FINAL REPORT

**INVESTIGATION OF THE EFFECTS OF PRESSURE ON THE COMPACTION AND
SUBSEQUENT SINTERING OF NANOSIZE POWDERS**

February 26, 1996

Report Prepared by
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for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
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INTRODUCTION

When the grain size in a material is reduced to the scale of a few nanometers, it is anticipated that the material will exhibit novel properties reflecting the contribution from the highly increased grain boundary area. This is true because the fraction of atoms on interface sites becomes comparable to the number of atoms on lattice sites in a nanograined material. Many physical properties are expected to be enhanced as a consequence of this effect. Thus, in view of these expected enhanced properties, the overall objective of this program was to produce a nanograined material and to evaluate its microstructure. Silicon nitride was selected as the prime candidate because of its superior overall physical properties for optical, structural and high temperature applications, but other materials such as transitional aluminas were also studied.

With current technology and available raw materials, we now know that it is very difficult, if not impossible, to produce a monolithic ceramic material with an average grain size of less than 100 nm. The grains of ceramic materials cannot be refined by cold working as is typically done in metals. Hence, the starting ceramic powder must be of a smaller or similar particle size as the desired grain size for the final product. The availability of nanosize (< 100 nm) ceramic powders, however, is limited. In many cases, the powders consist of polymorphic mixtures, precursors, or amorphous phases of the desired material. Phase transformation during sintering is difficult to control, and when it does occur it usually is accompanied by significant microstructural changes and grain growth. An example of such a powder is Al_2O_3 . To the best of our knowledge, high purity nanosize $\alpha\text{-Al}_2\text{O}_3$ powder is unavailable commercially. However, a variety of nanosize transitional forms of Al_2O_3 , including the γ and δ polymorphs, are commercially available in large quantities as mixtures. Results on the compaction and sintering of nanosize $\gamma\text{-Al}_2\text{O}_3$ powder are reported below.

Densification and Sintering of $\gamma\text{-Al}_2\text{O}_3$

A significant amount of published research exists on the sintering of $\alpha\text{-Al}_2\text{O}_3$ from transitional aluminas. From experimental work, it appears that standard dry compaction and pressureless sintering of these transitional aluminas results in a porous vermicular-type structure which is extremely difficult to densify at relatively low sintering temperatures [1,4]. As a consequence, a number of different routes have been explored to achieve sintering and high density at relatively low temperatures while still maintaining fine grain size. For example, dense $\alpha\text{-Al}_2\text{O}_3$ ceramics were made by sintering transitional alumina green bodies seeded with α phase crystals at temperatures as low as 1200°C [1]. The resulting compacts had a grain size comparable to the seed size (100 nm to 400 nm). In that study, it was shown that seeding the

sol-gel boehmite system significantly reduced the boehmite-to- α phase transformation temperature, thereby inhibiting grain growth during the transition because of the lower temperature while still permitting α -phase sintering. However, in that study, minimum grain size was limited by the initial size of the α -phase seeds used. Another method of increasing the rate and lowering the temperature of the phase transformation in alumina was reported by Ishitobi *et al.*, [2], and later by Dynys and Halloran [3]. Ishitobi demonstrated that hot-pressing nanosize η - Al_2O_3 powder under pressures of several gigapascals significantly decreases the transformation temperature. Dynys and Halloran, on the other hand, showed that cold compaction of fine powders at different pressures also affects the transformation kinetics during subsequent pressureless sintering. The mechanisms by which pressure affects transformation temperatures and kinetics in Al_2O_3 are not clear. A synchro-shear model accompanied by a restacking of oxygen atoms for the γ -to- α transformation in the structurally related Fe_2O_3 system has been reported, however [4].

