5 MPa. The reactant mixture consisting of loose porous agglomerates were taken in a graphite crucible and not ground in order to look at the change in morphology and development of microstructure during the whole process. The weight change has been noted after each experiment. After nitridation of the composite powder the product was decarbonised by heating in ambient atmosphere at 973 K for 2 h and the weight change has been noted after each experiment.

### Adsorption studies

Adsorption of $Al(NO_3)_3$ on carbon particles was studied by adding fixed amount of carbon black (5 g) to $Al(NO_3)_3$ solutions of different concentrations in conductivity grade water and shaken in a mechanical shaker for 4 h. The adsorbed amount of $Al(NO_3)_3$ was determined gravimetrically after evaporation to dryness and subsequent decomposition at 1323 K of a fixed amount of clear supernatant obtained after keeping the dispersion for seven days.

In another study similar experiments have been carried out with carbon black sol in water produced by addition of non-ionic surfactant (Tween 80) for comparison.

### Characterisation

Characterisation of the product has been made in the following ways:

(i) Scanning Electron Micrograph (SEM) analyses had been performed in a LEO S430i instrument of Leo Electron Microscope Ltd., UK to look at the morphologies of the particles. In this analysis a drop of the suspension of particles in aqueous medium has been dropped on a glass plate: dried and coated with a conductive layer of gold before introduction into the Microscope to avoid charging under electron beam.

(ii) Particle size analyses had been carried out with a Zetasizer, Malvern Instruments, UK.

(iii) Surface area measurements of the agglomerates had been performed in the Sorpty 1750 instrument of Carbo Erba Strumentazione, Italy.

(iv) X-Ray Diffraction (XRD) analyses had been carried out in X'Pert PRO instrument of Phillips, Holland with Cu-K$\alpha$ radiation ($\lambda$?=1.54056 Å) at 40 kV and 20.0 mA to analyse the phases.

(v) Carbon–Hydrogen–Nitrogen Content Analyses (CHN) of the product powder had been carried out with an Elemental Analyser of Perkin Elmer Instruments, UK. to determine the Carbon, Hydrogen and Nitrogen content of the powder.

(vi) Differential Thermo Gravimetry/Differential Thermal Analysis (DTA/TG) of $Al(NO_3)_3{\cdot}9H_2O$ has been carried out in STA409C instrument of NETZSCH, Germany to find out the decomposition temperature.

## Results and discussion

An extremely stable sol of carbon particles in presence of an electrolyte like $Al(NO_3)_3$ was obtained by incorporating a non-ionic lyophillic surfactant like Tween 80. A minimum amount of surfactant has been determined by carrying out the stability experiments of carbon sol after addition of $Al(NO_3)_3$ to the carbon sol having a fixed amount of carbon content. A typical value of Tween 80 for a 1:2 ($Al_2O_3$: C by wt.) composition and an initial solid loading (5.6% w/w) is 10% w/w with respect to carbon and 1% w/w with respect to the quantity of water. The results of carbon sol stability and adsorption studies show that addition of $Al(NO_3)_3$ to the sol does not cause any adsorption on the surface of the Tween 80 polymer micelles in water medium. However, sufficient adsorption has been noticed when $Al(NO_3)_3$ was added to carbon particles in water and the mixture was shaken for 4 h without addition of the surfactant (Fig. 1). In Fig. 1, *x/m*, the ratio of adsorbed $Al_2O_3$ ($x$) to Carbon content ($m$) has been plotted against the equilibrium concentration of $Al_2O_3$ ($C$, g $L^{-1}$). The concentrations of $Al_2O_3$ was determined from those of $Al(NO_3)_3$ on the assumption that the nitrate gets converted fully to $Al_2O_3$ on

