

Effect of Sintering Conditions on Texture Development of Silicon Nitride Processed in a Strong Magnetic Field (Postprint)

Authors: Yang Zhigang, Yu Jianbo, Li Chuanjun, Deng Kang, Ren Zhongming, Yunbo Zhong, Wang Qiuliang, Dai Yinming, Wang Hui

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Abstract

Silicon nitride ceramic green bodies were prepared by gel-casting in a 6T longitudinal strong magnetic field, and textured silicon nitride ceramics with a-axis or b-axis orientation were fabricated via pressureless sintering outside the magnetic field. The influence of sintering temperature and holding time on texture formation in silicon nitride ceramics was investigated. The results show that under the sintering conditions of this study, α -Si₃N₄ completely transformed into β -Si₃N₄. Increasing the sintering temperature promoted texture development in silicon nitride ceramics, with the degree of texture increasing from 0.40 at 1700°C to 0.76 at 1800°C. When the sintering temperature was 1750°C, extending the sintering time had almost no effect on the development of the degree of texture.

Full Text

Abstract

Si₃N₄ ceramics with preferential texture along the a or b axis were shaped by gel-casting in a magnetic field of 6T and then pressureless sintered. The effect of sintering temperature and time on texture formation of the Si₃N₄ ceramics was investigated. It was found that the phase transformation from α to β was completed for the Si₃N₄ ceramics prepared by the present process. With increasing sintering temperature, the texture formation of Si₃N₄ ceramics was enhanced, with the degree of texture increasing from 0.40 at 1700°C to 0.76 at 1800°C. Extension of sintering time at 1750°C had little effect on texture development of Si₃N₄ ceramics.

KEY WORDS: inorganic nonmetallic materials, silicon nitride, texture, gel-casting, strong magnetic field

Introduction

Textured silicon nitride ceramics exhibit excellent anisotropic properties and have found extensive applications in many fields [1-3]. Magnetic field alignment is one of the methods for preparing textured ceramic materials and has been widely studied in recent years [4-6]. Research on textured non-cubic crystal structure diamagnetic ceramic materials, such as alumina [7], titania [8], and zinc oxide [9] ceramics, represents one of the hot topics in this area. Under strong magnetic fields, ceramic particles suspended in liquid solvents experience anisotropic magnetic energy, causing them to rotate to specific orientations to achieve system stability [10]. Preparing textured silicon nitride ceramics in strong magnetic fields requires combination with colloidal forming methods. S.Q. Li et al. [11, 12] and X.W. Zhu et al. [13, 14] prepared green bodies by slip casting in strong magnetic fields and obtained textured silicon nitride ceramics through sintering outside the magnetic field. However, the slip casting process relies on capillary forces generated by porous plaster or alumina molds to absorb liquid solvent from the slurry along the mold walls, forming solidified green bodies. This process is time-consuming and produces samples with non-uniform grain distribution, leading to gradient texture formation. Particularly for large-size and complex-shaped samples, the process presents certain difficulties. Gel-casting is a near-net-shape ceramic forming method offering advantages such as short forming cycles, high green strength, and ease of preparing high-quality, complex-shaped, and thick-walled ceramic components [15], which can overcome the problems associated with slip casting.

After forming ceramic green bodies in a magnetic field, sintering outside the magnetic field environment is required to achieve densification and microstructural development to obtain ceramic components with desired properties. During the sintering process, microstructural evolution leading to texture formation occurs. This study utilizes magnetic alignment technology combined with pressureless sintering to prepare textured silicon nitride ceramic materials and investigates the effects of sintering temperature and time on the development of texture in silicon nitride ceramics.

Experimental Procedures

1.1 Raw Materials

The starting powder was α - Si_3N_4 with an average particle size of approximately 0.5 μm . β - Si_3N_4 powder with an average particle size of about 0.8 μm was used as seed particles. Yttria and silica were used as composite sintering additives. The gel system consisted of acrylamide as monomer, N,N'-methylenebisacrylamide as crosslinker, ammonium persulfate as initiator, N,N,N',N'-tetramethylethylenediamine as catalyst, 25% (mass fraction) tetramethylammonium hydroxide solution as dispersant, and deionized water as solvent. The pH of the slurry was adjusted using 5% HCl solution and 5% NaOH solution.

