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We have examined the effects of reactor pressure, gas velocity and carrier gas on nanocrystalline AlN powder microstructure and sinterability. A helium/ammonia gas stream produced AlN powders of smaller crystallite sizes but with needle-like morphologies. Such powders required hot-pressing at 1900 C for densification; the resulting materials are highly textured and may be of interest to piezoelectric applications. In contrast, a nitrogen/ammonia gas stream generated lower surface area AlN powders without needle-like morphologies. These AlN powders displayed superb sinterability, allowing pressureless, additive-free densification at a remarkably low temperature of 1700 C.

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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, 1999 – June 30, 1999

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Nanocrystalline Aluminum Nitride

Powder Synthesis Results

As described in a previous report [1], the forced-flow reactor conditions can have a large effect on the surface area and crystallite size of the powder produced. As is generally observed for these type of reactors, a decrease in surface area and increase in crystallite size occurred as the reactor pressure was increased. Gas velocity has also been shown to have an effect on the particle surface area and crystallite size, though it is a more complex phenomena. One variable which had not been previously investigated, however, was the choice of carrier gas.

In earlier studies, it was found that the amount of AlN produced with nitrogen as the nitriding gas was negligible, and only in conjunction with the microwave plasma could a reasonably high degree of nitridation (80%) be achieved. However, by using ammonia as the nitriding gas, full conversion was achieved and a high-purity nanocrystalline AlN powder could be produced with either nitrogen or helium as the carrier gas. In order to optimize the powder yield, helium was chosen as the carrier gas during the initial powder synthesis experiments. The nanocrystalline AlN powders synthesized, however, were difficult to sinter and required hot pressing at temperatures of 1900°C to obtain >90% dense specimens. The resulting samples were highly textured with an unusually intense (002) X-ray diffraction peak. Texturing in this orientation might make this material useful for piezoelectric applications.

Despite the interesting texturing result, the sinterability of the nanocrystalline AlN powder was quite low. After many attempts at correlating the various reactor conditions to powder sinterability, it was discovered that the carrier gas had the largest effect. Powders synthesized in a N_2/NH_3 stream were much more easily sintered than those produced in a He/NH_3 gas stream as shown in Figure 1. The source of this difference in sinterability is believed to be the different powder morphologies produced in the two different carrier gases. The TEM micrographs in Figure 2 show that the powders produced in a He/NH_3 gas stream (Figures 2(c,d)) contained a larger number of needle-like particles than the powders produced in a N_2/NH_3 gas stream (Figures 2(a,b)). Figures 3 and 4 show that the crystallite sizes and surface areas are also strongly affected by the choice of carrier gas, with the helium gas stream producing powders with higher surface areas and smaller crystallite sizes.

Pressureless Sintering of Nanocrystalline AlN

Processing and handling of the powders was performed in an argon-filled glovebox in which the oxygen and water content was generally maintained at <1 ppm. The powders were transferred from the forced-flow reactor into the glovebox without exposure to the atmosphere. Several batches of powder were then combined by passing them through a 325 mesh sieve to facilitate mixing. The pellets were formed by pressing the powder in a BN-lubricated stainless steel die at ~7 MPa and cold isostatically pressing them to 410 MPa. After removal from the CIP bags, the pellets were placed into a BN casket and covered with AlN packing powder (H. C. Starck Grade B). The BN casket containing the pellets was then placed in a covered molybdenum crucible which was sealed with Parafilm® to prevent exposure to the atmosphere during the brief transfer from the glovebox to the furnace. The casket assembly was then rapidly transferred to the graphite furnace which was pumped to $<2\text{x}10^{-2}$ mbar and refilled with 99.999% pure nitrogen three times prior to heating. The vacuum was maintained during the heating ramp until approximately 1000°C, when the furnace was backfilled to 4 psig and purged (0.4 slpm) with high-purity nitrogen which had been passed through an oxygen trap. The standard heating cycle included a ramp of 10°C/min to the sintering temperature, followed by a 2-hour soak. The sample and furnace were then allowed to cool fairly rapidly (~50°C/min) back to room temperature.

