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Hydrolysis control of alumina and AlN mixture for aqueous colloidal processing of aluminum oxynitride

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Abstract

AlN powder, surface modified by phosphoric acid treatment was employed for the aqueous colloidal processing of Aluminum Oxynitride (AlON). The hydrolysis of AlN leads to the formation of $Al(OH)_3$ and NH_3. On mixing of alumina to the phosphoric acid treated AlN in aqueous medium this reaction reoccurred. The phosphoric acid shield around AlN particles is ruptured by alumina addition thus exposing AlN surface to hydrolysis reactions. Hence hydrolysis can be effectively controlled by providing a phosphoric acid treatment to the alumina, prior to its addition to AlN. AlON precursor mixture thus obtained can be successfully shaped by an aqueous slip casting process and sintered to phase pure AlON at 1925 °C for 2 h. Viscosity, pH, SEM, FTIR, and XRD measurements are employed to elucidate the effect of Al_2O_3 addition on surface modified AlN for colloidal processing of AlON.

Keywords: Aluminum Nitride; Hydrolysis; Aluminum Oxynitride; Surface modification

1. Introduction

Combinations of AlN and alumina are widely used for the syntheses of various compounds such as Aluminum Oxynitride [1–11], MgAlON [12–14], SiAlON [15–17], and their composites [18–30]. The synthesis route generally employs organic solvents as the dispersing medium due to the tendency of AlN to undergo hydrolysis reaction in aqueous medium, which results in the formation of AlOOH followed by $Al(OH)_3$ and NH_3 [31–35] according to the following reactions:

$$AlN + 2H_2O \rightarrow AlOOH + NH_3 \quad (a)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (b)$$

$$AlOOH + H_2O \rightarrow Al(OH)_3 \quad (c)$$

It is therefore difficult to maintain the molar ratio between Al_2O_3 and AlN in order to obtain the required phase stoichiometry of the final product. Moreover, aqueous colloidal shaping processes require slurries with high solid loading content. In such processes that involve AlN powder, the hydrolysis reaction of AlN consumes the water from the slurry and transforms it into a high viscous paste, unsuitable for casting. Employing organic solvents as a processing medium and compaction as a shaping technique generally alleviates the said problems. The colloidal processing route, by virtue of its advantages provides defect free products with complex shaping made simple. This is also a cost effective technique for the fabrication of ceramic materials.

The hydrolysis of AlN was effectively used by Kosmac and co-workers. They used this to develop the colloidal based consolidation technique known as hydrolysis assisted solidification [34,36,37]. This technique has further been used for the fabrication of dense β-SiAlON by employing a mixture of treated and untreated AlN powders [38]. Miller and Kaplan added AlN powder into aqueous alumina slurry and limited their milling time for 2 h after the addition of AlN to avoid its hydrolysis reaction [9], for the synthesis of AlON.

The hydrolysis of AlN has been effectively controlled or the incubation period of AlN in water has been prolonged by treating AlN with various surface modifiers such as butyl acid phosphate, ammonium phosphate, poly phosphoric acid, aluminum dihydrogen phosphate, ortho phosphoric acid, citric acid, sebacic acid and stearic acid etc. [10,39–45]. The passivated powders thus obtained were further made to slurries

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of >76% solid loading in aqueous medium and the samples were casted and sintered successfully.

In the present work, the effect of addition of alumina on surface modified AlN in aqueous medium for the colloidal processing of AlON has been investigated. Samples of AlON were casted using this process, sintered and characterized for its phase and micro structural properties. The effectiveness of phosphoric acid treatment of AlN for surface passivation is examined in the presence of alumina and modified techniques are presented to retain the surface passivation of AlN, in order to enable the aqueous colloidal processing of AlON.

2. Experimental procedure

High purity alumina (SM8, Baikowski Chemie, France, d_{50} – 0.4 μ, BET surface area – 14 m^2/g) and AlN powders (Grade-C, H.C. Starck, Germany, d_{50} – 1.12 μ, BET surface area – 4.06 m^2/g) were used for the entire process.