1.2 Sample Preparation

Monomer, crosslinker, and deionized water were mixed at a mass ratio of 14:0.7:100 to form a premixed solution. 1% tetramethylammonium hydroxide dispersant was added to the premixed solution. After uniform mixing, appropriate amounts of silicon nitride powder (with 9% β -silicon nitride seed particles added), composite sintering additive powder, and premixed solution were combined to prepare a silicon nitride ceramic slurry with 30 vol% solid content. The slurry was ball-milled for 6 hours, then the pH was adjusted to approximately 11.5 using HCl and NaOH solutions, followed by 10 minutes of vacuum treatment. Appropriate amounts of initiator and catalyst were added to the slurry, which was then placed in a 6T longitudinal magnetic field [Figure 1: see original paper]. By controlling the amount of initiator and catalyst added, the polymerization time in the magnetic field was approximately 15 minutes. After gel polymerization was complete, the samples were dried and subjected to debinding treatment at 600°C in air for 2 hours, followed by pressureless sintering under 0.1 MPa N₂ atmosphere with powder bed embedding using pure boron nitride powder. Sintering temperatures were 1700°C, 1750°C, and 1800°C with a holding time of 2 hours; additional sintering was performed at 1750°C for 4 hours and 6 hours.

The prepared samples were cut along directions parallel and perpendicular to the magnetic field, and the surfaces were polished.

1.3 Sample Characterization

Phase composition and orientation analysis of the top surface (perpendicular to the magnetic field) and side surface (parallel to the magnetic field) were performed using a D/MAX-2550 X-ray diffractometer. The degree of texture was evaluated using the Lotgering orientation factor according to the formula [16]. For a,b-axis orientation, the formula is:

$$f = \frac{P - P_0}{1 - P_0}$$

where $I(hk0)$ is the sum of all (hk0) peaks in the plane perpendicular to the magnetic field, $I(hkl)$ is the sum of all (hkl) peaks in the plane perpendicular to the magnetic field, and the diffraction angle range is 10° to 70°. P is calculated from the prepared sample, and P_0 is calculated from the standard PDF card of β -silicon nitride. $f = 0$ indicates no orientation formation, while $f = 1$ indicates complete orientation formation. Fracture morphology was observed using a JSM-6700F field emission scanning electron microscope. The density of sintered bodies was measured by the Archimedes method using the water boiling technique. Room-temperature flexural strength was measured by three-point bending on a WDW-300 universal testing machine with a span of 20 mm and loading rate of 0.5 mm/min. All data represent the average of three samples.

Results and Discussion

2.1 Effect of Magnetic Field on Grain Orientation

Figure 2 [Figure 2: see original paper] shows XRD patterns of samples prepared at 1750°C for 2 hours after forming in 0T and 6T magnetic fields. No α - Si_3N_4 phase was detected in Figure 2, indicating complete transformation from α to β phase under these temperature conditions. For samples formed in a 0T magnetic field, no difference was observed in diffraction peaks between the top and side surfaces, indicating no grain orientation in Si_3N_4 . After forming in a 6T magnetic field, significant differences in diffraction peak intensity were observed between the top and side surfaces of the sample, with (210) and (200) diffraction peaks being the strongest in the top surface, while the (101) diffraction peak was strongest in the side surface. This indicates that Si_3N_4 grains were clearly oriented, with the a or b axis of Si_3N_4 grains tending to align along the magnetic field direction.

The principle of magnetic field-induced crystal orientation can be analyzed from an energy perspective according to the magnetic energy formula [4]:

$$U = -\frac{1}{2\mu_0} \cdot N \cdot \chi \cdot B^2$$

where N is the demagnetization factor, χ is the magnetic susceptibility, B is the applied magnetic flux density, and μ_0 is the vacuum permeability. Grains experience torque that rotates them to a stable orientation until the magnetic energy reaches a minimum. Silicon nitride has a hexagonal crystal structure with magnetic anisotropy characteristics, where magnetic susceptibility differs along different directions, resulting in different magnetic energies. For silicon nitride crystals, since the magnetic susceptibility along the c-axis is smaller than that along the a or b axis ($\chi_c < \chi_{a,b}$), the magnetic energy is higher ($U_c > U_{a,b}$), making the a or b axis of the crystal preferentially orient parallel to the magnetic field direction, while the c-axis randomly arranges in the plane perpendicular to the magnetic field [13].