Since the nanocrystalline AlN synthesized with nitrogen as the carrier gas gave the best densification results, the powders used in subsequent sintering experiments were synthesized with nitrogen as the carrier gas. This resulted in pure AlN powders with a crystallite size of 80-100 nm and surface areas of 40-50 m^2/g. The additive-free sintering curve for the nanocrystalline AlN powder created in the forced-flow reactor is shown in Figure 5, along with that of a commercial AlN powder (H. C. Starck, Grade B). Our nanocrystalline material densified much more readily than the H. C. Starck AlN powder (3.6 μm), achieving >95% of theoretical density by 1700°C. Interestingly, the sintering curve of our nanocrystalline AlN powder followed closely with that of Hashimoto *et al.*'s AlN sample which attained the best sintering results in the literature [2]. Hashimoto *et al.* produced their powder by carbothermal nitridation of a mixture of basic aluminum chloride (BAC) and glucose. By carefully controlling the BAC:glucose ratio and the nitridation conditions, and using several post-synthesis oxidation and nitridation steps to remove the residual carbon and reduce the oxygen content, they were able to produce a sinterable powder with a moderate surface area (16 m^2/g) and a low oxygen content (1-2 wt%). The sintering results obtained with our nanocrystalline powder were excellent since even the best commercially available AlN powders would require several hours at 1900°C to obtain >95% of theoretical density in additive-free sintering.

X-ray diffraction and SEM Characterization

X-ray diffraction patterns for the nanocrystalline and H. C. Starck AlN samples sintered at 1900°C are shown in Figure 6. All peaks present corresponded to AlN. The fact that no secondary phases were detected suggested that either the oxygen content of these samples was below the solubility limit for oxygen in AlN, or the secondary phases were present at very low levels. Several authors have attempted to correlate the oxygen contents with crystallographic cell parameters. However, since the method of defect incorporation changes depending on the oxygen level, the cell parameters go through a maxima making oxygen determination via X-ray diffraction very difficult. The oxygen content of these samples, determined by fast-neutron activation analysis, will be reported later.

Scanning electron micrographs of the fracture surfaces of AlN pellets after sintering at 1600°C, 1700°C and 1900°C for two hours are shown in Figure 7. Samples were fractured, coated with gold, and examined using a JEOL 6320FV field emission gun scanning electron microscope. It was noted that the densification of nanocrystalline powders (Figures 7(a) and (b)) was superior to that of the commercial microcrystalline powders (Figure 7(c)). The grain growth of the nanocrystalline AlN was quite rapid so that when >90% of the theoretical density was attained, the grain size was on the order of 2-3 microns. The final grains were over 20 times larger than the initial grain size (<100 nm). Therefore, over 99.98 vol% of the AlN had crossed a grain boundary and been consumed by a growing grain during sintering. In contrast, the commercial AlN would have to grow to a final grain size of ~50 μm to achieve the same degree of material transport. Although this might be possible, the long diffusional paths and relatively slow diffusion rates meant that achieving a grain size of ~50 μm would take a very long time at high temperatures. This result suggested that if oxygen has to be at a grain boundary in order to be removed (by either an additive or a highly reducing atmosphere), then nanocrystalline AlN would have an important advantage in rapid processing of ceramics with low lattice oxygen contents.

