Synthesis of nanosized AlN powder using novel nitridation route

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Nanosized AlN powders were prepared by nitridation of coarse aluminium powder in flowing N\textsubscript{2} and NH\textsubscript{3} gases, using NH\textsubscript{4}Cl and KCl as additives. XRD analysis indicated that the pure phase of AlN powder could be obtained by nitridation at 1000°C for 4 h with NH\textsubscript{3} gas. The average particle size of the AlN powder estimated from the XRD pattern is about 29 nm. FE-SEM micrograph revealed the spherical morphology of the powder particles whose sizes are in the range of 26-43 nm.

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AlN has generated a lot of interest over the past decade because of its excellent physico-chemical properties, such as high thermal conductivity, high electrical resistivity, low dielectric constant, low thermal expansion coefficient (similar to that of silicon and GaAs), good thermal shock resistance as well as good chemical stability\textsuperscript{1-3}. As far as application of AlN is concerned, this is especially considered for use in heat dissipation applications such as IC packaging materials, heat sinks as well as high thermally conducting composites. AlN is considered an ideal material for semiconductor substrates and refractory applications. AlN powder can be produced by various methods, such as carbothermal reduction of alumina and direct nitridation of aluminium-metal powder\textsuperscript{4,5}. Combustion synthesis and self-propagating high temperature synthesis (SHS) are the cost-effective methods that utilize the potential advantages of low process cost, energy efficiency and short reaction time\textsuperscript{6-9}. The important properties mentioned above can be realized when the material is in fully dense form. A very fine AlN powder is the major requirement for good sinterability to obtain a fully dense material. Therefore, the synthesis of nanosized AlN particles following a cost effective route is a worth-while exercise. Direct nitridation route has the advantages of simplicity and cost effectiveness. In this method, aluminium-metal powder is reacted with N\textsubscript{2} or NH\textsubscript{3} at high temperature. The formation of protective AlN layer on the surface of the aluminium-metal inhibits the diffusion of N\textsubscript{2} gas to the aluminium core and therefore, an intermediate grinding operation is required to complete the nitridation, which results in a high impurity concentration. In order to avoid such protective layer formation, the nitridation of aluminium-metal powder was carried out in flowing NH\textsubscript{3} gas, using NH\textsubscript{4}Cl, KCl as additives\textsuperscript{10}. This process being simple and cost-effective, is considered to be novel. However, this was not studied in sufficient detail by other researchers. In the present work, an attempt has been made to synthesize nanosized AlN powders by nitridation of commercial grade coarse aluminium powder, using NH\textsubscript{4}Cl and KCl as additives. The nitridation reaction has been carried out in a specially designed stainless steel tube inserted into a cylindrical muffle furnace.

**Experimental Procedure**

Coarse aluminium powder (commercial grade), NH\textsubscript{4}Cl (99.0%, s.d. fine) and KCl (99.0%, s.d. fine) were wet mixed (wt. ratio of 1:1:1) in acetone medium for sufficiently long time. The mixture was then dried at about 80°C and placed into a specially designed stainless steel long reaction tube inserted in a tube furnace. The reaction tube was purged with N\textsubscript{2} gas for half an hour to remove air in it before the furnace was turned on. The one end of the reaction tube is connected to the gas supply and the other end is connected with a rubber tube for outletting the gases after the chemical reaction of powder mixture. Each sample (powder mixture) of 4 g in weight was taken for study. In the first case, the samples were heated at 900°C, 1000°C and 1100°C for 3, 4 and 5 h in flowing N\textsubscript{2} gas (high purity) and then furnace cooled to room temperature in the flowing gas.
Thereafter, the resultant powder was collected from the reaction tube. Similar procedure was followed for the samples, in the second case, in the flowing NH₃ gas. X-ray diffraction (XRD) analyses of the resultant powders were carried out on a X-ray diffractometer (Bruker AXS, D8 Advance) with a step size of 0.05º and a scan speed of 3 s per step in the 2θ range of 10º-80º. The diffraction patterns were taken using CuKα radiation (λ = 1.5418Å). The chemical compound formation was identified from the patterns. The crystallite sizes (D) were calculated from peak broadening of principal peaks (from the FWHM of the peaks expressed in radians) by using Scherrer’s formula:\(^{11,12}\)

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D = \frac{0.94\lambda}{\beta \cos \theta}
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where β is the full width at half maximum of the corresponding peak.

The particle size and the morphology of the as synthesized nitride powders were observed using FE-SEM (Quanta 200 FEG). In order to prepare the test specimen for FE-SEM observation, a small quantity of powder agglomerates were broken using mortar and pestle. Separated powder particles were got stucked on one side of the double sided tape attached on the specimen holder. The powder particles mounted on the holder were gold coated and thereafter inserted into the specimen chamber for microscopic observations.

**Results and Discussion**

XRD patterns of all the samples processed at 900ºC, 1000ºC and 1100ºC in N₂ gas were registered. However, in no case, the pure phase of AlN was obtained through the reaction schedules with N₂ in the present study. The patterns showed that the resultant powders consist of AlN, Al₂O₃ and AlON compounds. The relative percentage of AlN in the...
mixed phases (of AlN, Al₂O₃ and AlON) increases with longer time period of heating and became highest in the sample synthesized at 1000ºC for 5 h. The XRD pattern of the sample synthesized at 1000ºC for 5 h is shown in Fig. 1.

In the case of samples synthesized in NH₃ gas, the reactions were carried out for 4 h at all the above mentioned temperatures (i.e. 900ºC, 1000ºC and 1100ºC). The XRD-patterns are shown in Figs 2-4. It can be seen from the figures that the formation of AlN phase pure to the highest degree, could be obtained by synthesizing at 1000ºC for 4 h. However, the peaks of Al₂O₃ and AlON compounds, though negligibly small in intensity, were found to be present in all the patterns. The crystallite sizes were calculated from the principal peaks of the patterns. The average crystallite size of the phase pure AlN has been found (from Fig. 3) to be about 29 nm.

The purpose of incorporating NH₄Cl and KCl into coarse aluminium powder at the precursor level is as follows. The nitridation temperature gets lowered significantly due to the NH₄Cl, which in turn prevents the coalescence of alumina particles. Due to the evaporation of KCl aperture generates and this enables NH₃ to diffuse to the interior of aluminium particles successfully to react with molten aluminium inside.

The powder for which the crystallite size has been reported from the XRD analysis, has also been observed for its morphology by Field emission scanning electron microscope (FE-SEM) and the micrograph is shown in Fig. 5. It can be seen from the
that the powder is nearly spherical and the particle sizes are found to lie in the range of 26-43 nm.

**Conclusions**

Nanosized AlN powders were synthesized by nitridation of coarse Al powder. High purity (X-ray) AlN powder could be prepared by nitridation with NH$_3$ at 1000°C for 4 h. FE-SEM study has shown that the powder consists of particles having almost spherical morphology and size ranging between 26 and 43 nm. The particle size calculated from X-ray principal peak broadening has been found to be 29 nm.

**References**