2.2 Effect of Sintering Temperature on Texture Formation

Figure 3 [Figure 3: see original paper] shows XRD patterns of samples obtained at different sintering temperatures for 2 hours after forming in a 6T magnetic field. As seen in Figure 3, the α phase had completely transformed to β phase within the studied sintering temperature range. In the top surface of sintered silicon nitride samples, the intensity of the (210) diffraction peak relative to the (101) diffraction peak gradually increased as the sintering temperature increased from 1700°C to 1800°C. Figure 4 [Figure 4: see original paper] further displays the orientation factor of silicon nitride samples held at different sintering temperatures for two hours. The orientation factor obtained at 1700°C was 0.40, which increased to 0.76 as the sintering temperature rose to 1800°C. Combined with

the results from Figure 3, this indicates that increasing sintering temperature promotes texture formation in silicon nitride ceramics. Figure 5 [Figure 5: see original paper] shows the fracture morphology of samples obtained at different sintering temperatures on the cross-section perpendicular to the magnetic field direction. The microstructure of each sample consists of elongated columnar β - Si_3N_4 grains. In the fracture surface of the sample sintered at 1700°C, the degree of orientation was not high (only 0.40), so numerous grains with hexagonal cross-sections were present. As the sintering temperature increased, the number of grains showing hexagonal cross-sections gradually decreased, with more grain long axes tending to arrange within the plane. Since the long axis direction of β - Si_3N_4 grains is the *c*-axis direction, more grains had their *c*-axes tending to arrange in the plane perpendicular to the magnetic field. Therefore, a microstructure of silicon nitride ceramics with a or b axis orientation—i.e., planar orientation structure—was obtained. From the microstructural evolution, it can be inferred that increasing sintering temperature promotes texture development. Meanwhile, the fracture surfaces show that the grain size (diameter) gradually increases with increasing sintering temperature.

According to previous research results [17], using initial raw β - Si_3N_4 powder, silicon nitride ceramics with relatively high texture degree were obtained in a 6T longitudinal magnetic field, particularly achieving highly textured silicon nitride green bodies during the forming stage, indicating that β - Si_3N_4 particles easily form orientation under 6T magnetic field conditions. In silicon nitride ceramic research, high-performance silicon nitride ceramics can be prepared using α - Si_3N_4 powder with β - Si_3N_4 seed addition. Using this raw material system, the sintering process involves particle rearrangement, dissolution-precipitation, and grain growth. During the dissolution-precipitation process, $\alpha \rightarrow \beta$ phase transformation occurs simultaneously with grain growth [18]. The 9wt% β - Si_3N_4 seed particles added to the α - Si_3N_4 powder act as nuclei to promote phase transformation and grain growth, with the orientation of β - Si_3N_4 grains determining the final orientation of the sintered body to a certain extent. If highly oriented β - Si_3N_4 nuclei are obtained in the green body stage through seed addition, these oriented β - Si_3N_4 grains preferentially undergo anisotropic grain growth through the dissolution-precipitation mechanism during sintering, and continue to grow through Ostwald ripening after phase transformation is complete, promoting texture development in silicon nitride ceramics to obtain highly oriented silicon nitride ceramics. Additionally, silicon nitride ceramics prepared using β - Si_3N_4 as initial raw material have microstructures composed of approximately spherical and short columnar silicon nitride grains [19]. In contrast, using α - Si_3N_4 powder with β - Si_3N_4 seed addition as raw material, the phase transformation process during sintering yields the microstructure of silicon nitride ceramics composed of elongated columnar grains as shown in Figure 5.

However, in this experiment, according to Figures 2 and 3, this transformation process was completed within the studied sintering temperature range. Therefore, the improvement of texture by sintering temperature primarily occurs

through grain growth, and is entirely a growth process among β - Si_3N_4 grains. Silicon nitride ceramics are sintered through a liquid-phase sintering mechanism. Increasing sintering temperature favors increased glass phase content and reduced viscosity, accelerating the dissolution of unoriented small β - Si_3N_4 particles, mass transfer in the liquid phase, and deposition on the surfaces of oriented grains [20]. These unoriented small β - Si_3N_4 particles may have precipitated from locally saturated solution in the liquid phase during phase transformation and did not have sufficient time to grow during subsequent sintering. Therefore, consumption of unoriented small particles and continued growth of oriented large particles promoted texture development in silicon nitride ceramics.

