Sintering of nanopowders of amorphous silicon nitride under ultrahigh pressure

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(Received 17 May 1999; accepted 31 January 2000)

Nanopowders of amorphous silicon nitride were densified and sintered without additives under ultrahigh pressure (1.0–5.0 GPa) between room temperature and 1600 °C. The powders had a mean diameter of 18 nm and contained ~5.0 wt% oxygen that came from air-exposure oxidation. Sintering results at different temperatures were characterized in terms of sintering density, hardness, phase structure, and grain size. It was observed that the nanopowders can be pressed to a high density (87%) even at room temperature under the high pressure. Bulk Si_3N_4 amorphous and crystalline ceramics (relative density: 95–98%) were obtained at temperatures slightly below the onset of crystallization (1000–1100 °C) and above 1420 °C, respectively. Rapid grain growth occurred during the crystallization leading to a grain size (>160 nm) almost 1 order of magnitude greater than the starting particulate diameters. With the rise of sintering temperature, a final density was reached between 1350 and 1420 °C, which seemed to be independent of the pressure applied (1.0–5.0 GPa). The densification temperature observed under the high pressure is lower by 580 °C than that by hot isostatic pressing sintering, suggesting a significantly enhanced low-temperature sintering of the nanopowders under a high external pressure.

I. INTRODUCTION

Silicon nitride ceramics (Si_3N_4) have superior physical, chemical, and high-temperature mechanical properties and have become one of the most studied advanced ceramics, as an important candidate for a variety of technical and engineering applications. Common dense Si_3N_4 polycrystalline materials are generally fabricated by liquid-phase sintering of powders with the addition of various sintering aids (such as Al_2O_3, Y_2O_3, Yb_2O_3, ZrO_2, etc.) at high temperature (1750–2000 °C). The existence of metallic glass phases at grain boundaries resulting from the additives greatly impairs the high-temperature mechanical properties of the materials.[1,2] Thus, the sintering of Si_3N_4 ceramics without additives is an important approach to reducing impurity phases in the sintered bodies and hence achieving Si_3N_4 ceramics with the intrinsic properties of the materials. Studies have shown that Si_3N_4 ceramics free of additives that were densified under high pressure exhibited improved mechanical and high temperature compared to those sintered with additives.[3]

Si_3N_4 ceramics cannot be densified in their "pure" state using traditional sintering routes, owing to their strong covalent bonding and much lower bulk diffusion rate. However, they can be densified under ultrahigh high pressure (UHP) (>1.0 GPa) and hot isostatic pressing (HIP), which were conducted by several groups of researchers.[3–7] Prochazaka *et al.*[4] and Yamada *et al.*[5] sintered Si_3N_4 powders at 5 GPa between 1500 and 1600 °C and observed that the densification behavior of the materials strongly depended on powder composition and phase structure. They observed that crystalline Si_3N_4 powders (α phase) were densified to a near full density under the conditions, but the amorphous powders with a stoichiometric composition exhibited poor sintering behavior.[4,5] The reason the amorphous powders were poorly sintered was not discussed.

In the above UHP sintering studies, common coarse particles (micrometers or submicron in diameters) were used as the starting powders. Densification of nano-size ceramic powders by the UHP method, as a main route to

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produce bulk nanophase ceramics, has received increasing interest in recent years and has been applied to a variety of ionically bonded oxide nanoceramics (such as TiO_2, ZrO_2, ZnO_2, etc.).[8,9] However, relatively less work has concentrated on densification of the covalent Si_3N_4 nanoceramics under ultrahigh high pressures. Recently, a HIP method was used to sinter amorphous Si_3N_4 powders by Symons and Danforth *et al.*[10–12] The densification of the powders was observed at very high sintering temperature (2050 °C) in this process, and such high temperature is unfavorable for the control of grain growth. Thus, application of higher pressures is expected to reduce the sintering temperature of the materials. Pechenik *et al.*[13,14] recently pressed nano Si_3N_4 powders by diamond anvil at 5.0 GPa from liquid-nitrogen temperatures to 500 °C and reported the formation of transparent amorphous Si_3N_4 samples by the cryogenic densification. However, densification of the nano-size powders at higher temperature under ultrahigh high pressure has not yet been reported.