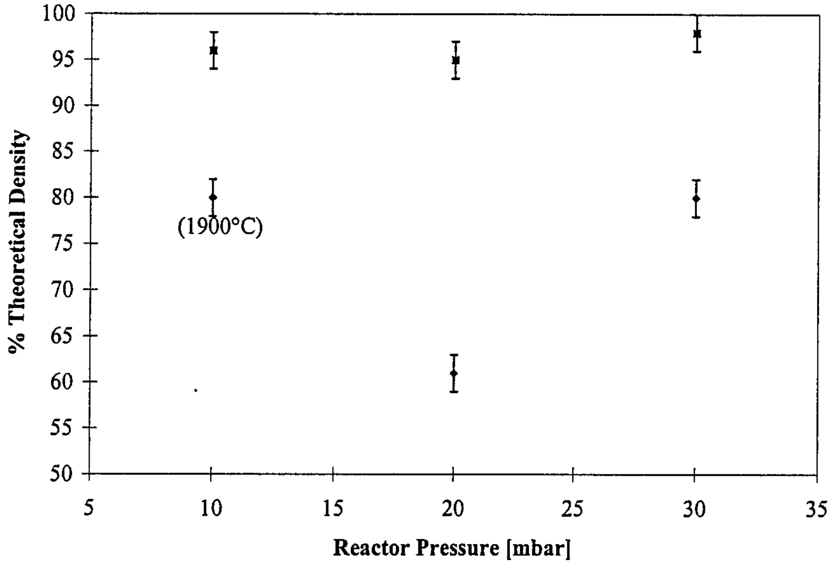

Figure 1. Effects of carrier gas and reactor pressure on the sinterability of nanocrystalline AlN powders. The carrier gas for in-situ nitridation synthesis was either (■) nitrogen or (◆) helium. All samples were pressurelessly sintered for two hours at 1700°C, unless otherwise indicated.

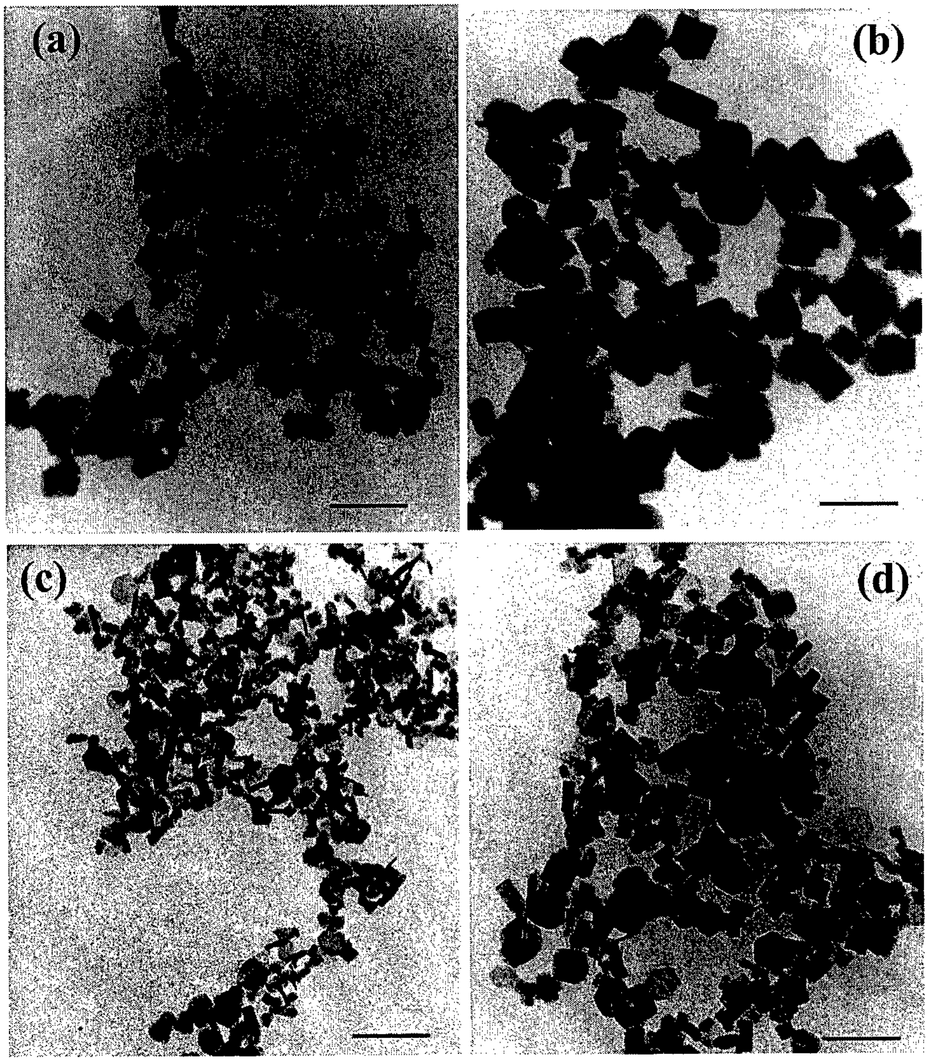

Figure 2. Transmission electron micrographs of nanocrystalline AlN powders synthesized in the forced-flow reactor via in-situ nitridation with NH_3. The powders were produced with (a,b) nitrogen or (c,d) helium as the carrier gas. The reactor pressure was 20 mbar for samples (a) and (c), and 30 mbar for samples (b) and (d). The scale bar is 100 nm.

