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13. ABSTRACT ( <i>Maximum 200 words</i> ) The direct synthesis of nanocrystalline AlN in the forced flow reactor is described, along with initial characterization and chemical analysis results. The AlN has a surface area in excess of 100 square meters per gram and a volume average crystallite size of 40 nm. The particles are not entirely spherical and show some faceting and elongation, which explains the discrepancy between the high surface area and the XRD determined crystallite size.			
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## “Processing of Nanocrystalline Nitrides and Oxide Composites”

Technical Report on ONR Grant No. N00014-95-1-0626

for the period of April 1, 1998 - June 30, 1998

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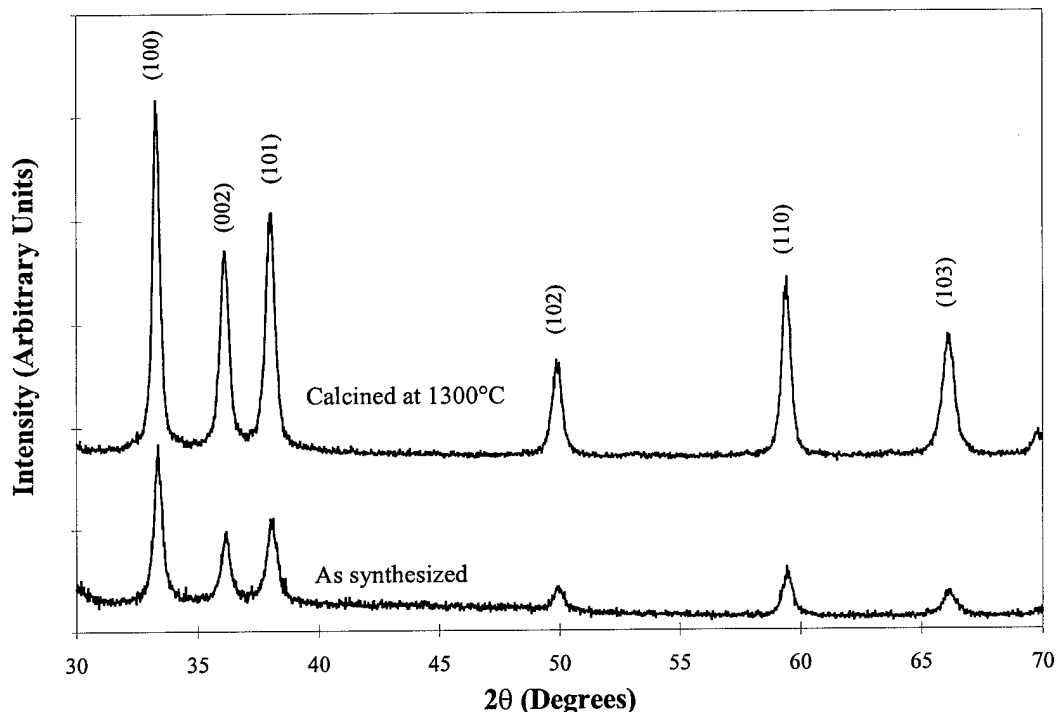
### *Nitridation of Nanocrystalline Aluminum*

As reported previously[1], the synthesis of nanocrystalline aluminum can be easily accomplished in the forced flow reactor. The material produced is ultrafine-grained (30-50 nm, depending on the synthesis conditions) and appears to be equiaxed from X-ray diffraction (XRD) and electron microscopy. The material is readily nitrided to 70% conversion by 660°C (the melting point of aluminum) and can be further nitrided to >90% pure AlN by continued heating to 1000°C under a nitrogen flow. Kinetic analysis and determination of the activation energy for the low-temperature nitridation have been difficult, possibly due to surface oxidation or particle agglomeration affecting the mass transport of nitrogen to the particles. Additional experiments are currently underway to determine which factors affect the nitridation, and may include changing the reactant gas from nitrogen to ammonia.