Because the nano-size Si_3N_4 powders are generally present in amorphous form, obtaining crystallized ceramics requires sintering at least above the crystallization temperature (>1000–1300 °C). On the other hand, sintering the amorphous powders below the crystallization temperature may generate bulk amorphous ceramics. In the present work, we report densification of nanosize powders without additives under ultrahigh pressure (1.0–5.0 GPa) between room temperature and 1600 °C. The sintering results obtained at different temperature regimes are presented, and the behavior of densification and grain growth were investigated.

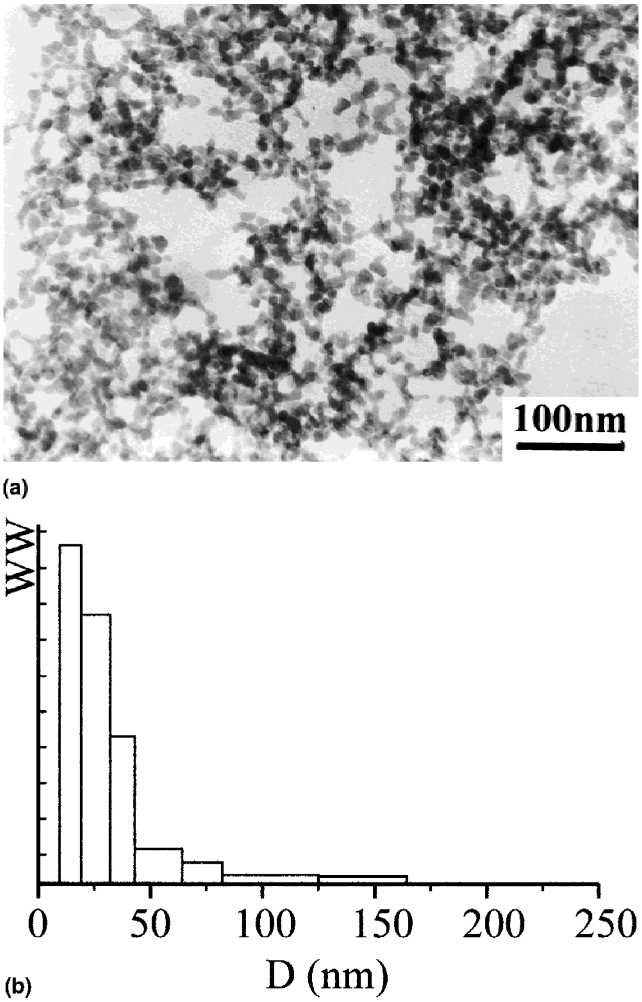

FIG. 1. (a) TEM micrograph and (b) particulate distribution [obtained by small-angle x-ray scattering (SAXS)] of the starting amorphous Si_3N_4 nanopowders.