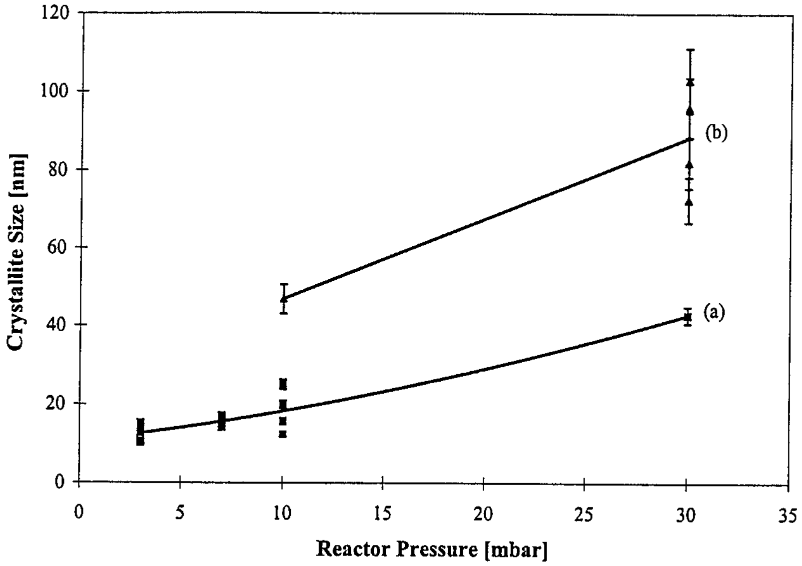

Figure 3. Crystallite sizes of AlN produced at various reactor pressures with (a) helium and (b) nitrogen as the carrier gas. The variability in the data was due to differences in the gas velocity used, and the increased error in Scherrer's analysis as the crystallite size approached 100 nm.

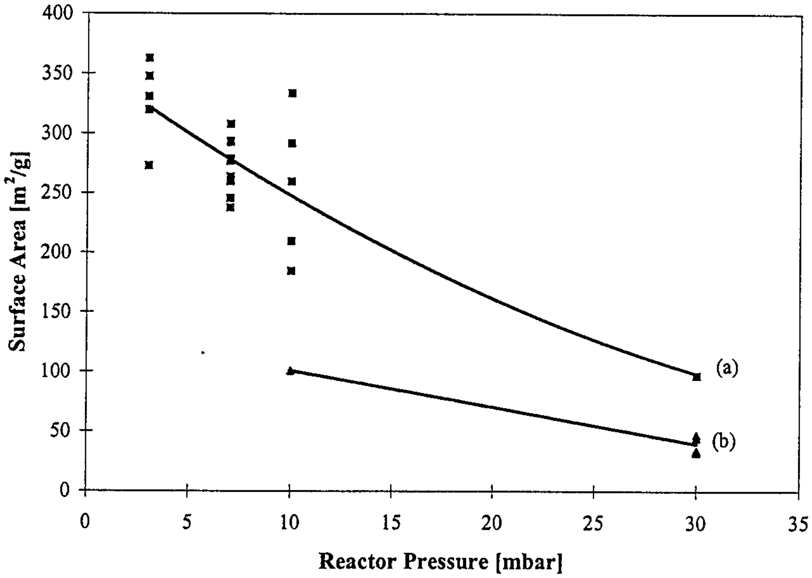

Figure 4. Surface areas of AlN produced at various reactor pressures with (a) helium and (b) nitrogen as the carrier gas. The variability in the data at a given pressure was due to differences in the gas velocity used.