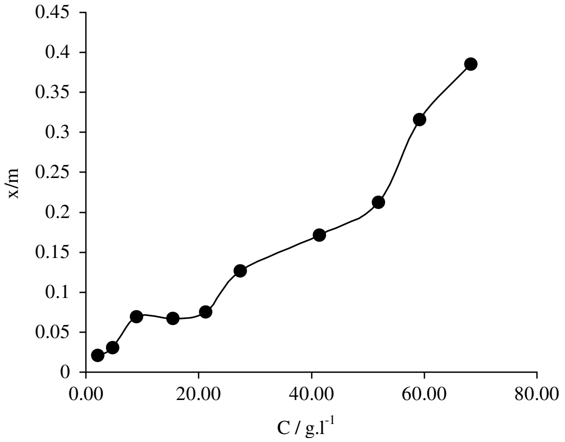

**Fig. 1** Adsorption of $Al(NO_3)_3$ on carbon particles, *x*—amount of adsorbed $Al_2O_3$ in g; *m*—amount of Carbon in g and *C*—the equilibrium concentration of $Al_2O_3$ in g $l^{-1}$ equivalent to $Al(NO_3)_3$ concentration present in the supernatant

decomposition. Increase in floc volume has also been noticed with addition of $Al(NO_3)_3$ (Fig. 2). The floc volume fraction ($V_f$) was determined from the increase in height of the flocculated mass in a graduated cylinder with the increase of $Al(NO_3)_3$ concentration expressed in terms of equivalent $Al_2O_3$ to C weight ratio, *c*.

Carbon particles are known [22] to have negative surface charge and $Al^{3+}$ should be adsorbed on its surface. Tween 80 reaches critical micelle concentration (CMC) at 0.1 mM in aqueous medium [23]. The sizes of these micelles have been determined by light scattering method and the average mean value is 11.2 nm. On addition of carbon black the particle size increases to 354.6 nm. The particles are almost mono-disperse in nature. Increase in particle size points towards either adsorption of carbon particles on the surface of the micelles or agglomeration of the carbon particles within the micelles. Encapsulations of carbon particles by polymer micelles are well known [24]. The absence of adsorption of $Al(NO_3)_3$ on Carbon sol particles produced by treatment with Tween 80 and their corresponding stability prove that an encapsulation process has actually taken place. During concentrating the sol $Al(NO_3)_3$ crystallites have precipitated on the surface of the encapsulated C-agglomerates. Decomposition of $Al(NO_3)_3$ at 623 K produces amorphous alumina as evident from X-Ray Diffraction analysis of the decomposed powder and DTA of $Al(NO_3)_3$. The metal nitrate salts are known [25] to decompose by evaporative decomposition. Amorphous alumina transforms to $\alpha$-$Al_2O_3$ through several intermediates such as $\gamma$, $\theta$, $\delta$ etc on heating. Decarbonisation of the decomposed product at 973 K for 2 h produced spherical white particles (Fig. 3a). X-Ray Diffraction of these particles show that they are $\gamma$-$Al_2O_3$ and no peak of Carbon, originally present, was found. Weight loss data show that Carbon has been removed in the decarbonisation step almost quantitatively.

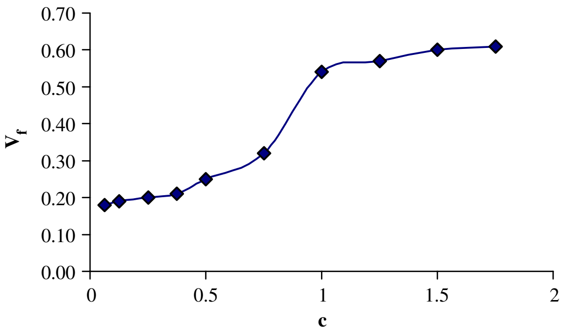

**Fig. 2** Change in volume fraction, $V_f$ of floc with $Al_2O_3$/C weight ratio, *c*

Figure 3(a) shows that surface of the spheres are porous and the average size of them is 10 μm. Decarbonisation of the Carbon black particles adsorbed with $Al(NO_3)_3$ did not produce spherical particles, instead, irregular shaped structure (Fig. 3c). Similarly, the product obtained after decomposition and subsequent heat treatment of $Al(NO_3)_3$ at 973 K for 2 h in ambient atmosphere shows no sphericity. (Fig. 3b). Formation of spherical $Al_2O_3$ particles in case of starting with carbon sol produced by miceller encapsulation of carbon agglomerates suggests that a core–shell structure was initially formed. The core–shell structure has been formed by the heterogeneous nucleation and crystallisation of $Al(NO_3)_3$ on carbon agglomerates encapsulated by the surfactant (Tween 80) on concentrating the sol. Decarbonisation in ambient atmosphere burns off carbon keeping the shell structure in tact (Fig. 3a). This has been confirmed by weight loss experiments and X-Ray Diffraction. A BET measurement of the decomposed agglomerates consisting of C@$Al_2O_3$ particles show the value of surface area is around 140 $m^2$/g indicating highly porous nature of the agglomerates and there is no hindrance for nitrogen or oxygen to reach the reacting interface. The shell has provided sufficient opportunity to allow oxygen to burn the core carbon particles since it is porous. Similar type of spherical $TiO_2$ particles have been observed [18] to form by adsorption of hydrolysed product of Ti-alkoxide on polystyrene spheres and subsequent calcinations of the core particles.