II. EXPERIMENTAL

A. Starting powders

The starting Si_3N_4 powders were produced by laser-induced vapor phase reactions from a mixture of silane and ammonia gases. Synthesis of the powders was carried out on a 5-kW CO_2 laser-assisted powder synthesis reactor with a yielding ability of 1 kg/day that was established in the Institute of Metal Research, Chinese Academy of Sciences. The synthesis principle is similar to that reported previously in detail by Cannon *et al.*[15,16] The powders are amorphous as checked by x-ray diffraction (XRD) and have a Brunauer–Emmett–Teller (BET) specific area of 109 m^2/g. The mean particle diameter was calculated to be 18 nm using the equation $d = 6/(\sigma\rho)$, where σ denotes the BET specific area and ρ represents the solid density of the amorphous Si_3N_4. The solid density of the amorphous Si_3N_4 powders was determined by pycnometry which is equal to 2.90 g/cm^3 as reported previous.[10] The BET-derived diameter is in good agreement with the particle size estimated by transmission electron microscopy (TEM) observation which is in range of 15–20 nm [Fig. 1(a)]. Small-angle x-ray scattering (SAXS) measurements showed that the particle diameter was distributed in a very narrow range below 50 nm [Fig. 1(b)]. The powders were pure white in color. Elemental analysis gave compositions (wt%) of Si 57, N 37.2, and O 5.8. The oxygen and nitrogen contents were determined by melt extraction method using a He and infrared (IR) detection (LECO TC 436 Nitrogen/Oxygen Determinator) with a standard deviation of <1%. The elemental compositions of the powders correspond to a Si/N ratio of 1.5, which is equal to that for stoichoimetric Si_3N_4. The appreciable amount of oxygen in the powders resulted from a hydrolysis reaction between the silylamino groups on the surface of as-synthesized powders and water vapors as the powders were exposed in the air.[10,17] The reaction is extremely pronounced for the powders of nano-sizes due to their very large specific area, which resulted in an oxygen content of 5.8 wt% in the powders after 0.5 year of storage in air. However, other metallic impurities in the powders are below ppm level. The low level of metallic impurities is one of many superior properties of the laser-synthesized nanopowders.[15,16]

B. Compaction, sintering, and characterization

The amorphous Si_3N_4 nanopowders were shaped using a pistol-cylindrical mold under uniaxial pressing prior to the high-pressure experiments. The shaped powder compacts were subsequently densified and sintered on a cubic-anvil pressure apparatus which can generate a pressure in range of 1–10 GPa. The cubic-anvil (WC), as used in the present study, has a larger pressure cell than that of diamond anvil cell (DAC), as used by Pechenik *et al.*[13] in their studies, hence allowing processing of relatively larger sized samples. Also, the cubic-type anvil can generate pressures more uniform in the pressure cell than that of the uniaxial pressure by the diamond anvil cell, which is expected to enhance densification of powders during pressing. For the shaping and compacting experiments, all the procedures were conducted in air without outgassing. About 3 g of each powder batch was pressed (400 MPa) in a stainless steel mold to form a cylindrical pellet 15 mm in diameter and 17 mm in height which fit the size of the high-pressure cell. The precompacted columns were then inserted in a graphite sleeve and capped with graphite discs at each end. The graphite sleeve was used as a heater during sintering. The sample was then placed inside a bulk pyrophyllite which served as solid pressure-transmitting medium during pressing. Sintering was done by first applying pressure to 1.0–5.0 GPa, raising the temperature, holding at the temperature for 30 min, and then turning off the heater and unloading. The temperature inside the pressure cell was detected by a 30 RhPt–6% RhPt thermocouple. The temperature in the pressure cell was calibrated against an electric current for heating that was actually monitored to control sintering temperatures (±20 °C). Pressure was calibrated by the standard method using the phase transition points of Bi, Ti, and Ba with a reading deviation of ±0.2 GPa.[18]

Samples sintered at various pressures and temperatures were cut and polished using 1-μm diamond paste and were then characterized in term of bulk density, phase composition, grain size, and hardness. Density was measured according to Archimedes' principle using water as the liquid medium. The density of porous or cracked samples was measured after coating a thin layer of organic resin to prevent water penetration into the samples during the measurements. Phase structure was identified by x-ray diffraction (Perkin D/max-rA diffractometry) using Cu K_α radiation. Grain size was calculated from the line broadening of the diffraction peaks (301), for α and (411) for β phases, according to the Scherrer equation ($D = 0.89\lambda/\beta \cos \theta$).[19] Hardness was performed on polished surface of specimens on a digital microhardeness tester (Micromet 11, Buehler Ltd. USA) under loading of 0.2–1.0 kg with a duration of 10 s. Ultraviolet and visible (UV/VIS) transmission spectra of the translucent/transparent specimens of Si_3N_4 glass obtained by pressing were recorded on the UV/VIS spectroscopy (model 721, Shanghai). The samples for the spectra measurements were a pellet of the sintered Si_3N_4 (2–5 mm thick) with two polished surfaces.

