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Hydrolysis protection and sintering of aluminum nitride powders with yttria nanofilms

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Abstract

Aluminum nitride (AlN) is a promising material for electronic substrates and heat sinks. However, AlN powders react with water that adversely affects final part properties and necessitates processing in organic solvents, increasing the cost of AlN parts. Small quantities of yttrium oxide (Y_2O_3) are commonly added to AlN particles to enable liquid phase sintering. To mitigate the reaction of AlN particles with water, particle atomic layer deposition (ALD) was used to coat AlN powders with conformal films of Y_2O_3 prior to densification and powder processing. When AlN particles were coated with 6 nm thick films of amorphous Y_2O_3, the hydrolysis reaction was significantly suppressed over 48 h, demonstrating that Y_2O_3 nanofilms on AlN powders act as a barrier coating in an aqueous solution. AlN powders with Y_2O_3 addition by particle ALD sintered to high relative densities ($\geq$90% theoretical) after sintering at 1800°C for 50 min.

KEYWORDS
aluminum nitride, atomic layer deposition, environmental barrier coatings (EBC), sinter/sintering

1 | INTRODUCTION

A high thermal conductivity (150–200 W m^{-1} K^{-1})[1–3] and low electronic conductivity make aluminum nitride (AlN) an ideal material for electronic heat sinks. Its thermal conductivity is much higher than most ceramic materials and is similar to that of metals.[4] However, AlN's low electronic conductivity enables the direct fabrication of integrated circuits on the heat sink, eliminating the dielectric layer needed to electrically isolate the metal heat sink from the LED.[5,6]

AlN has many desirable properties, but it is expensive to produce due to the high sintering temperatures required to reach near-theoretical density and reactivity with water.

AlN degrades in water, forming Al_2O_3 that dissolves into the AlN lattice to produce vacancies on aluminum sites (V_{Al}''')[7–10]:

$$2AlN + 3H_2O \rightarrow Al_2O_3 + 2NH_3 \qquad (1)$$

$$Al_2O_3 \xrightarrow{AlN} 2Al_{Al} + 3O_N^{\cdot} + V_{Al}''' \qquad (2)$$
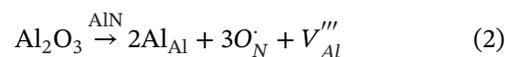
These vacancies scatter phonons traveling through the lattice, thereby reducing the thermal conductivity.[11,12] To mitigate this reaction, AlN powders must be handled in organic solvents which increases processing costs.

AlN requires sintering temperatures of ~1800°C to reach high densities, even with the addition of sintering aids. Conventionally, AlN densifies by liquid phase sintering with the addition of Y_2O_3,[1–3,13,14] CaO,[14–16] and/or other materials[2,13,17,18] as sintering aids. These secondary phases also react with Al_2O_3 impurities produced during AlN powder synthesis, sequestering them to grain boundaries and triple points to avoid the formation of V_{Al} (Equation 2) and increasing the thermal conductivity.[1,2]

Typically, sintering aids are added by ball milling[1,14,15,18–20] or vibratory milling[2,13] of sintering aid particles with AlN powders. In this work, we propose a novel method of liquid phase sintering aid addition, particle atomic layer deposition (ALD). Particle ALD is a thin film deposition technique that uses sequential surface-limited reactions to grow thin films that are chemically bonded to the surface of substrate particles.[21] Here, particle ALD is used to add Y_2O_3 to AlN particles as a conformal nanoscale surface coating, homogeneously dispersing the sintering aid prior to densification. Additionally, ALD-coated powders have shown reduced reactivity toward environmental species, including SiC in steam[22] and ZrO_2 in H_2.[23] By adding the Y_2O_3 as a nanofilm instead of particles, it acts as a barrier coating and protects the AlN particle surface from reaction with water to enable aqueous processing.

2 | EXPERIMENTAL SECTION

Commercial AlN powder (Tokuyama Soda, Grade E, 3.4 m^2/g) was coated with nanoscale films of Y_2O_3 in a fluidized bed reactor at 300°C. Nitrogen was used as the carrier gas. The yttrium precursor (Arya, Air Liquide) was supplied using a bubbler and oxygen was the oxygen source. Typically, after the precursor reacts with all available functional groups on the particle surface, "breakthrough" occurs where a characteristic atomic mass signal increases in the mass spectrometer, indicating that an unreacted precursor is flowing through the powder bed.[24] Precursor breakthrough was not observed when dosing the yttrium precursor, so it is unknown if the surface reaction reached completion. Therefore, the number of ALD cycles is not reported.