X-Ray Diffraction of decomposed composite powder after heating under $N_2$ atmosphere upto 1723 K and then cooling reveals the presence of $\alpha$-$Al_2O_3$ along with carbon at 0 h (Fig. 4). Ultimately at the nitridation temperature the reaction takes place between $\alpha$-$Al_2O_3$, carbon and nitrogen. It has been observed [6] earlier that distribution of carbon particles have a definite role to play in the carbothermal reduction & nitridation of $Al_2O_3$. Oxidation of carbon has been suggested [6] to be the rate-limiting step in formation of AlN particles. Acting as templates C@$Al_2O_3$ composite

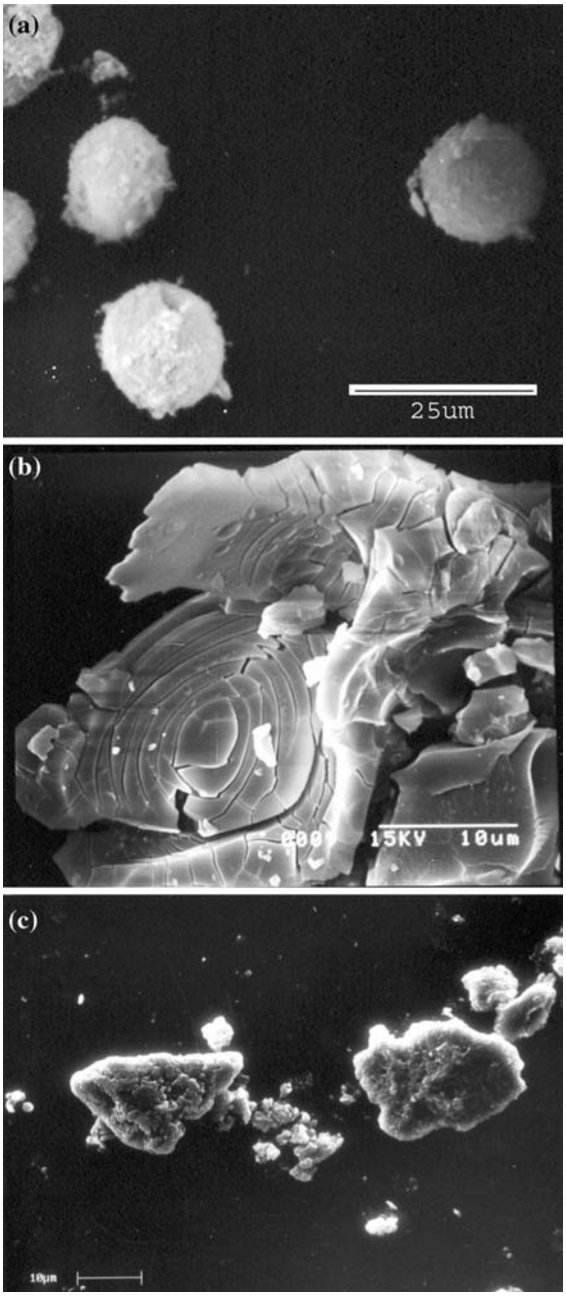

**Fig. 3** (**a**) SEM photograph of spherical $\gamma$-$Al_2O_3$ particles obtained after decarbonisation at 973 K, 2 h of the C@$Al_2O_3$ composite powders. (**b**) SEM photograph of amorphous alumina obtained after drying and calcining of $Al(NO_3)_3$ at 673 K. (**c**) SEM photograph of partially crystalline $\gamma$-$Al_2O_3$ particles obtained after decarbonisation of carbon particles chemisorbed with $Al(NO_3)_3$ at 973 K