III. RESULTS AND DISCUSSION

A. Compacting at room temperature

The amorphous Si_3N_4 nanopowders were first pressed at room temperature (~25 °C) between 1.0 and 5.0 GPa in order to study their compaction behavior without heating. It was observed that the powders can be densified to a high density even at room temperature under the high pressure. Two typical pressing results, together with those sintered at high temperature, are listed in Table I. A bulk density of 2.49–2.53 g/cm^3 was obtained for the compacts pressed between 1.0 and 5.0 GPa for 30 min. The corresponding relative density is between 84 and 87%, taking 2.90 g/cm^3 as the solid density of the amorphous Si_3N_4 as determined by He pycnometry.[10–12] This compact density is much higher than the theoretical

TABLE I. Typical results on the densification and sintering of the amorphous Si_3N_4 nanopowders under high pressure.

Samples	Pressure (GPa)	Sintering temp. (°C)	Sintering density (g/cm^3)	Relative density[a] (%)	Phase composition (XRD)	Sample appearance
1	1.5	25	2.49 ± 0.05	84	Amorphous	Brown opaque
2	5.0	25	2.53 ± 0.05	87	Amorphous	Brown translucent
3	5.0	850	2.63 ± 0.03	90	Amorphous	Brown translucent
4	5.0	950	2.75 ± 0.03	95	Amorphous	Brown translucent
5	5.0	1000	2.95 ± 0.02	93	α phase	Dark opaque
6	5.0	1300	3.01 ± 0.01	95	$\alpha + \beta$	Gray opaque
7	5.0	1420	3.02 ± 0.01	93	β phase	White opaque

[a] Calculated using 2.90 g/cm^3 as theoretical density of amorphous sample and 3.18 g/cm^3 as that of crystalline Si_3N_4.[10]

packing density of 74% for equal-size, closely packed hard spheres, which indicates the occurrence of significant plastic deformation of the nano-size particles under the high pressure. It was observed that the green bodies compacted at room temperatures exhibited strong bonding characteristic and can be ground and polished to form a mirrorlike surface. Figure 2(a) shows the appearance of one specimen which was obtained by pressing at 5.0 GPa for 30 min. It is noted that, after the pressing, the samples changed their appearance from the off-white color of the starting powders to brown or light brown ones. Vicker hardness measurements performed on the polished surface of a compact pressed at 5.0 GPa gave hardness values in the range of 710–752 kg/mm^2. The high compaction density and the strong bonding characteristics of the nano-size powder compacts formed under the high pressure are not exhibited commonly by Si_3N_4 green bodies pressed from coarse powders, indicating the enhanced densification behavior of the nanosize powders under a high external pressure.

