Effect of Si$_3$N$_4$ nanowires on the mechanical properties and dielectric constant of porous Si$_3$N$_4$ ceramics

Tianxiang ZHANG$^1$, Xinghong ZHANG$^1$ and Wenbo HAN$^{1,\dagger}$

$^1$National Key Laboratory of Science and Technology for National Defence on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin, 50080, China

The high strength and low dielectric constant of silicon nitride (Si$_3$N$_4$) ceramics are an irreconcilable conflict. It is a compromise to introduce a suitable reinforcing phase in Si$_3$N$_4$ ceramics to receive well dielectric properties without excessive loss of mechanical properties. In this paper, Si$_3$N$_4$ nanowires were in-situ synthesized by pyrolysis of polysilazane with Si$_3$N$_4$ nanopowders as catalyst without introduction of impurities in Si$_3$N$_4$ porous ceramics. The formed Si$_3$N$_4$ nanowires not only improve the mechanical property but also reduce dielectric constant of porous Si$_3$N$_4$ ceramic.

©2019 The Ceramic Society of Japan. All rights reserved.

Key-words : Si$_3$N$_4$, Si$_3$N$_4$ nanowires, Mechanical property, Dielectric constant

[Received February 21, 2019; Accepted June 17, 2019]

1. Introduction

Silicon nitride (Si$_3$N$_4$) ceramics with excellent mechanical and dielectric properties are promising electromagnetic-wave-transparent materials. The porous structure of Si$_3$N$_4$ ceramics are essential to ensuring their high dielectric property considering the low dielectric constant of air. However, effectively decreasing in dielectric constant and density of Si$_3$N$_4$ results in high porosity, which leads to a degradation in the mechanical properties of Si$_3$N$_4$ composites. Various kinds of second-phase materials, such as SiC nanowires, ZrO$_2$ nanofibers, carbon fibers and graphene platelets have been used as reinforced phase to enhance the mechanical property of Si$_3$N$_4$ ceramics. Nevertheless, the existence of a reinforced second phase causes dielectric-property degradation for Si$_3$N$_4$ composites. Thus, selecting a suitable reinforced phase that does not degrade the dielectric property and keeps adequate mechanical properties of porous Si$_3$N$_4$ is imperative. Si$_3$N$_4$ nanowires (SN$_{NWs}$) present excellent mechanical and dielectric properties, and the in-situ formed SN$_{NWs}$ in porous Si$_3$N$_4$ ceramics could keep adequate mechanical properties and don’t attenuate dielectric properties.

In this work, SN$_{NWs}$ were synthesized by precursor pyrolysis of polysilazane (PSN) with nano Si$_3$N$_4$ powders as catalyst to prevent the introduction of impurities. The effect of SN$_{NWs}$ on microstructure, flexural strength, fracture toughness, and dielectric constant of porous Si$_3$N$_4$ ceramics were systematically investigated.

2. Experimental procedure

2.1 Material preparation

Micron-sized $\alpha$-Si$_3$N$_4$ (D$_{50}$ = 0.5 $\mu$m, Beijing HWRK Chem. Co., Ltd., China), nanosized $\beta$-Si$_3$N$_4$ (25 nm, Hefei kaier nanometer energy technology co., LTD, China), Yb$_2$O$_3$ sintering additive (purity >99%; Tianjin Bodi Chem. Co., Ltd., China), and PSN (molecular weight = 1443, Institute of Chemistry, Chinese Academy of Sciences, China) were used to prepare composites. SN$_{NWs}$ were synthesized by precursor pyrolysis of PSN at 1300°C in nitrogen atmosphere. Three different Si$_3$N$_4$ composite powders were mixed. The compositions of composites are listed in Table 1.

The porous SN-5N, SN-6P and SN-6P5N composites were shaped by cold isostatic pressing at 175 MPa and processed by pressureless sintering (ZT-150-20, Shanghai CH Co., Ltd., China) in nitrogen atmosphere. The pressureless sintering parameters are as follows: (i) heating to 1300°C with a heating rate of 2 °C/min and then holding for 4 h, (ii) heating to 1750°C at 4 °C/min and then holding for 2 h, and (iii) cooling to room temperature by nature.

2.2 Measurement and characterization

The phase composition of Si$_3$N$_4$ composite was analyzed by X-ray diffraction.

Table 1. Compositions of SN-5N, SN-6P and SN-6P5N composites

| Composites | Matrix (wt%) | Addition |
|------------|-------------|----------|
| SN-5N      | $\alpha$-Si$_3$N$_4$ $\cdot$Yb$_2$O$_3$ | —        | 5 wt %  |
| SN-6P      | $\alpha$-Si$_3$N$_4$ $\cdot$Yb$_2$O$_3$ | 6 wt %  | —        |
| SN-6P5N    | $\alpha$-Si$_3$N$_4$ $\cdot$Yb$_2$O$_3$ | 6 wt %  | 5 wt %  |

$^\dagger$ Corresponding author: W. Han; E-mail: wbhan@hit.edu.cn
alyzed by X-ray diffraction (XRD) and the microstructure was observed by field emission scanning electron microscope (Quanta 200FEG, FEI). The relative density and porosity of Si₃N₄ ceramics were measured through the Archimedes method. Si₃N₄ samples with sizes of 3 mm × 4 mm × 20 mm were prepared for measurement of flexural strength. Single-edge notched beams with sizes of 2 mm × 4 mm × 22 mm were used to evaluate the fracture toughness of Si₃N₄ samples. These mechanical experiments were performed with an Instron-5569 machine at a loading rate of 0.5 mm/min. The dielectric constant (ε) was measured by the high Q cavity method at room temperature with a fixed frequency of 10 GHz and calculated with a vector network analyzer. The open porosities of composites were measured by mercury intrusion method (Auto Pore IV 9500 V1.09, Micromeritics Instrument Corporation).