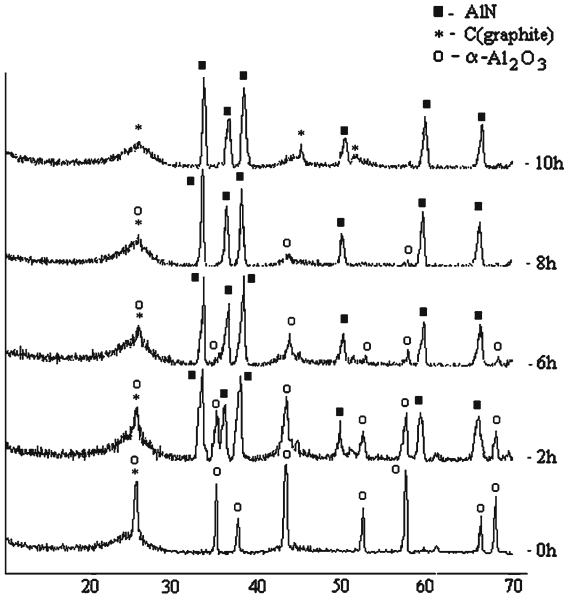

**Fig. 4** XRD of products with the progress of reaction at 1723 K, 0.4 MPa $N_2$, 0.05 l $min^{-1}$ gas flow

particles on nitridation produced spherical AlN particles. The core–shell structure ultimately converted to spherical AlN particles and also acted as substrates of growing whiskers (Fig. 5a, b). The average size of these spherical AlN particles are ~8 µm. These spheres are aggregates of small AlN crystallites, which have dimensions in the range of 30–50 nm determined by X-Ray Diffraction line broadening (Scherer's method). Retention of the shape of starting $Al_2O_3$ particles during nitridation reaction has been observed by earlier workers [5, 6, 9]. The observation of

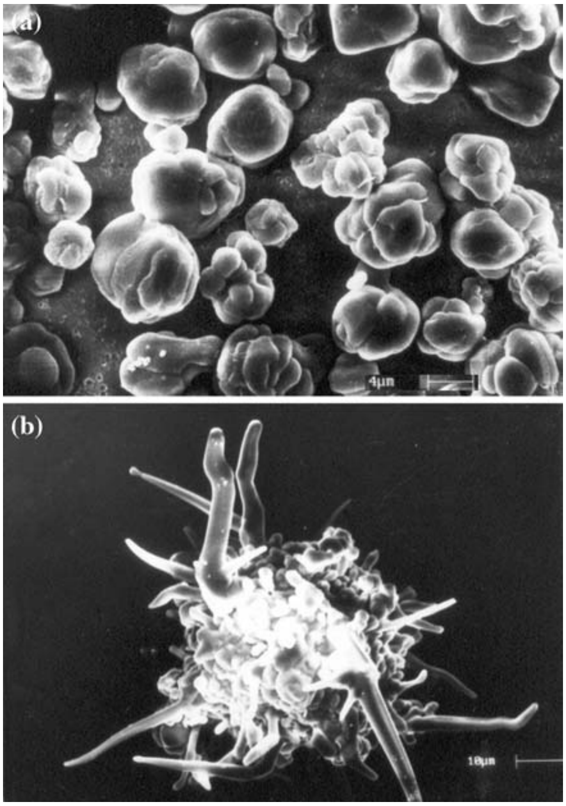

**Fig. 5** (**a**) Spherical AlN particles obtained from C@$Al_2O_3$ composite particles. (**b**) Whiskers protruding out from the spherical AlN particles

the shape retention during nitridation contradicts earlier observations [7] where a vapour transport process has been suggested to be the main mechanism of nitridation under elevated nitrogen pressure. However, whisker formation on the spherical particles (Fig. 5b) suggests that vapour transport is also occurring simultaneously. AlN whiskers have also been obtained by different means [26, 27]. From Fig. 5b it could be observed that the main mechanism operating is Vapour–Solid mechanism. No liquid droplet could be identified on the tip of the whiskers. The whiskers are not always straight and follow a deviation from their growth direction. Non-directional growths of whiskers have been observed in the present study (Fig. 5b). The reason of this type of growth may be the activation of different crystallographic planes for the necessary growth of the whiskers as suggested by other workers [26, 27].