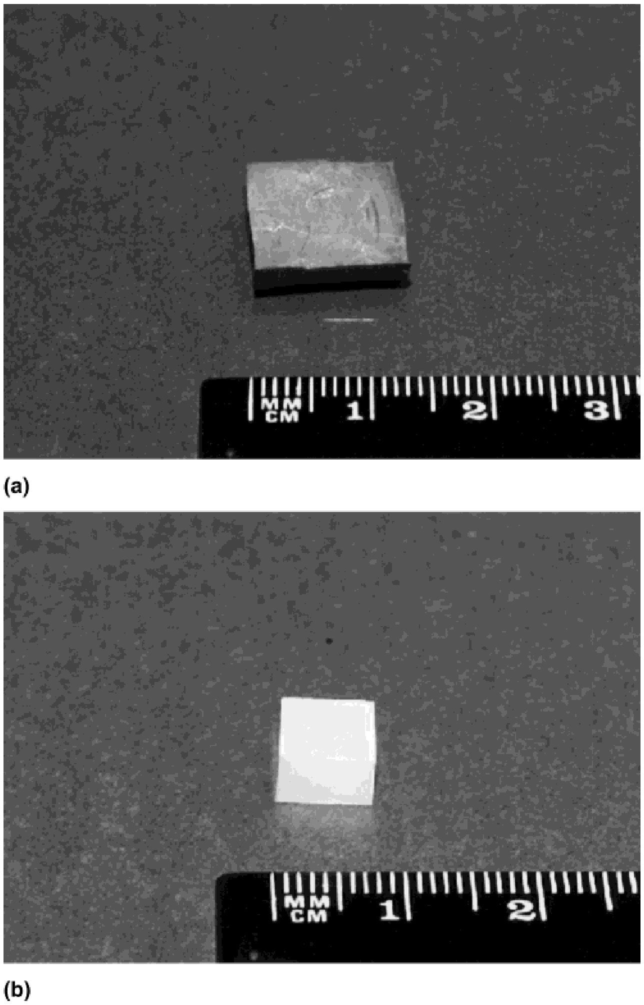

FIG. 2. (a) Appearance of the amorphous Si_3N_4 compacts pressed from the amorphous Si_3N_4 nanopowders at 5.0 GPa at room temperature for 30 min and (b) the crystalline Si_3N_4 (β phase) sintered at 1420 °C at 5.0 GPa for 30 min. Note the pure white color of the sintered and crystallized Si_3N_4 ceramic, which is a result of nonadditive sintering and differs from the normal gray or dark-gray color of sintered Si_3N_4 with additives.

Pechenik *et al.* pressed laser-synthesized amorphous Si_3N_4 powders by a diamond anvil at 5.0 GPa using liquid nitrogen as lubricants and obtained transparent Si_3N_4 specimens, from which they deduced that a high density was achieved in the compacted amorphous Si_3N_4 ceramics.[13] But no compact density was reported, perhaps due to the small size of their specimens (0.15 × ϕ 0.2 mm), precluding a routine determination of the compact density of the specimens. The amorphous samples pressed in the present study at room temperature were not transparent in appearance. But the hardness value (710–752 kg/mm^2) is nearly equal to, and even slightly higher than that, ~700 kg/mm^2, of their cryogenically pressed amorphous Si_3N_4 materials. Also, the hardness of our amorphous Si_3N_4 ceramics (710–752 kg/mm^2) is significantly higher than that of the compacts pressed by Pechenik *et al.* at room temperatures at 5.0 GPa (~450 kg/mm^2). The enhanced densification at room temperature in our case was probably ascribed to the application of cubic-anvil pressure, which could generate “quasi-isostatic” pressure and hence promoted interparticle sliding during densification, compared with the uniaxial pressure as used by Pechenick *et al.*[13]

B. Sintering below crystallization temperature (<1000-–1100 °C)

Sintering experiments were done between 500 and 1600 °C under 1–5 GPa. XRD identified that sintered specimens obtained below 1000–1100 °C remained amorphous. The sintered density of the amorphous specimens obtained between 800 and 950 °C was between 2.63 and 2.75 g/cm^3, depending on sintering temperatures (Table I). A sintered density of 2.75 g/cm^3, obtained at 950 °C at 5.0 GPa, corresponds to a relative density of 95%. This high relative density indicates that the nano-size powders can be almost fully densified below the crystallization temperature under sufficient high pressure. Therefore, bulk Si_3N_4 amorphous ceramics can be formed at sintering temperatures slightly below that of the onset of crystallization. The Vicker hardness of the amorphous Si_3N_4 bodies sintered between 800 and 950 °C was determined to be in the range of 830–1206 kg/mm^2, depending on sintering temperatures.