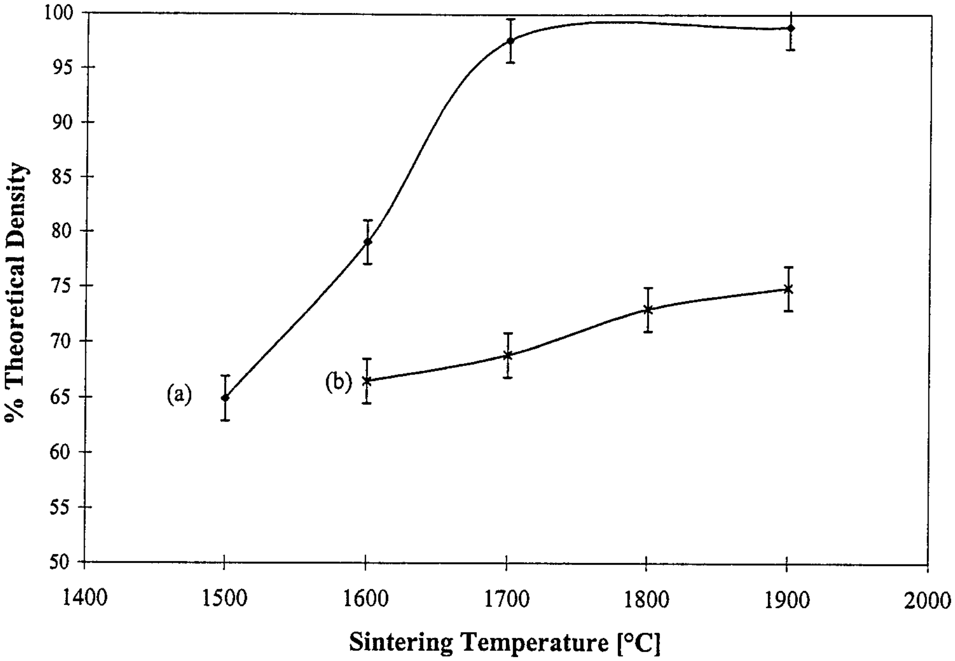

Figure 5. Pressureless, additive-free sintering curves of (a) nanocrystalline AlN (surface area = 44 m^2/g) and (b) H. C. Starck Grade B AlN. The samples were soaked at the sintering temperatures for 2 hours.

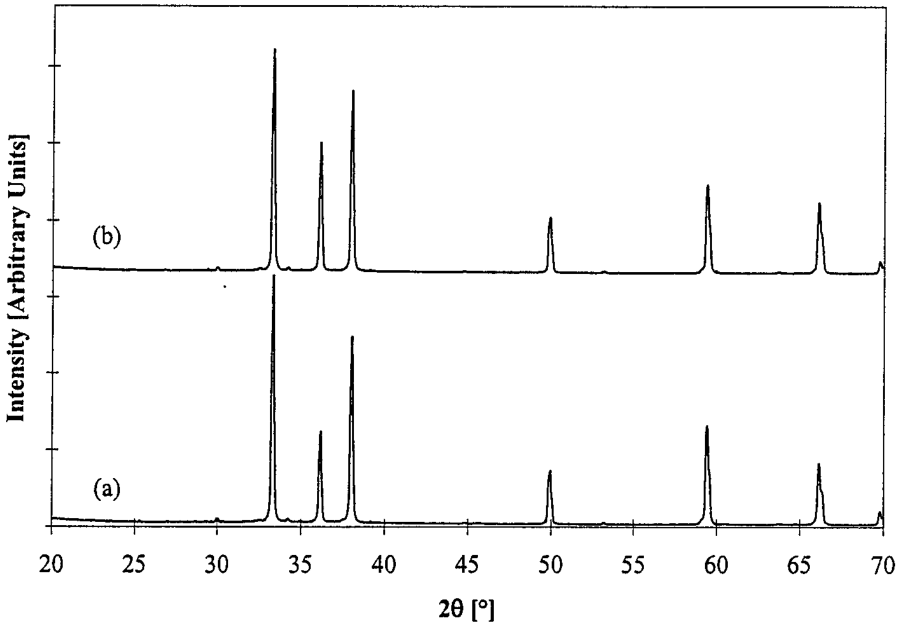

Figure 6. X-ray diffraction patterns of (a) nanocrystalline AlN and (b) H. C. Starck Grade B AlN after pressureless, additive-free sintering at 1900°C for 2 hours.