Finally, it is important to note that Yeh and Sacks [5] made dense alumina samples with small grain size from slurries of fine grain α - Al_2O_3 (200 nm to 300 nm) using conventional suspension techniques. The slurries were slip-cast into pellets of relatively high green density (69% of theoretical). These pellets were sintered at 1150°C to almost full density with very little increase in grain size. Their results also established that the polymorphic transformation is unnecessary to sinter α - Al_2O_3 at low temperatures. In the cases described above, the grain size of the sintered material was determined by the initial size of the seed or the starting powder used, which, in all instances, was greater than 100 nm.

From these earlier studies, three important conclusions can be drawn: (1) sintering can be achieved at low temperatures with fine starting powders; (2) densification at low temperatures can be achieved by avoiding the porous, vermicular structure which is formed during the phase transformation; and, (3) a reduction in the phase transformation temperature and kinetics can be achieved by the application of high pressure to the precursor powder in the fabrication of the green body.

OBJECTIVES

The objectives of the present work are to study the densification process and the microstructure that evolves from the γ -to- α transformation in nanosize γ - Al_2O_3 powder, and to show how they are affected by the magnitude of the initial compaction pressure used to fabricate the green body. From our earlier work, we know that at very high pressures (> 3 GPa), the development of a porous, vermicular structure during the γ -to- α transformation can be avoided entirely, and, as a result, a dense sample of α - Al_2O_3 can be sintered with a grain size of ≈ 150 nm. To explore this phenomenon further, we studied the effects of 1.0 GPa and 2.5 GPa compaction pressures on the consolidation and subsequent sintering of nanosize γ - Al_2O_3 powder.

EXPERIMENTAL PROCEDURES*

Materials

The nanosize γ - Al_2O_3 starting powder used in this work is Aluminum Oxide C, commercially available from Dugussa, AG, Geschäftsbereich Anorganische Chemieprodukt, Frankfurt, Germany. In an earlier study, the powder was found to consist of primarily γ phase with <10% by volume of δ phase, as determined by transmission electron microscopy (TEM) and x-ray diffraction (XRD) techniques [6]. The powder was also shown to consist of equiaxed particles with an average diameter of 20 nm. Typical of nanosize powders, it is strongly agglomerated. Moreover, even after compaction and heat treatment at 800°C, no evidence of necking or partial sintering was resolved by TEM. It appears that the agglomeration of the powder and/or integrity of the compact is essentially the result of strong van der Waals type surface forces.

Compaction

Green body samples of 3 mm diameter were made by dry, cold compaction of the powder to 1 GPa and 2.5 GPa utilizing a single-acting WC/Co piston/cylinder die. Specific details about the compaction procedures and equipment used are described elsewhere [7]. After compaction, samples were sintered in an alumina tube-furnace under vacuum. Samples were sintered at 1000°C, 1100°C, 1200°C, 1300°C, 1500°C and 1600°C for 5h, employing heating and cooling rates of 300°C/h. An estimate of bulk density of the green bodies and sintered bodies was calculated from the physical dimensions and weight of the fabricated disks, which were assumed to be perfect right circular cylinders. To further understand the densification process, optical microscopy, XRD, and TEM were used to characterize the microstructure of the samples.

To apply even higher compaction pressures to the alumina powder, additional samples were compacted in a diamond anvil high pressure cell (DAC). The nanosize γ - Al_2O_3 powder and a ruby sphere used as a pressure sensor were encapsulated in the DAC using an Inconel X750 gasket with a 250 μm hole. The DAC technique used here has been described extensively and no detailed description is given here [6,8]. The powder was dry compacted to (2, 3, 4, and 5) GPa. In some cases, liquid nitrogen (LN_2) was used as a lubricant to achieve a more homogeneous packing of the powder. Details on the effects of LN_2 also have been described previously [8]. Sintering of these samples was done at 1150°C for 1 and 2 h in air. Due to their small size, $\approx 150 \mu\text{m}$ - 200 μm in diameter, the DAC processed samples were characterized by SEM and energy dispersive x-ray methods.