Interest in the bulk amorphous Si_3N_4 arises in part from its optical transmittance. As mentioned above, Pechenik *et al.*[13,14] pressed amorphous Si_3N_4 nanopowders at 5.0 GPa at liquid-nitrogen temperature and observed the formation of transparent amorphous Si_3N_4 under this condition. In our case, the dense amorphous compacts obtained at room temperature are opaque. But the amorphous materials pressed between 800 and 950 °C at 5.0 GPa are visibly translucent (2–5 mm thick). The lack of transparency for our materials may be due to the larger dimensions of our specimens (2–5 mm thick) than those demonstrated by Pechenik *et al.* (0.1 mm thick).[14] It was observed that the degree of transparency increased with sintering temperatures between 25 and 950 °C and changed with powder compositions: low oxygen powders (2.0 wt% oxygen) and Si-rich powders gave less translucent or opaque specimens. The amorphous Si_3N_4 ceramics obtained at 950 °C at 5.0 GPa were characterized by UV/VIS absorption spectrum in the wavelength ranging from 250 to 850 nm, showing a gradually decreased absorption with the increasing wavelength above 450 nm. The absorption behavior is similar to that shown by Pechenik *et al.* for their cryogenically compacted specimens.[14] Furthermore, an optical transmission spectrum between wavelength of 250 and 850 nm was recorded for a translucent amorphous Si_3N_4 plate (2 mm thick), which shows an increasing transmission above wavelength of ~450 nm, with a transmittance attaining ~85% at 850 nm (Fig. 3).

C. Sintering above crystallization temperature (>1000 °C)

1. General sintering results

Crystalline Si_3N_4 specimens were obtained when sintering temperature was above 1000 °C. XRD analysis revealed that the specimens sintered between 1000 and 1100 °C at 5.0 GPa contained predominately α–Si_3N_4 phases with β as a minor phase. At $T = 1100$ to 1420 °C, a mixture of α and β phase was obtained, and at $T > 1350$ to 1420 °C, the sintered bodies were almost entirely β phase.

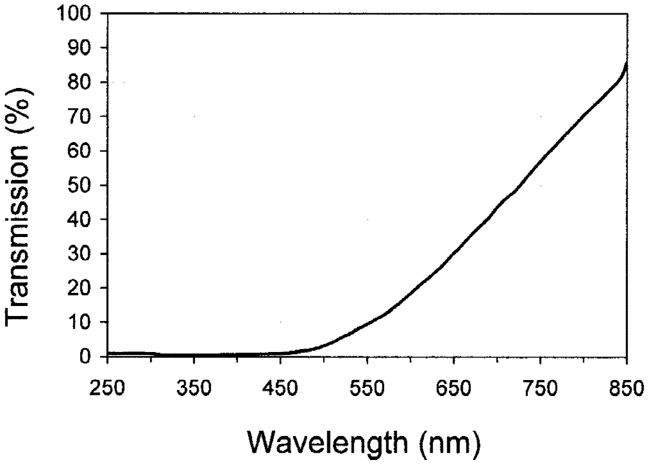

FIG. 3. UV/VIS transmission spectrum of the amorphous Si_3N_4 ceramics sintered at 950 °C at 5.0 GPa. The sample for the measurement was a thin plate, 2 mm thick with polished surfaces.

It was observed that the appearance of the sample after sintering changed greatly with sintering temperature at $T > 1000$ °C. The samples sintered between 1000 and 1350 °C were generally irregularly broken into small pieces, while crack-free specimens were easily obtained at $T > 1350$ to 1420 °C. Different from the translucent and brown appearance of the amorphous Si_3N_4 that formed below 1000–1100 °C, the samples obtained at $T > 1350$ to 1420 °C were translucent and pure white in color [Fig. 2(b)]. The white color of the Si_3N_4 ceramics is seldom observed in conventional sintered Si_3N_4 ceramics. It is a result of the high purity of the starting Si_3N_4 powders and of nonadditive sintering.

Figure 4 shows the variation of Vicker hardness with sintering temperatures at 5.0 GPa. The hardness increases steeply between 850 and 1000 °C which may be due to the increase of bulk density of the specimens with the increasing temperatures in this temperature range. At $T > 1000$ °C, the hardness increases slowly with sintering temperature. The sintered bodies obtained at 1420 °C consisted of β phase exhibited a hardness around 1648 kg/mm^2. This hardness value is comparable to that of the hot-isostatically sintered Si_3N_4 ceramics with addition of sintering aids (Y_2O_3 + Al_2O_3).[20]