The weight loss data and X-Ray Diffraction results of the decarbonised nitrided powder indicates that ~90% conversion to AlN is possible by this method at a temperature of 1723 K and hold time of 10 h for a 2 g batch size. The size of the AlN crystallites increases with the progress of the reaction and increase of temperature as evidenced from narrowing and increase of the height of the XRD peaks. A comparison of the specifications of AlN particles (Table 2) produced by (1) mechanically mixing $Al_2O_3$ and Carbon powders and (2) nitridation of composite $C@Al_2O_3$ powder in the same (1:2) ratio shows that particle sizes reduce drastically when the starting material is a composite $C@Al_2O_3$ particle. Similarly nitrogen content is also increased to almost theoretical value (34.14%). The size of the AlN particle reduces (100–500 nm) when the solid content and concentration of $Al(NO_3)_3$ in the starting Carbon sol are decreased (Fig. 6). This process has, therefore, the possibility of controlling the size of the final AlN particles from nanometre to micron level without introducing a hazardous and costly grinding step normally encountered.

Burning out the residual carbon (decarbonisation) is a delicate process. Porosity in the material should control the access of air/oxygen to the carbon particles. Moreover, the hold time at the temperature of decarbonisation should be as low as possible to minimise oxidation of AlN. Although a detailed study in this area is beyond the scope of this paper, it has been observed that the amount of residual carbon is more in samples obtained from C particles which were not pre-encapsulated by the non-ionic surfactant (Tween 80) or mechanically mixed with $Al_2O_3$ (Table 2) whereas, $C@Al_2O_3$ particles formed by encapsulation of carbon particles produces much less carbon content on decarbonisation (Table 2). This proves indirectly that less aggregation occurs in $C@Al_2O_3$ particles after nitridation and the product layer is porous in nature.

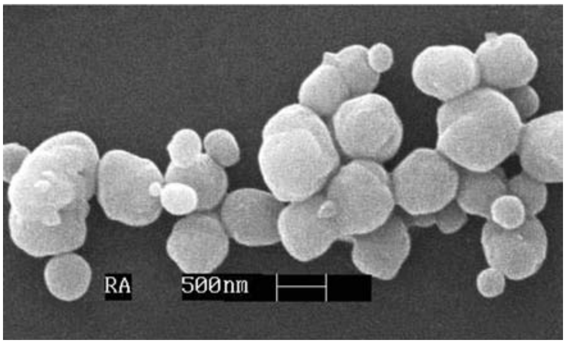

**Fig. 6** SEM photograph of nano-sized AlN powder prepared from $C@Al_2O_3$ composite particles with decreased $Al_2O_3$ content

## Conclusion

Spherical and porous $Al_2O_3$ particles have been prepared by decarbonisation of $C@Al_2O_3$ composite particles. $C@Al_2O_3$ particles have been synthesised by encapsulation of C-nanoparticles with a non-ionic surfactant (Tween 80) and subsequent nucleation, crystallisation and decomposition of $Al(NO_3)_3$ on the surface of the core particles/agglomerates. Nitridation of these core shell structures ultimately leads to spherical particles of AlN. When $Al(NO_3)_3$ is adsorbed on carbon particles directly no spherical $Al_2O_3$ particle was formed. The micro-encapsulation process could reduce particle sizes of AlN drastically by properly selecting the solid content and concentration of $Al(NO_3)_3$ in the sol. Retention of shapes of spherical $Al_2O_3$ particles and the formation of whiskers proves that both solid–gas as well as vapour phase reaction takes place simultaneously during nitridation of $C@Al_2O_2$ composite at elevated temperatures.

**Table 2** Specifications of AlN produced by different carbothermal preparation methods

| Method of preparation of reactant mixture | Average particle size | C and N content | Morphology | Nitridation temperature, duration |
|---|---|---|---|---|
| Mechanically mixed binary $C/Al_2O_3$ particles | 11–20 microns | C—0.61%, N—31.4% | Large aggregates | 1600 °C, 2 h |
| $C@Al_2O_3$ composite particles | 100 nm–8 microns | C—0.37%, N—33.33% | Spherical as well as whiskers | 1600 °C, 2 h |

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