RESULTS

Piston/Cylinder Compaction and Sintering

Sintering results for samples compacted in the piston/cylinder die to pressures of 1 GPa and 2.5 GPa are summarized in Figure 1. For both sample pressures, the sample bulk density increases

with sintering temperature over the range 1000°C to 1600°C. At sintering temperatures below 1300°C, the density of the samples compacted to 2.5 GPa was significantly higher than the 1 GPa samples. At 1300°C and higher, however, both compaction pressures produce essentially the same final density which is below theoretical density. Thus, even after heat treatment for 5 h at 1600°C, these compacts could not be sintered to full density. By comparison, commercial α - Al_2O_3 powder with a submicrometer particle size typically can be sintered to full density at 1600°C [9].

Figure 1. Bulk density of alumina compacts as a function of sintering temperatures for 1 GPa and 2.5 GPa green compaction pressures. The compacts were fabricated utilizing the 3 mm diameter piston/cylinder die. The estimated uncertainty in the density is indicated by the vertical lines associated with each measurement.

Figure 2 shows a TEM micrograph of a γ - Al_2O_3 green body compacted at 2.5 GPa. Both XRD and electron diffraction results confirmed that the grains are predominantly γ phase with an average size of 20 nm and an equiaxed morphology. Moreover, microstructural observations on samples compacted to 1.0 GPa and 2.5 GPa indicate a random dense packed particle structure with uniform interconnected porosity. For both compaction pressures, the pore dimensions were less than the particle size. The microstructural differences in packing density between the samples compacted at 1 GPa and 2.5 GPa could not be resolved by TEM.

XRD characterization was done on the sintered samples. The results indicated that samples sintered at 1100°C and higher for 5 h were completely converted to α phase for both 1 GPa and 2.5 GPa compaction pressures. Samples pressed to 2.5 GPa and sintered at 1000°C were also completely transformed to α phase. However, a mixture of γ and α phases was identified in the samples pressed to 1 GPa and sintered at 1000°C.

Figure 2. A TEM brightfield image shows the microstructure of a green body compact of nanosize γ - Al_2O_3 powder pressed to 2.5 GPa in the piston/cylinder die. X-ray and electron diffraction measurements confirm the existence of predominantly γ phase.

TEM examination of selected sintered samples confirmed the results of the effect of compaction pressure on densification during sintering as well as XRD characterization. Figures 3a and 3b compare the microstructures of samples sintered at 1000°C after compaction at 1.0 GPa and 2.5 GPa, respectively. The sample compacted at 1 GPa (Figure 3a) consists of a mixture of equiaxed particles of γ phase and isolated clusters of porous α phase grains each approximately 250 nm in size. At 1000°C, necking between γ particles, indicative of partial sintering, was not observed by TEM. Sintering of the porous α phase grains, however, was apparent and resulted in a spongy or vermicular structure with continuous porosity. By contrast, samples pressed to 2.5 GPa and sintered at 1000°C consisted of all α phase (Figure 3b), with a vermicular microstructure morphology and continuous porosity similar to the isolated α phase clusters in the 1 GPa pressed samples. It is evident from these results that increased compaction pressure can reduce the time required for complete transformation at 1000°C.

At higher sintering temperatures, as shown in Figure 4 for a 2.5 GPa compacted sample sintered at 1300°C for 5 h, significant porosity remains in the form of closed pores situated both interstitially and within the grains. Theoretical density was never achieved in these samples, regardless of compaction pressure or sintering temperature. In addition, the final grain size was of the order of several micrometers.

Figure 3. Brightfield images in TEM show the typical microstructure of γ - Al_2O_3 samples compacted in the piston/cylinder die and sintered at 1000°C for compaction pressures of (a) 1 GPa and (b) 2.5 GPa. The 1 GPa compacted sample consists of a mixture of γ phase particles (G) and isolated vermicular type clusters of α phase. (A) The 2.5 GPa compacted sample consists of all α phase with a vermicular microstructure morphology and continuous porosity.

