Variation of porosity and pore size during post-sintering of reaction-bonded silicon nitride doped with Y2O3 and MgO additives

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Sintering of reaction-bonded silicon nitride (SRBSN) is a method of preparing Si3N4 ceramics with high thermal conductivity and good mechanical properties. In the present study, by using a high purity silicon powder as the starting material and 2 mol % of Y2O3 and 5 mol % of MgO as sintering additives, the phenomena including phase transformation, grain growth, densification, and pore size evolution occurred in the SRBSN process were studied. It was found that the α- to β-Si3N4 phase transformation could complete at 1700°C. Obvious grain growth started at around 1700°C. Substantial densification took place at temperatures between 1800 and 1900°C. When sintered at 1900°C for 30 min, not only the total number of pores drastically decreased as a result of the shrinkage of the compact, but also a fraction of open pores turned to be closed pores due to microstructural changes such as grain growth and pore coalescence.

Key-words : Silicon nitride, Silicon, Nitridation, Reaction bonding, Sintering

1. Introduction

With the replacement of Si by the wide-bandgap semiconductors such as SiC and GaN, power devices are expected to work under higher voltage, larger current and smaller size.1) The greater power density requires the ceramic substrates installed in the power devices to have better performance such as more efficient heat dissipation and higher mechanical strength. Aluminum nitride (AIN) has been used as a major ceramic substrate material for power devices since it exhibits high thermal conductivity of over 200 W m⁻¹ K⁻¹ and good heat dissipation capability. However, recent studies have found that AIN substrates might get cracked after a few heat cycles when tested in the temperature range from −40 to 250°C, due to its inadequate mechanical strength (typical bending strength of 300–400 MPa and fracture toughness of 3–4 MPa m¹/²).2) The electronics industry is eager to seek alternative high-thermal-conductivity substrate materials with better mechanical properties.

Recently, our research group has succeeded in fabricating Si3N4 with both high thermal conductivity and high strength by a sintering of reaction-bonded silicon nitride (SRBSN) method.3)⁵ After investigating the influences of a variety of parameters, such as the oxygen content in silicon powder,6)⁷ aluminum content,⁸ iron content⁹) and sintering additives employed,¹⁰)¹¹) Zhou et al. could fabricate an Si3N4 with a record-high thermal conductivity of 177 W m⁻¹ K⁻¹ and a fracture toughness of 11.2 MPa m¹/².¹²) These results indicate that silicon nitride should be a promising substrate material for application in the next-generation power devices.

SRBSN is a process including two steps, i.e., nitridation and post-sintering. A silicon compact, which is usually doped with a small amount of additives, is nitrided and turns to be a porous silicon nitride compact, which is called a reaction-bonded silicon nitride (RBSN) compact, followed by a high temperature post-sintering process where the porous silicon nitride compact is converted to a dense sintered body.¹³) In order to improve the thermal conductivity as well as the mechanical properties of the SRBSN material, it is important to optimize the processing parameters for nitridation and post-sintering. The authors recently investigated the influences of nitriding temperature, holding time, and sample thickness on the nitridation behavior of silicon compacts doped with 2 mol % of Y2O3 and 5 mol % of MgO sintering additives.¹⁴)

For the second step of SRBSN method, densification behavior of SRBSN compacts has been reported in some literatures. Wakahara et al. reported that the post-sintering of a RBSN compact might exhibit different behaviors compared to the conventional sintering of a Si3N4 powder compact.¹⁵) Using an in situ dilatometry technique, they measured the shrinkage behaviors of a RBSN compact and a Si3N4 powder compact, both doped with 5 wt % of Y2O3.
and 2 wt % of Al₂O₃ additives, during sintering at temperatures till 1850°C. They found that the shrinkage of the RBSN compact started at around 1750°C, whilst the Si₃N₄ powder compact started to shrink at around 1400°C. They claimed that the restriction of sintering of the RBSN compact seemed to result from neck growth and strong aggregation among the reacted Si₃N₄ particles. Joeng et al. succeeded in fully densifying reaction bonded Si₃N₄ specimens with the same sintering additive system by post-sintering at 1800°C for 2 h, which result is consistent with the Wakahara’s report. From a view point of porosity variation, Morita et al. measured the open and closed porosities of RBSNs added with Y₂O₃ and MgO nanometer size powder before and after post sintering, and found that open porosities of the RBSN specimens before post-sintering were higher than closed porosities however after post-sintering open porosities was lower than closed porosities. Although they examined the porosity change of SRBSNs, the relationship between shrinkage behavior and variation of amount and morphology of pores during heating for post sintering has not yet clarified.

The peculiar shrinkage behavior should affect the evolution of shape and size of pores in the compact during post-sintering, which was not discussed in the study of the above papers. Therefore, in the present work, porosimetry was used to monitor the changes of porosity and pore size during post-sintering of a RBSN compact, along with phase transformation examination and microstructural characterization, in order to investigate the post-sintering behavior of RBSNs, especially the evolution of porosity and pore size during post-sintering.