To characterize the composition of the ALD-coated powders, the yttrium content was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and LECO light element analysis (LECO TC600 and LECO C200) was used to determine carbon and oxygen content. Transmission electron microscopy (TEM; Tecnai ST20) was used to characterize the film.

For comparison to the ALD-coated powders, AlN powder samples with equivalent Y_2O_3 content added by

TABLE 1 Y_2O_3 wt% and method of addition for all samples

| Sample	Y_2O_3 content (wt %)	Addition method
0%ALD	0	NA
0.4%ALD	0.4	ALD
6.5%ALD	6.5	ALD
0.4%MIX	0.4	Mechanical mixing
6.5%MIX	6.5	Mechanical mixing

mechanical mixing were prepared (Table 1). AlN powder was mixed with 0.4 and 6.5 wt% Y_2O_3 powder (Sigma Aldrich, 99.99% trace metal basis, 3.3 m^2/g) for 24 h in a drum roller with isopropanol and yttria-tetragonally stabilized zirconia milling media (Tosoh) in a 10:1 media to powder ratio. The solvent was then removed by drying under vacuum for ~2 days.

To characterize the hydrolysis behavior of coated and uncoated AlN powders, 1.5 g of 0%ALD, 0.4%ALD, and 6.5%ALD powders were placed in 150 ml of distilled water at 30°C under stirring. As the AlN powders react with water, ammonia is produced resulting in an increase in pH (Equations 1–2). The pH was monitored over ~48 h using a pH meter (Sartorius) and was stored on a computer at various time intervals. Pure Y_2O_3 powder (Sigma Aldrich, 99.99% trace metal basis, 3.3 m^2/g) was also tested as a control.

All powders were mixed with 6 wt% polyethylene glycol (Alfa Aesar polyethylene glycol 8000) and isopropanol in a mortar and pestle. The mixture was then placed under a vacuum overnight for solvent removal. Then, the powder/binder mixture was placed in a stainless-steel die and pressed at 350 MPa for 90 s to form 6 mm diameter powder compacts. For each sintering experiment, the pellet was placed in a boron nitride protective sleeve. The temperature was then raised to 600°C at a rate of 2°C/min followed by a 10 min isothermal hold for the removal of binder and then from 600 to 1800°C at 10°C/min followed by a 50 min isothermal hold. After sintering, the final density of the specimen was determined by geometric measurement. A fracture surface of the dense samples was characterized using backscattered electron-scanning electron microscopy (BSE-SEM, Hitachi SU3500) with an accelerating voltage of 10 kV.