Figure 4. The microstructure of the 2.5 GPa alumina sample compacted in the piston/cylinder die and sintered at 1300°C for 5 h. The morphology shows significant porosity (p) which was permanently trapped inside the grains preventing the attainment of full densification. Intergranular voids are designated by "v".

Compaction and Sintering in the DAC

To further investigate the effects of compaction pressure on the sintered structure, the nanosize alumina powder was compacted to even higher pressures of (3, 4 and 5) GPa utilizing a diamond anvil cell. For comparison with the piston/cylinder results, some samples were also compacted in the DAC to 2.1 GPa and sintered at 1150°C for 2 h. The sintering temperature was limited to 1150°C to avoid significant oxidation of the Inconel X750 gasket used in the DAC compaction arrangement. In agreement with the piston/cylinder results, samples compacted at 2.1 GPa developed an α phase vermicular microstructure as shown in Figure 5. Here, the morphology of the α phase grains and the distribution of porosity is similar to that seen in Fig. 3b. In contrast, the formation of this vermicular structure was completely eliminated in samples compacted at 3 GPa and higher. As illustrated in Figure 6, samples compacted to 3 GPa developed smaller grains having an equiaxed morphology after sintering at 1150°C. For sintered 3 GPa compacts, an average grain size of 223 nm was measured using the line intercept method on a plane of polish. The grain size distribution was fairly broad, however, with a breadth of distribution of 37 nm (one standard deviations). A volume fraction of porosity of 11% was measured from the micrographs by the point count method. Most of the resolved porosity appeared to be isolated at grain interstices.

Sintered samples precompact to 4 GPa had an even finer microstructure with less porosity than was found for the 3 GPa compacted sample as shown in Figure 7. These samples had an average grain size of 192 nm. Likewise, the grain size distribution was fairly broad, 22 nm (one standard deviations). Therefore, it is difficult to statistically assert a decrease in grain size at this compaction pressure. Nevertheless, the measured volume fraction of porosity also decreased to 7%.

Figure 5. Microstructure of an alumina sample compacted in a diamond anvil cell to 2.1 GPa and pressureless sintered at 1150°C for 2 h. The vermicular microstructure shown here agrees with results obtained for samples prepared in the piston/cylinder die for similar processing conditions.

Figure 6. Microstructure of an alumina sample compacted in the DAC to 3 GPa and pressureless sintered at 1150°C for 2 h. Under these processing conditions the formation of the vermicular structure was severely inhibited compared with the 2.1 GPa DAC compacted sample.

Figure 7. Samples compacted in the DAC at 4 GPa and pressureless sintered for 2 h at 1150°C, an example of which is shown here, exhibit even a finer microstructure and with less porosity than the 3 GPa compacted sample.

In a similar analysis of sintered 5 GPa compacted samples, the average grain size was determined to be 189 nm with a standard deviation of 26 nm, and the volume fraction of porosity was 7% (Figure 8). Pores are exclusively accommodated at grain interstices. As can be seen from the measured grain sizes, there is no statistical difference between the average grain size of the 4 GPa and 5 GPa compacted samples, nor was there a measurable difference in the volume fraction of porosity.

Figure 8. Microstructure of an alumina sample compacted at 5 GPa in the DAC and pressureless sintered at 1150°C for 2 h. This microstructure is similar to that found for the 4 GPa compacted sample shown in Fig. 8.

A series of samples compacted to 5 GPa were also sintered at 1150°C for 1 h to study the effects of time. Observations from these samples support the contention that once the α phase nucleates, the α grains grow rapidly. For these samples, the average grain size within the central portion of the sample did not decrease significantly by reducing the sintering time to 1 h (Figure 9a).