2. Experimental procedure

High-purity Si powder (>99.99% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) was used as the starting powder. Y₂O₃ powder (>99.9% purity, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) and MgO powder (>99.9% purity, Ube Material Industries, Ltd., Yamaguchi, Japan) were added as sintering additives. The starting powder and sintering additives were mixed in ethanol using a planetary mill (250 rpm, 2 h) in a Si₃N₄ jar with Si₃N₄ balls. The molar ratio of the starting composition was Si₃N₄:Y₂O₃:MgO = 93:2:5 by assuming the Si powder being completely nitrided to Si₃N₄. After vacuum drying and sieving, the mixed powders were uniaxially pressed in a 15 mm diameter stainless-steel die and then cold isostatically pressed at a pressure of 300 MPa. The compacts obtained had diameters of approximately 14 mm and thicknesses of 6 mm. The compacts were nitrided at 1400°C for 4 h under a nitrogen pressure of 0.1 MPa in a graphite resistance furnace. Then, by further heating up the furnace and introducing more nitrogen, post-sintering of RBSN compacts was carried out at 1500, 1600, 1700, 1800°C for 10 min, and at 1900°C for 10 and 30 min under a nitrogen pressure of 1 MPa. In order to monitor the nitridation process, several nitrided compacts were taken out for characterization without going to the second step of post-sintering.

X-ray diffraction (XRD, RINT-2500, Rigaku, Tokyo, Japan) with monochromatic Cu Kα radiation (40 kV/100 mA) was used to identify the phases in the cross-sectional surfaces of all compacts. In addition, quantitative analysis of the α- and β-phases in the compacts was conducted according to the method reported by Pigeon and Varma. The morphologies of the nitrided compact and the sintered materials were observed using scanning electron microscopy (SEM, JSM-6340F, JEOL, Tokyo, Japan). Bulk density was measured by the Archimedes method. Theoretical density (TD) was calculated according to the rule of mixtures. Relative density (RD) was given by the ratio of bulk density and TD. Total porosity was calculated as (100-RD). Pore size distributions and open porosities of the nitrided compact and the sintered Si₃N₄ samples were measured using mercury intrusion porosimetry (AutoPore IV 9520, Micromeritics corporate Headquarters, Norcross, USA). The difference between total porosity and open porosity was calculated as closed porosity.

3. Results and discussion

Figure 1 shows the XRD patterns of the nitrided compact and the sintered materials. In the nitrided compact, the main crystalline phases were α-Si₃N₄ and β-Si₃N₄, and the minor phases were Y₂Si₃O₇N₄ and YSiO₂N. No Si peaks were observed, indicating that the nitridation of Si was complete. For the main crystalline phases, the peaks of β-Si₃N₄ were stronger than that of α-Si₃N₄. Quantitative analysis revealed that the β/α ratio was 52:48. The minor crystalline phases, Y₂Si₃O₇N₄ and YSiO₂N, might be formed through the reaction between the SiO₂ originally existing on the surface of the Si powder, the Y₂O₃ additive, and Si₃N₄. Compared to the nitrided compact, the sintered materials contained higher β-Si₃N₄ contents, which increased with increasing sintering temperatures. The β/α ratios for the materials sintered at 1500 and 1600°C were 55:45 and 78:22, respectively. When the sintering temperatures were 1700°C or higher, all the diffraction peaks of α-Si₃N₄ disappeared, indicating that the α-Si₃N₄ phases

![Fig. 1. XRD patterns of (a) the nitrided compact and the materials sintered at (b) 1500, (c) 1600, (d) 1700, (e) 1800, and (f) 1900°C for 10 min.](image-url)
completely transformed to $\beta$-$\text{Si}_3\text{N}_4$. As for the oxynitride minor phases of the sintered materials, their diffraction peaks became weaker with increasing sintering temperatures, implying more loss of secondary phases at higher sintering temperatures.

**Figure 2** shows the SEM images of the fracture surfaces of the nitrided compact and the sintered materials. In the nitrided compact [Fig. 2(a)], the grains were quite fine. A few elongated grains having lengths less than 2 $\mu$m could be observed, and they should be $\beta$-$\text{Si}_3\text{N}_4$ grains, which would serve as nuclei for the $\alpha$- to $\beta$-$\text{Si}_3\text{N}_4$ phase transformation during the post-sintering process. The sintered material obtained by sintering at 1500°C for 10 min showed a microstructure very similar to that of the nitrided compact, indicating no obvious grain growth [Fig. 2(b)]. When the sintering temperature increased to 1600°C, the microstructure became a little bit coarser and a few elongated grains having lengths around 5 $\mu$m were observed [Fig. 2(c)]. With the sintering temperature increasing to 1700°C, the number of elongated grains increased and the grains became larger [Fig. 2(d)]. When the sintering temperature was 1800°C, almost all the grains turned elongated and their sizes further increased [Fig. 2(e)]. With the sintering temperature further increasing to 1900°C, the sintered material showed a coarser microstructure composed of interlocked elongated grains [Fig. 2(f)].