3 | RESULTS AND DISCUSSION

The Y_2O_3 content determined by ICP-OES was 0, 0.4, and 6.5 wt% Y_2O_3 for 0%ALD, 0.4%ALD, and 6.5%ALD, respectively, where the wt% Y_2O_3 is denoted in the sample name (Table 1). The uncoated AlN powder had an oxygen and carbon content of 1.2 ± 0.2 and 0.13 ± 0.01 wt%,
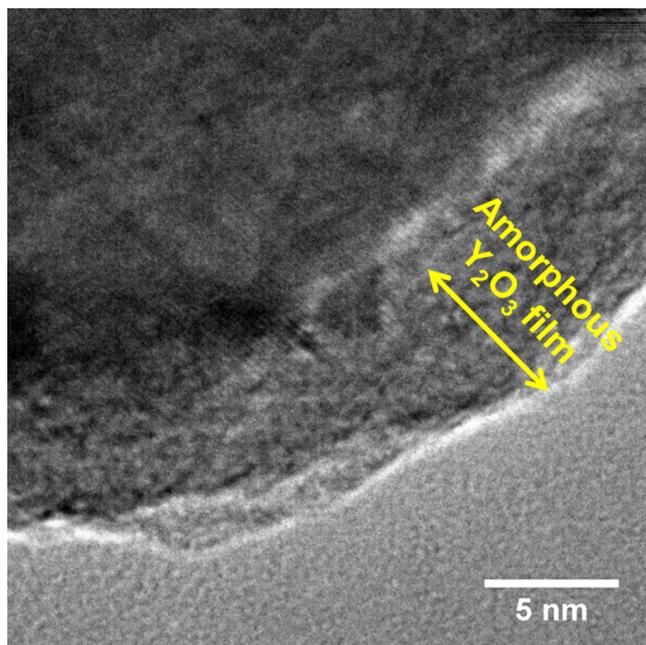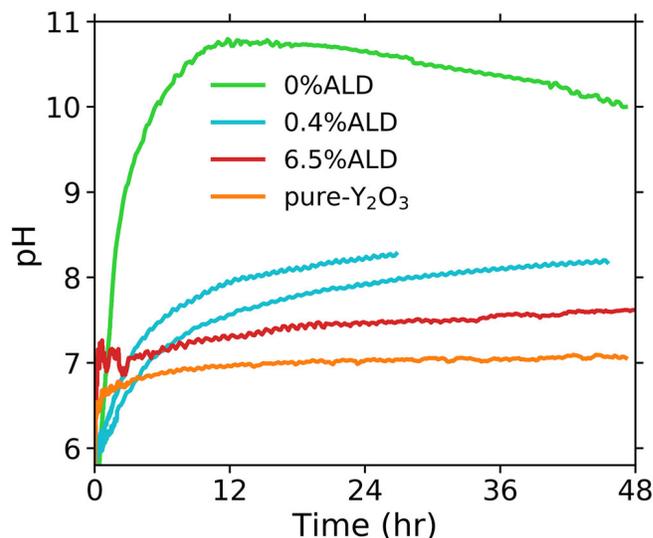
FIGURE 1   Transmission electron microscopy (TEM) of aluminum nitride (AlN) powder with 6.5 wt% Y_2O_3 added by particle ALD, where the AlN particle is coated with an amorphous film of Y_2O_3 that is ~6 nm in thickness

FIGURE 2   The hydrolysis behavior of the uncoated and ALD-coated aluminum nitride (AlN) powders, along with pure-Y_2O_3 powder run as a control. The addition of 6.5 wt% Y_2O_3 by particle ALD significantly reduces AlN hydrolysis over ~48 h

respectively, as determined by LECO light element analysis. For 6.5%ALD, the carbon content after the ALD process increased to 0.41 ± 0.02 wt%, showing that some carbon impurities are present in the film. TEM was used to characterize the Y_2O_3 film of 6.5%ALD (Figure 1). The lattice of the AlN particles is apparent, and the AlN particles were coated with conformal thin films of amorphous Y_2O_3. The film thickness was ~6 nm with 6.5 wt% Y_2O_3 addition.

The hydrolysis behavior of the uncoated powders was measured by determining the change in pH over time of a water/powder mixture (Equation 1). The pH of 0%ALD increases quickly from 6 to ~10.5 over 10 h, suggesting that the uncoated powder quickly hydrolyzes in the presence of water (Figure 2). After 10 h, the pH decreases possibly due to the volatilization of NH_3 from the solution. The pH of 0.4%ALD reaches ~8.25 after 48 h, suggesting that adding a Y_2O_3 nanofilm by particle ALD suppresses the hydrolysis reaction. However, a gradual increase in pH is observed over the first 10 h, suggesting that the film is incomplete with only 0.4 wt% Y_2O_3 addition.

With 6.5 wt% Y_2O_3 addition, the final pH is ~7.6 after 48 h, less than the final pH of both 0%ALD and 0.4%ALD. The hydrolysis behavior of 6.5%ALD more closely resembles that of pure-Y_2O_3, suggesting that the Y_2O_3 film effectively protects the surface of the particles from reaction with water. However, the pH of 6.5%ALD still increases slightly from 7 to 7.6 over 48 h. This is likely because of the slow dissolution of the amorphous Y_2O_3 film into solu-

tion, as some amorphous ceramics have limited solubility in water at relatively low temperatures.[25,26] This slowly creates porosity in the film, as reported previously for amorphous Al_2O_3 films in water.[25]