Here though, it can be noted that sintering for only 1 h did not result in a uniform microstructure. As illustrated in Fig. 9, the center of the sample, Figure 9a, exhibits an average grain size of (181 ± 21) nm (one standard deviation), whereas areas near the edge of the sample, Figure 9b, had an average grain size of (144 ± 16) nm. In these peripheral areas, the grain size distribution is very uniform and porosity was not resolved, suggesting that a more uniform stress distribution was developed in these regions during green body compaction. The existence of these uniform areas also suggests that it may be possible to develop a uniform microstructure by a suitable high pressure compaction process. Thus, in an effort to promote a uniform stress distribution throughout the green body, a series of samples was compacted under liquid nitrogen (LN_2), which acts as a lubricant to reduce interparticle friction thereby increasing packing density [8].

Figure 9. Microstructures for alumina compacted in the DAC at 5 GPa and sintered at 1150°C for 1 h. (a) at the center of the sample, (b) at the edge or circumference of the sample. In (b) the grain size is much finer and more uniform than in (a) suggesting that stress distribution plays an important role in determining grain-size.

Samples compacted in the DAC under LN_2 and sintered at 1150°C for 1 h exhibited an even more uniform grain size population than was obtained under dry compaction conditions as shown in Figure 10. Average grain size was found to be (146 ± 15) nm (one standard deviation) and porosity was not resolved. In contrast with the samples compacted under dry conditions at room temperature, the average grain size is uniform throughout the entire cross-section of the sample. This result provides additional evidence of the lubricating properties of LN_2 on the compaction of nanosize powders. The microstructure of this sample indicates a substantial population of grains well below 100 nm in size, an observation not made with the same frequency in the dry compacted samples.

DISCUSSION

Compaction and Sintering

Dry compaction of nanosize powders to high packing densities is inherently difficult. High pressure is usually necessary to overcome surface forces and to promote sliding and rearrangement

of the particles. In our work with γ - Al_2O_3 , compaction pressures higher than 0.5 GPa were necessary to obtain green body structural integrity. In addition, samples compacted to pressures of 1 GPa and higher were typically translucent to visible light indicating that porosity is homogeneously distributed on a fine scale. As expected, green density increased with increased compaction pressure. The highest green density attained in the piston/cylinder die was $\approx 65\%$ of theoretical. The pressure required to do this was 2.5 GPa, the maximum achievable pressure for the piston/cylinder apparatus.

Figure 10. Microstructure for alumina sample compacted at 5 GPa under LN_2 in the DAC and pressureless sintered for 1 h at 1150°C . The microstructure observed here is finer and more uniform than that obtained for any other sample in our experiments. The result confirms that LN_2 does, indeed, act as a lubricating medium to achieve full densification of the nanosize powder with a minimum stress distribution in the green body.

Proposed nucleation grain-growth mechanism

The results of this study show that a vermicular α -phase microstructure forms when γ -alumina samples compacted at pressures below 2.5 GPa are sintered at low temperatures. The vermicular microstructure consisted of interconnected individual grains, ranging in size from about 100 nm to nearly 300 nm and relatively high volume fraction of both closed and open porosity. As illustrated in Figure 3b, where regions of dark contrast define areas of common orientation, the grains have a complex morphology. Furthermore, careful study of the microstructure in TEM revealed that the size of the vermicular grains is related to the compaction pressure. For the same sintering conditions, the α phase grains are typically larger in samples compacted at 1 GPa as compared to samples compacted at 2.5 GPa. These results suggest two things: (1) the transformation is nucleation limited, and, (2) the density of nuclei increased with increased compaction pressure. For example, the results indicate that low compaction pressures create a smaller number of nucleation sites where the transformation initiates. These nuclei grow very fast forming vermicular clusters that consume all adjacent γ phase particles. The clusters stop growing when they impinge on each other. Thus, the size of the vermicular structured grains is determined by the number of