### *Nanocrystalline Aluminum Nitride Synthesis*

Our recent investigations into producing nanocrystalline aluminum nitride directly in the reactor have been met with considerable success[2]. Previously, we were able to synthesize only small amounts of pure AlN if we sublimed AlN powder into a nitrogen stream with the microwave plasma applied. This procedure required very high temperatures (~2000°C) to sublime the AlN and, partially due to the microwave plasma, produced only a small amount of powder. Larger quantities of a lower purity AlN powder (with excess aluminum) could also be produced if we evaporated aluminum metal under similar conditions. The excess aluminum was most likely due to periods of rapid evaporation and spattering just after an evaporation pellet has been added, producing significant amount of molten aluminum. By redesigning the feed stream and changing the operating conditions, a more even evaporation of material has been achieved. The feed material was changed from pellets to high-purity aluminum wire, and the nitriding gas was changed from nitrogen to ammonia. By heating the graphite crucible to approximately 1500°C before adding the aluminum, flash evaporation conditions can be attained. The aluminum wire also allows the addition of smaller amounts of aluminum each time, producing a more uniform evaporation and preventing the accumulation of molten aluminum. In the current configuration, the ammonia is added upstream of the crucible and can nitride the molten aluminum in the crucible unless high temperatures are used to rapidly and completely evaporate

the aluminum wire as it is introduced. Since the ammonia begins to decompose spontaneously at temperatures greater than 200°C [3] and is then free to react with the aluminum, the microwave plasma is not needed. X-ray diffraction patterns of the white as-synthesized powder and the heat treated sample are shown in Figure 1. The as-synthesized powder has a crystallite size of approximately 40 nm, which increases to approximately 45 nm after heat



**Figure 1.** X-ray diffraction pattern of AlN powder as synthesized and after calcining at 1300°C in nitrogen for three hours.

treatment at 1300°C. The surface area of the powder as synthesized is 119 m<sup>2</sup>/g, which corresponds to an equivalent spherical diameter of 16 nm. However, the particles are not entirely spherical, as observed by transmission electron microscopy, but range from brick-shaped particles with an aspect ratio of approximately 2 or 3 to nearly spherical particles. In these preliminary runs, the reactor pressure increased from 3 mbar to 25 mbar as the run proceeded, so it is difficult to determine under what conditions the various particle morphologies were produced. The effect of various synthesis parameters, such as reactor pressure, ammonia concentration, ammonia inlet location and gas velocity, on particle size, morphology, and purity will be examined in future experiments.

Unlike the particles produced from subsequent nitridation of nanocrystalline aluminum which displayed an obvious XRD orientation preference for the (002) direction[1], the relative intensities of the XRD peaks for directly nitrided nanocrystalline AlN (Figure 1) are nearly identical to those of uniform polycrystalline AlN. In addition, the in-situ synthesized aluminum nitride does not display any oxygen-containing phases (such as  $\gamma$ - or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or any of the aluminum oxynitride phases) after calcination, whereas the post-synthesis nitrided nanocrystalline aluminum exhibited these secondary phases.

These preliminary runs resulted in a material that was approximately 31.55 wt% N, and 57.3 wt% Al. (The stoichiometry of pure AlN is 34.2 wt% N and 65.8 wt% Al.) The missing mass is made up of carbon (~1 wt%), hydrogen (~0.65 wt%), and, most probably, oxygen (by difference, ~9.5 wt%). The source of the carbon may be adsorbed hydrocarbon on the high surface area AlN or contamination from the graphite crucible. The chemistry of the carbon in the sample is unknown since both graphite and aluminum carbide ( $\text{Al}_4\text{C}_3$ ) are present in the crucible at these high temperatures and both could be transported in the gas stream along with the AlN. The source of the oxygen is undetermined; however, since the powder is exposed to the air for a short period of time before chemical analysis, it could pick up surface oxygen, water, or hydrocarbons during this time. The stoichiometry of these powders is apparently nitrogen-rich and roughly corresponds to a formula of  $\text{AlN}_{1.06}(\text{OH})_{0.28}\text{C}_{0.04}$ . Direct analysis of oxygen content in unexposed samples using fast neutron activation analysis is being planned. Future work on improving the chemical purity of the AlN will involve changing the reactor conditions and raw materials (aluminum supply, gas purity, etc.), as well as improving powder handling methods if deemed necessary.

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[1] Ying, J.Y. "Technical Report on ONR Grant No. N00014-95-1-0626 for the period of January 1, 1998 - March 31, 1998"

[2] Panchula, M.L. and Ying, J.Y., M.I.T., unpublished results.

[3] Huseby, I. C. "Synthesis and Characterization of a High-Purity AlN Powder" *J. Am. Ceram. Soc.* **66** [3] 217-220, (1983).