For 0%ALD, only 70% theoretical density was achieved after sintering. When a small quantity of Y_2O_3 is added (≥ 0.4 wt%) by ALD or mechanical mixing, all samples reach high densities that are $\geq 90\%$ theoretical. The fracture surfaces of dense samples were characterized by BSE-SEM (Figure 3). In samples with 6.5 wt% Y_2O_3, the Y_2O_3 phase migrated significantly as the Y_2O_3 is not uniformly distributed throughout the final microstructure. The addition of Y_2O_3 by both mechanical mixing and particle ALD leads to a non-uniform distribution of the secondary phase at this concentration.

4 | CONCLUSION

Particle atomic layer deposition (ALD) was used to coat AlN powders with conformal thin films of amorphous Y_2O_3, demonstrating a novel method for the addition of liquid phase sintering aids to AlN powders. Hydrolysis experiments revealed that an ~6 nm Y_2O_3 film (6.5 wt%) significantly reduced the hydrolysis of the AlN particles over 48 h, illustrating that deposition of Y_2O_3 nanofilms on AlN particles by ALD protects the AlN particle surface from hydrolysis. However, a gradual increase in pH over this time interval suggested that the amorphous Y_2O_3 slowly dissolved in water to form porosity.
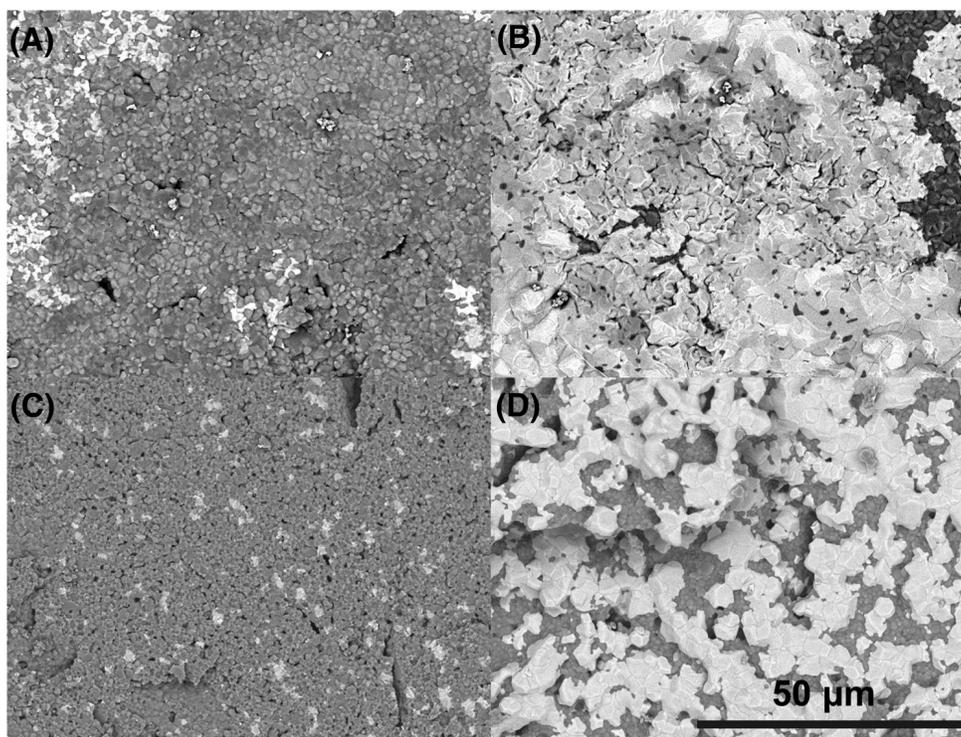
FIGURE 3 Micrograph of (A–B) 6.5%ALD and (C–D) 6.5%MIX in two different locations. The gray grains are AlN and the white phase is Y_2O_3 which is non-homogeneously dispersed after sintering

Samples with Y_2O_3 addition by either mechanical mixing or particle ALD achieved $\geq$90% relative density after sintering at 1800°C and contained a non-uniformly dispersed Y_2O_3 phase throughout the microstructure.

CONFLICT OF INTEREST
A.W. Weimer has a significant financial interest in Forge Nano, Inc.

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