nuclei created during compaction. Because more nuclei are created at higher compaction pressures and grain growth is constrained by grain impingement, the size of the vermicular grains is reduced. Following this same line of reasoning one expects that at even higher pressures each particle can act as an individual nucleation site and transformation can occur within each particle, thus avoiding the formation of the vermicular structure entirely. This proposed growth mechanism is illustrated in the schematic drawing shown in Figure 11. At low compaction pressures (Figure 11a), a few particles initiate transformation and grow into a vermicular microstructure. At high pressures (Figure 11b), each individual γ particle, in principle, can transform to the α phase, thus avoiding the vermicular microstructure. Furthermore, Chou and Nieh [10] indicate that the close lattice match between selected crystallographic planes of γ and α phases of Al_2O_3 suggest that growth can proceed with minimal rearrangement of atoms, which might explain the explosive growth of α phase during the γ -to- α transformation.

Figure 11. Proposed nucleation growth mechanisms for low and high pressure compaction to form the green body.

As one might expect, densification of the porous, vermicular microstructure at low temperatures is very difficult because the pore geometry and radius of curvature is unfavorable for pore closure. For pressureless sintering, temperatures higher than 1300°C were found to be necessary to initiate densification of the vermicular structure.

Compaction and Sintering in the DAC

Results of compaction in the piston/cylinder die suggested that higher pressures might be necessary to avoid formation of the vermicular structure. Therefore, we compacted the nanosize powder to even higher pressures of (3, 4 and 5) GPa utilizing a diamond anvil cell. The results show that at a compaction pressure of 3 GPa and sintering at 1150°C, the formation of the vermicular structure can be avoided completely. The results from both the piston/cylinder arrangement and the DAC are summarized in Table 1. The vermicular structure can be avoided by compaction to pressures higher than 2.5 GPa and pressureless sintering at 1150°C. In addition, the higher the compaction pressure the smaller the grain size in the microstructure of the final sintered body.

Table 1

Compact Pressure (GPa)	Sintering Temperature (°C)	Sintering Time (h)	Al ₂ O ₃ Polymorph	Grain Size
1	1000	5	γ & α	-
2.5	1000	5	α	-
2.5	1300	5	α	> 1000 nm
3*	1050	2	α	223 ± 37 nm
4*	1050	2	α	192 ± 22 nm
5*	1050	2	α	189 ± 26 nm
5* (LN ₂)	1050	1	α	144 ± 16 nm

* Compaction in DAC

The grain size of these samples, however, is not comparable to the original particle size of the γ -Al₂O₃ powder. If we consider the size of each individual grain in these high pressure compacted samples, each one constitutes a combination of roughly 1500 γ phase particles. During transformation, these particles must sinter fairly rapidly, because no grain entrapped porosity was observed. The result suggests a strong driving force for the necessary transport processes for densification even at the relatively low sintering temperature of 1150°C. The initial explosive growth slows down fairly rapidly once a grain size of 100 nm to 200 nm is achieved. This behavior can be explained by considering the driving force for sintering. If the only driving force in these samples is proportional to $2E_s/r$, where E_s is the surface free energy and r is the radius of curvature of the boundary surfaces, it is clear that the initial driving force for sintering can be very high for a 20 nm particle size. As grains grow, the driving force decreases and the rate of grain growth is reduced significantly, explaining why it is possible to have densification at 1150°C in a relatively short time. The large distribution of grain sizes probably occurs as a result of a nonuniform distribution of nucleation sites created during compaction. This behavior is expected since large density gradients are created during

dry compaction of powders. Furthermore, the high surface area of nanosize powders makes interparticle friction more relevant and homogeneous compaction more difficult. However, as demonstrated, compaction under liquid nitrogen can reduce interparticle friction resulting in a more homogeneous and finer microstructure.

These results lead us to the conclusion that average grain size can be reduced further, perhaps by applying even higher pressures or by mechanically inducing strain in the powder prior to compaction. Obviously, applying pressures of several GPa is impractical for industrial purposes, but milling the powder may be a sensible alternative approach.