Figure 6 [Figure 6: see original paper] shows the relative density of samples held for 2 hours at different sintering temperatures. As seen in Figure 6, density increased slightly as sintering temperature increased from 1700°C to 1750°C, but did not continue to increase significantly as temperature rose to 1800°C. The reason is that formation of large abnormal grains during later sintering stages hinders densification. Since the sintered density of obtained samples was relatively low and the density difference between samples sintered at 1700°C and 1800°C was small, density differences cannot be clearly observed from Figure 5. The orientation formation process involves only particle alignment and does not affect densification degree, yet the orientation factor can differ by nearly a factor of two between the two temperatures. Macroscopic analysis (Figure 4) clearly shows that orientation degree increases with temperature. In microscopic analysis, no obvious difference in grain orientation is observed in the plane perpendicular to the magnetic field direction in Figure 5 for two reasons: first, the prepared material is a porous textured ceramic with high porosity, and fracture morphology was used to observe and analyze the microstructure; second, completely oriented silicon nitride was not obtained under current conditions, causing the *c*-axis (long axis) of silicon nitride grains to tend to arrange in the plane perpendicular to the magnetic field, with some elongated columnar grains forming various angles with this plane and producing different-sized or numerous fracture surfaces after fracture, making clear distinctions unobservable.

Figure 7 [Figure 7: see original paper] shows the room-temperature flexural strength of textured samples obtained at different sintering temperatures. As seen in Figure 7, the flexural strength on different loading surfaces increases with sintering temperature. Meanwhile, the strength in the plane perpendicular to the magnetic field direction is slightly higher than that in the plane parallel to the magnetic field direction. Compared with previous research on silicon nitride ceramics prepared using β - Si_3N_4 as initial raw material [17], both raw material systems exhibit anisotropic flexural strength properties in textured silicon nitride ceramics, though the flexural strength does not show particularly large differences at different temperatures.

2.3 Effect of Holding Time on Texture Formation

Figure 8 [Figure 8: see original paper] shows XRD patterns of samples formed in a 6T magnetic field and sintered at 1750°C for different times. As seen in Figure 8, as sintering time extended from 2 hours to 6 hours, almost no obvious change occurred in the relative intensity of all (hkl) diffraction peaks in the top surface of sintered samples, and the orientation factor of these samples also showed little change, remaining at approximately 0.48 as shown in Figure 9 [Figure 9: see original paper]. These results demonstrate that within the studied sintering time range, extending sintering time has minimal effect on the development of a or b axis orientation in silicon nitride ceramics.

As also seen in Figure 8, phase transformation was already completed after reaching the sintering temperature of 1750°C in the textured silicon nitride ceramic sintering process. Moreover, the mass transfer process is constant during this holding period, and smaller unoriented particles also grew during the holding period up to 2 hours. As time continues to extend, these grown particles exhibit the same sintering activity as already-oriented large particles. On the other hand, interlocking among larger elongated β -Si₃N₄ particles may limit further grain growth in silicon nitride [21]. Thus, extending sintering time within the studied range has little effect on texture degree development in silicon nitride ceramics.

Conclusions

1. Using α -Si₃N₄ powder with 9% β -Si₃N₄ seed addition as raw material, a or b axis oriented silicon nitride ceramics can be prepared by gel-casting in a 6T longitudinal static magnetic field to form green bodies followed by pressureless sintering.
2. Increasing sintering temperature favors increased texture degree in silicon nitride ceramics, primarily achieved by promoting grain growth. The texture degree of silicon nitride ceramics sintered at 1700°C was 0.40, reaching 0.76 for those sintered at 1800°C. The sintered textured samples exhibited anisotropic flexural strength properties.
3. Extending holding time from 2 hours to 6 hours had minimal effect on the texture degree of silicon nitride ceramics, with the texture degree remaining at approximately 0.45 after sintering at 1750°C.

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