**Figure 3** shows the relative densities of the nitrided compacts and the materials sintered at 1500, 1600, 1700, 1800, and 1900°C for 10 min. The nitrided compact and the materials sintered at 1500–1700°C had almost the same relative densities of around 76%. When the sintering temperature exceeded 1700°C, the relative densities started to increase. This was similar to the result of Wakihara et al.\textsuperscript{15} that post-sintering shrinkage did not occur until 1750°C, although the sintering additive doped in the RBSN was 1800, 1900°C for 10 min.
different from the one used in the present work. They considered that higher densification temperature was caused mainly by the following reasons; the nitrided compacts had neck formation and aggregation among Si₃N₄ grains, and then densification of nitrided compacts during sintering might be inhibited by mainly a lack of the grain rearrangement without shrinkage. Further, because the densification of RBSN specimens is promoted only by the grain growth of β-Si₃N₄ (dissolution and recrystallization of β-Si₃N₄), that is shrinkage starts at higher temperature. Such microstructure futures were also observed in our investigator as shown in Fig. 2. After sintering at 1900°C for 10 min, the relative density reached 87.5%.

Figure 4 shows the total porosities, open porosities and closed porosities of the nitrided compact and the materials sintered at 1500, 1600, 1700, 1800, and 1900°C for 10 min. Certainly, the changes of total porosities were in accordance with the changes of relative densities shown in Fig. 3. Similar to the total porosities, open porosities hardly changed until 1700°C. Above 1700°C, open porosities started to obviously decrease, similar to the total porosities. After being sintered at 1900°C for 10 min, the open porosity was still close to the total porosity. However, after being sintered at 1900°C for 30 min, while the total porosity was 7.5%, the open porosity dropped to 0.7%, and the closed porosity was 6.8%. It means that when sintered at 1900°C for 30 min, not only the total number of pores drastically decreased as a result of the shrinkage of the compact, but also a fraction of open pores turned to be closed pores due to microstructural changes such as grain growth and pore coalescence. Morita et al. reported that open porosity of SRBSN tuned to closed porosity around the relative density of about 90%; the specimen sintered at 1850°C for 2 h had 8.7% closed porosity and 0.7% open porosity. These results is consistent with our results when focusing on the disappearance of open porosity during sintering though the post sintering conditions were slight difference between two experiments.

Figure 5 shows the pore size distributions of the Si powder compact, the nitried compact and the sintered materials, which were measured by the mercury intrusion porosimetry method. The median pore sizes calculated from the pore size distribution plots shown in Fig. 5 were listed in Table 1. The pore size distribution plot of the Si powder compact covered a very broad range, from 0.02 to 3 μm, and its median pore size was 0.33 μm. The nitried compact showed a narrower pores size distribution plot, and its median pore size was smaller (0.28 μm), which could be attributed to the 22% volume expansion resulted from the conversion from Si to Si₃N₄ during nitridation. Sintering at 1500 and 1600°C resulted in the shift of pore size distribution to the smaller size direction, and the median pore sizes were 0.27 and 0.25 μm, respectively. However, when the sintering temperature increased to
1700°C, the trend of decreasing pore size got reversed. The material sintered at 1700°C had a median pore size of 0.30 μm. This could be attributed to the grain growth occurred during sintering at 1700°C. The larger elongated grains formed larger pores. Sintering at 1800°C resulted in further increasing of the pore sizes, where the median pore size was 0.35 μm. However, when the sintering temperature was 1900°C, the trend of change in pore size got reversed once again. The material sintered at 1900°C had a median pore size of 0.28 μm, smaller than that of the material sintered at 1800°C. Compared to the sintering at 1800°C, the sintering at 1900°C led to larger grain sizes which would cause the formation of larger pores [Figs. 2(f) vs. 2(e)]; however, sintering at 1900°C also resulted in larger shrinkage and greater densification (Fig. 3). It was the larger shrinkage that resulted in the smaller pore size of the material sintered at 1900°C than that of the material sintered at 1800°C.

4. Summary

While the SRBSN method had been proven to be an effective way of preparing Si₃N₄ ceramics with high thermal conductivity and good mechanical properties in the previous studies, the sintering behavior was not well studied. In the present study, the phenomena including phase transformation, grain growth, densification, and changes in pore size distribution occurred in the nitridation and the post-sintering processes were studied. While the nitrided compacted consisted of almost equally α- and β-Si₃N₄ phases, the α- to β-Si₃N₄ phase transformation could proceed to complete by sintering at 1700°C for only 10 min. Obvious grain growth during post-sintering started at around 1700°C. Substantial densification did not take place until the sintering temperature was higher than 1700°C. Once densification was initiated, it could proceed rather fast, as evidenced by the rapid decreasing of the open porosity when sintering at temperatures between 1800 and 1900°C. The open porosity became nearly zero after sintering at 1900°C for 30 min. It was also found that the change in pore size distribution during post-sintering was very dynamic due to the interaction between grain growth and densification.

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