Processing of Nanosize Silicon Nitride Powder

We continued our work on the processing of nanosize amorphous Si_3N_4 powder by high pressure compaction methods. In our present studies, we used a newly prepared amorphous Si_3N_4 nanosize powder provided by Richard R. Buss of Sandia National Laboratory. According to Dr. Buss, the powder was prepared using special procedures designed to produce a high purity, stoichiometric nanosize powder. With this new powder we were able to fabricate transparent green compacts using 1.5 GPa, a pressure much lower than the 3 GPa to 5 GPa required for achieving transparency in our earlier experiments with a different material source. The substantially lower compaction pressure needed to achieve transparency is attributed to the new material's high purity and improved stoichiometry. The powder was compacted at room temperature into 3 mm diameter disks about 0.6 mm thick in a piston/cylinder die apparatus. To study the sintering behavior of the transparent Si_3N_4 compacts, the green samples were sintered at (1200, 1300, 1400 and 1500) °C for 5 h in N_2 . The bulk density of these compacts increased from 1.41 g/cm³ to 1.73 g/cm³ with increasing sintering temperature as shown in Figure 12. The maximum density obtained corresponds to about 60% of the theoretical density of amorphous Si_3N_4 . The samples sintered below 1500 °C remained transparent with no evidence of crystallization. Above 1500 °C partial crystallization occurred resulting in an opaque material. Preliminary infrared absorption measurements on these sintered samples suggest a correlation between sintering temperature and the degree of transmittance, particularly between 3750 cm⁻¹ and 7000 cm⁻¹. The microstructure and hardness of these compacts are presently being studied.

Figure 12. Bulk density of Si_3N_4 compacts as a function of sintering temperature. Sintering time was 5 h under N_2 . Vertical lines for each point indicated the estimated uncertainty in the density measurement.

CONCLUSIONS

The compaction pressure on nanosize $\gamma\text{-Al}_2\text{O}_3$ powder has an enhancing effect on: (1) the green body density, and (2) the γ -to- α transformation rate and temperature of transformation. In general, samples compacted in the piston/cylinder die to 1 GPa and sintered at temperatures below 1300°C yielded consistently lower bulk densities than the samples pressed to 2.5 GPa and sintered at the same temperatures. The density of both samples approached the same value ($\approx 3.2 \text{ g cm}^{-3}$) for sintering at temperatures near 1300°C. For these samples, full density was never attained even at higher temperatures. In contrast to these results, the microstructures of samples compacted in the DAC to pressures higher than 3 GPa and sintered at 1150°C for 1 h show very limited porosity. In addition, these samples maintained a small grain size. These results demonstrate that high pressure compaction alone can create a sufficient number of nucleation sites to inhibit the formation of the vermicular structure which normally follows the γ to α transformation of Al_2O_3 .

In summary, the results on γ - Al_2O_3 powder demonstrate that green body density increases with increasing compaction pressures. For compaction pressures less than 3 GPa, microstructures containing significant porosity developed at all sintering temperatures studied. This result is due to the development of a highly porous or vermicular structure during the γ -to- α phase transformation, which occurs at temperatures of 1000°C to 1150°C. At higher compaction pressures (> 3 GPa), however, the formation of the vermicular structure was avoided and near theoretical densities (estimated from SEM micrographs) with grain size > 150 nm were obtained.

Concerning the processing of nanosize amorphous silicon nitride, transparent green compacts were prepared by compaction of the powder to 1.5 GPa, a pressure much lower than the 3 GPa to 5 GPa required for achieving transparency in our earlier experiments with a different material source. Unlike previous powders studied, the present material was heat-treated in a reducing atmosphere of excess ammonia to remove unwanted species produced during synthesis. Thus, it appears that compaction behavior of silicon nitride powder is strongly related to purity and stoichiometry. Nevertheless, even the transparent compacts fabricated here never sintered to full theoretical density.

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