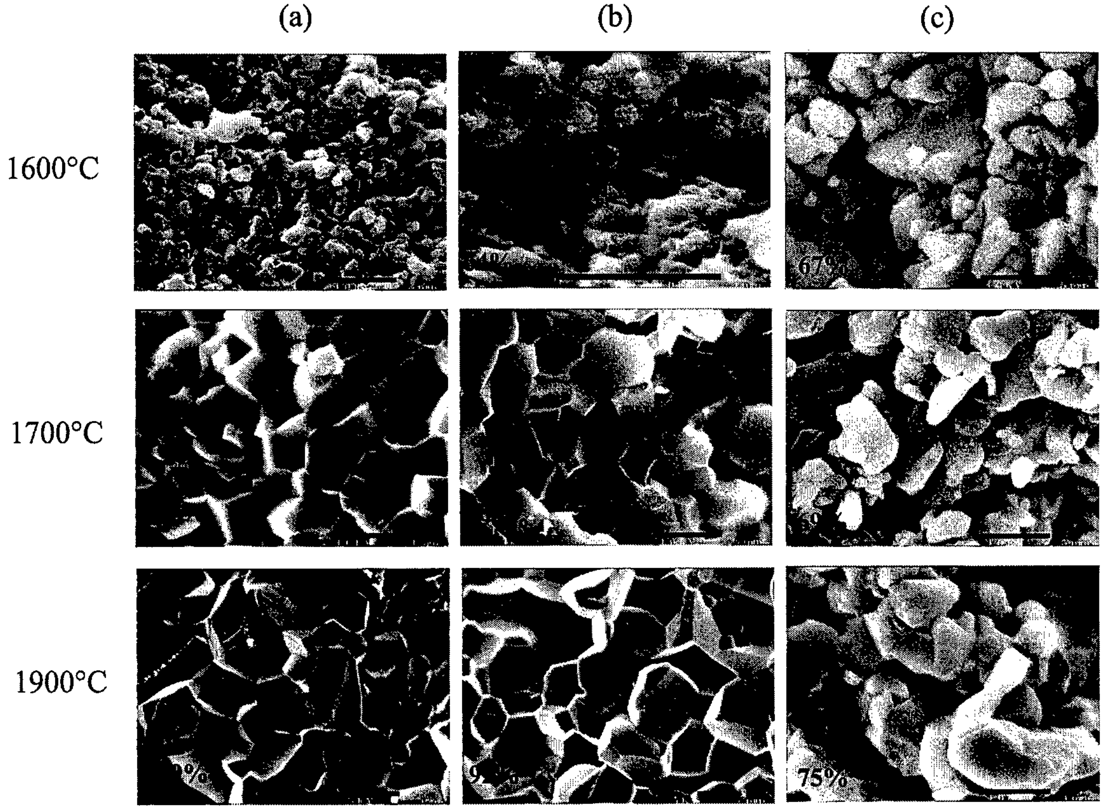

Figure 7. SEM micrographs of fracture surfaces for AlN pellets after pressureless sintering for 2 hours at the given temperature. Samples were prepared from (a) nanocrystalline AlN synthesized at 30 mbar, (b) nanocrystalline AlN synthesized at 10 mbar, and (c) commercial H. C. Starck Grade B AlN. The scale bar represents 1 μm; the % theoretical density attained during additive-free sintering of the samples is noted in the lower left corner of each micrograph.

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[1] J.Y. Ying, Technical Report on ONR Grant No. N00014-95-1-0626 for the period of July 1, 1998 – September 30, 1998.

[2] N. Hashimoto, H. Yoden, and S. Deki, "Sintering Behavior of Fine Aluminum Nitride Powder Synthesized from Aluminum Polynuclear Complexes," *J. Am. Ceram. Soc.*, **75** [8] 2098-106 (1992).