2. Grain growth

The grain size of the crystallize Si_3N_4 sintered at 5.0 GPa above crystallization temperatures (>1000 °C) was measured by XRD according to the line broadening of diffraction peaks. The grain size of α–Si_3N_4 formed at 1000 °C was determined to be 160 nm, which is almost 1 order of magnitude greater than the starting particle diameter (18 nm). This indicates that a rapid grain growth occurred following the nucleation of α phase during crystallization. Figure 5 shows the variation of grain size with sintering temperature which was obtained at 5.0 GPa. With increasing temperature, the grain size in-

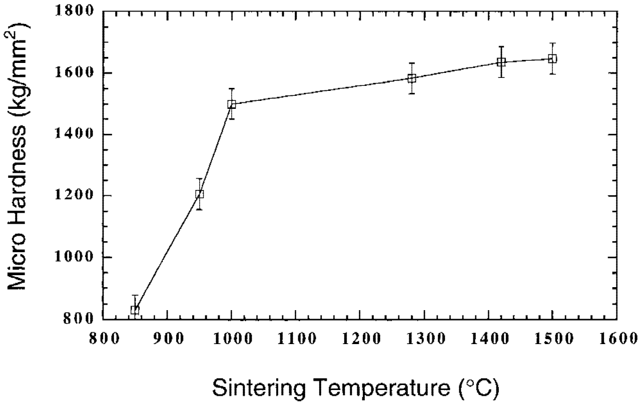

FIG. 4. Variation of Vicker hardness with sintering temperatures at 5.0 GPa.

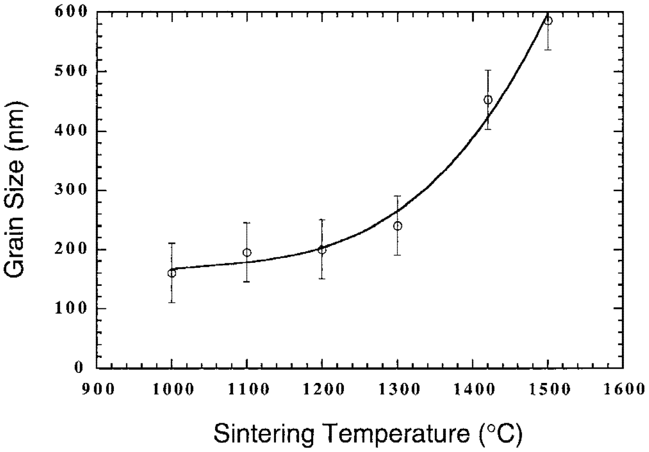

FIG. 5. Variation of grain size with sintering temperature at 5.0 GPa.

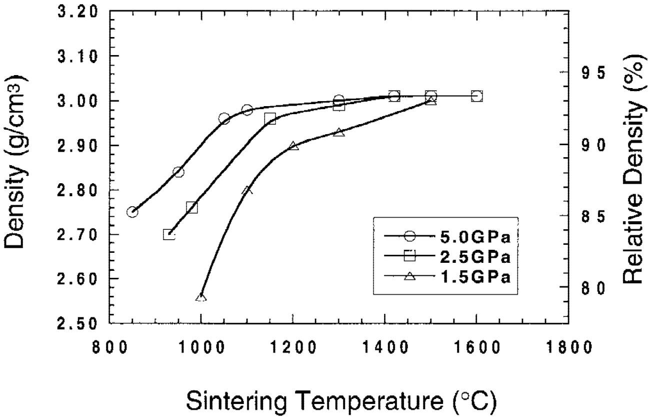

FIG. 6. Variation of sintered density with sintering temperatures at three different pressures (1.0, 1.5, and 5.0 GPa).

creases slowly between 1100 and 1350 °C, followed by an accelerated growth above 1300 °C. The slower grain growth between 1100 and 1350 °C may be related to the dynamically controlled solid nucleation and growth of new β phases in the α-phase matrix that first crystallized from the amorphous structure during crystallization. The accelerated grain growth at $T > 1350$ °C is attributed to the growth by combination of β grains that occurred after the completion of α/β phase transition. The rapid grain growth at the sintering temperature right above the crystallization temperature makes it difficult to control grain size below 100 nm. However, because most of densification is nearly completed below 1300 °C, it is possible to control the grain size below 200 nm while simultaneously ensuring a higher bulk density (~93%). To acquire nanocrystalline bodies with a grain size below 100 nm, an alternative possible route is to process the dense amorphous bodies by a subsequent high-temperature anneal, as another approach which is currently being undertaken.