2.1. Hydrolysis of AlN

As received AlN powder was dispersed in distilled water with 60 wt% solid loading using 1 wt% Darvan 821A (R.T.Vanderbilt Co., Inc., Norwalk, CT, USA) as a dispersant. Dispersion was carried out in a magnetic stirrer at ambient temperatures. The slurry was checked for pH and the viscosity was measured (MCR 51, Anton Paar GmbH, Austria) at 30 min interval until the slurry turned into a high viscous paste. The paste was dried at 50–60 °C and the powder was characterized for its micro structure by SEM (Hitachi, FEG SEM, Japan) and for the phase analysis by XRD (D8, Bruker, Germany). FTIR analysis (Spectrum GX, Perkin Elmer, U.S.A) was also carried out to elucidate the bond characteristics. For this characterization, 10 mm diameter and 0.1–0.2 mm thick pellets were compacted uniaxially at 10 tons load using a mixture of 200 mg KBr and 2 mg hydrolyzed AlN powders.

2.2. Surface modification of AlN

AlN was dispersed in distilled water containing 1–2 wt% ortho phosphoric acid (98% H_3PO_4, Qualigens, India) using Darvan 821A as a dispersant. Dispersion was carried out in a magnetic stirrer at 60–70 °C for 15 min. The excess water was filtered out from the slurry after the dispersion and the filtrate was dried at 50–60 °C for 24 h in air. The dried powder was characterized for its morphology by SEM. The dried powder was then made into slurry, with 60 wt% solid loading in water using Darvan 821A as a dispersant. The slurry was checked for its pH and the corresponding viscosity was measured every 30 min. The dried powder was further analyzed for phases by XRD and for functional groups by FTIR.

2.3. Addition of alumina in surface modified AlN

65–70 mol% of alumina that corresponded to the AlON ($Al_{23}O_{27}N_5$) composition was added to the surface modified AlN for all the done experiments. Aqueous slurry of alumina and AlN with 60 wt% solid content was prepared using Darvan 821A as a dispersant. The slurry was stirred in a magnetic stirrer for 5 h and the pH and viscosity was measured at every 30 min. The slurry was further dried at 50–60 °C and subjected to micro structural, FTIR and phase analyses.

2.4. Addition of surface modified alumina in surface modified AlN

Alumina was also subjected to surface modification as per the procedure followed for AlN and the AlON precursor slurries with 60 wt% solid loading was prepared using the surface modified AlN and alumina powders using Darvan 821 A as dispersant. The slurry was stirred in a magnetic stirrer for 5 h with periodic measurements of pH and viscosity. The slurry was further dried at 50–60 °C in air and subjected to SEM, FTIR and XRD analyses.

2.5. Shaping by slip casting

Aqueous suspensions of surface modified alumina and AlN were prepared with 76–80 wt% solid loading using Darvan 821A as a dispersant. The slurry was casted in a porous alumina mould and dried at ambient conditions for 24 h followed by drying at 80 °C for 24 h. Dried samples were then subjected to heat treatment at 500 °C for 2 h in air and further sintered at1925 °C in nitrogen atmosphere for 2 h. Sintered samples were characterized for their density by Archimedes principle and phase analysis by XRD.

3. Results and discussion

Fig. 1a and b shows the morphology of alumina and AlN respectively used for the processing. Alumina particles have size distribution in a narrow range and the average particle size is in the range of 200–400 nm while AlN particles were found to have a wider distribution of sizes ranging from 500 nm to 3 μm.

3.1. Hydrolysis of AlN

Fig. 2 shows the plot of pH and viscosity with time. The pH values of untreated AlN slurry started changing within the first 30 min confirming the vigorous tendency of AlN to hydrolysis forming AlOOH followed by $Al(OH)_3$ and NH_3. It was observed that the pH of initial slurry rises to 10.3 from 8.5 within 5 h due to the evolution of NH_3 from the hydrolysis reaction. The viscosity of the slurry also increased reaching a value of 10.6 mPa s from 2 mPa s. An abrupt change in viscosity was observed after 2 h. The change in viscosity is due to the consumption of water by AlN from the slurry for its hydrolysis to form AlOOH followed by $Al(OH)_3$.

Fig. 1c shows the microstructure of AlN that had undergone hydrolysis reaction and clearly indicates the presence of needle like boehmite particles on the surface. Most of the particles were covered with hydroxide whereas some particles remained unaffected.