3. Effects of pressure and sintering temperature on densification

The variation of density with sintering temperature at three different pressures (1.5, 2.5, and 5.0 GPa) is shown in Fig. 6. It is seen that the density increases with temperature along a similar trend at the three different pressures (1.5, 2.5, and 5.0 GPa), i.e., a remarkable increase at lower temperature, typically below the crystallization temperature (1000 °C), followed by a slow increase at higher temperatures. In the low-temperature region, the effects of pressure on density are more pronounced than that in the high-temperature region, indicating a large contribution of pressure to the densification of the amorphous powders at lower temperatures. As temperature increases above 1350–1420 °C, the sintered density under different pressures trends to approach the same final density, which seems to be independent of the pressure applied (1.0–5.0 GPa). This may be caused by generation of viscous flow of silicon oxide phases in the sintered bodies at the elevated temperature which allow densification of the materials at a relatively low pressure. The reduction of viscosity of the silicon oxide phases may be caused by the existence of OH groups in the starting powders[12,17] which was found to have a remarkable effect on lowering the viscosity of silica even in ppm level, in particular, above 1420 °C.[12,21]

It is noted that the final density (3.02 ± 0.01 g/cm^3) attained at $T > 1420$ °C is lower than the theoretical density of crystalline Si_3N_4 (3.18 g/cm^3), which corresponds to a relative density of 94% with respect to crystalline Si_3N_4. However, this does not mean that the sintered bodies were not fully densified under the sintering conditions. The lower relative density was due to the existence of low density silicon oxide or silicon oxynitride phases (Si_2ON_2 density: 2.82 g/cm^3). Assuming all the 5.8 wt% oxygen is present as silicon oxynitride in the sintered bodies (formation of Si_2ON_2 phases were detected under certain conditions), calculation gives a compromise density value of 3.03 g/cm^3 for the two phase composite (Si_3N_4–Si_2ON_2). This value is nearly equal to the bulk density of the specimens sintered at $T >$1420 °C, implying that the materials were fully densified at $T > 1420$ °C.

Finally, it is interesting to note that the relative density of 94% (with respect to crystalline Si_3N_4; density 3.18 g/cm^3) obtained in this experiment is equal to that obtained by HIP sintering of similar powders as reported by Symons and Danforth.[10,11] However, the densification temperature of 1420 °C in the present case is 580 °C lower than that of HIP sintering, in which the final density was attained at temperature as high as 2050 °C. This indicates that application of high pressure can significantly enhance densification of the amorphous Si_3N_4 ceramics and reduce sintering temperatures.

IV. SUMMARY AND CONCLUSIONS

Amorphous Si_3N_4 nanopowders were densified under 1.0–5.0 GPa at room temperature and 1600 °C. It was observed that the nanopowders can be compacted to a high density (87%) even at room temperature. Upon heating, dense bulk amorphous Si_3N_4 ceramics were obtained at temperature slightly below that of the onset of crystallization (1000–1100 °C). Crystalline Si_3N_4 ceramics that were pure white in color were obtained at sintering temperatures above 1420 °C. However, a rapid grain growth occurred during crystallization which made it difficult to control grain size below 100 nm by the high-pressure sintering. Under an applied pressure of 1.0–5.0 GPa, a final density of 95–98% was attained at 1420 °C which seems to be independent of the pressure. This densification temperature is 580 °C lower than that previously achieved in HIP sintering for the same sintered density, indicating the significantly enhanced densification of the amorphous Si_3N_4 at relatively lower temperatures under high pressure.

ACKNOWLEDGMENT

This work was supported by the Chinese Foundation of Nature and Science under Grant No. 159472013.

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