3. Results and discussion

To investigate the effects of α-Si₃N₄ nanopowders on the formation of SN₃NWs, the SN-6P and SN-6P5N samples were prepared by curing at 170°C and pyrolysis at 1300°C in nitrogen atmosphere prior to sintering. The scanning electron microscopy (SEM) images of the above composites are shown in Fig. 1. SN₃NWs cannot be observed in SN-6P sample [Fig. 1(a)], whereas a large number of SN₃NWs uniformly distributed in microsized SN-6P5N composite powders [Fig. 1(b)]. The results indicate as, Si₃N₄ nanopowders could act as the catalyst and effectively promote the formation of SN₃NWs in pyrolysis of PSN at 1300°C.

The SEM images of fracture morphology for SN-6P5N and SN-5N samples are shown in Figs. 2(a) and 2(b), respectively. SN₃NWs presented a homogeneous dispersion in Si₃N₄ matrix for SN-6P5N sample, whereas SN-5N sample presented elongated β-Si₃N₄ grains without SN₃NWs. The difference in grain sizes between SN-6P5N and SN-5N samples was attributed to the inhibition of SN₃NWs to the growth of Si₃N₄ grain during pressureless sintering. The energy dispersive X-ray spectrometry results in the yellow frame region of SN₃NW provided in Fig. 2(a) showed that SN₃NWs consisted primarily of Si and N, with a small amount of O probably related to the surface oxides of SiO₂. The Si:N atomic ratio was 2:1, indicating that SN₃NWs were silicon rich. These results suggested that SN₃NWs can be in-situ formed with Si₃N₄ nanopowders as catalyst during the pressureless sintering process.

The XRD patterns of SN-6P5N and SN-5N samples are provided in Fig. 3. Both SN-6P5N and SN-5N samples mainly comprised β-Si₃N₄, whereas the initial α-Si₃N₄ phase was undetected in the final ceramics. Si₃N₂O and Yb₂Si₂O₇, as grain boundary phase, were observed for both samples. The results indicate the phase transformation of Si₃N₄ was almost complete during pressureless sintering.
sintering, and that the generated SNNWs cannot alter the composition of grain-boundary phase reacted between sintering additive Yb₂O₃ and Si₃N₄ raw powders.

The flexural strength and fracture toughness of Si₃N₄ composites are presented in Fig. 4(a). The flexural strength of SN-5N and SN-6P5N samples were 263 and 296 MPa, respectively. The fracture toughness of SN-5N and SN-6P5N were 5.15 and 6.53 MPa·m⁰.², respectively. The excellent mechanical properties of Si₃N₄ ceramics are attributed to the specific interlocking microstructure formed by the elongated β-Si₃N₄ grains. Combined with the microstructure, SNNWs can effectively increase the mechanical properties of Si₃N₄ ceramics, even with fewer elongated β-Si₃N₄ grains. A possible explanation for the higher flexural strength of SN-6P5N was grain refining and support of SNNWs, and the higher fracture toughness was ascribed to the bridging and pull-out of SNNWs, which preventing crack propagation.

The porosity and dielectric constant of Si₃N₄ samples are shown in Fig. 4(b). The dielectric constant of SN-5N and SN-6P5N samples were 4.47 and 4.38, respectively. The results demonstrate in-situ formed SNNWs can reduce the dielectric constant of porous Si₃N₄ ceramics. The SN-5N and SN-6P5N samples have high porosity of 37.99 and 35.13%, respectively. The open porosities of SN-5N and SN-6P5N composites were measured by mercury intrusion method. The pores of SN-5N and SN-6P5N composites with porosities >35% are mainly open pores. The open porosities of SN-5N and SN-6P5N composites are 36.78 and 33.49%, respectively, and the remaining closed porosities are 1.21 and 1.64%, respectively. A positive correlation existed between the porosity and dielectric constant of Si₃N₄ porous ceramics, but for all of that, the dielectric constant and porosity of SN-5N were both higher than those of SN-6P5N. The porous Si₃N₄ ceramic after chemical vapor infiltrating with Si₃N₄, the mechanical properties were significantly improved due to the increase in the joint strength between the β-Si₃N₄ particles and the loading capacity of the β-Si₃N₄ particles, and at the same time, the dielectric properties were lowered due to a slight decrease in the porosity. Moreover, the dense Si₃N₄, BN and B₄C coatings can improve their mechanical properties of porous Si₃N₄ ceramic, but their dielectric constants also will increase. However, the S13N4 nanowires could reduce the dielectric constant of porous Si₃N₄ ceramic. The Si₃N₄ nanowires could reduce the dielectric constant of porous Si₃N₄ ceramic. The porous Si₃N₄ (SN-5N) has a dielectric constant of 4.47 which is higher than the 4.38 of Si₃N₄ ceramic added with Si₃N₄ nanowires (SN-6P5N). Thus, the SNNWs could promote the dielectric properties of Si₃N₄ porous ceramics, which was probably attributed to fine β-Si₃N₄ grains and high porosity. To investigate the effect of Si₂N₂O phase on the dielectric constant of porous Si₃N₄ ceramic. Si₃N₄ ceramic without of Si₂N₂O addition has a dielectric constant of 4.53, which is slightly higher than the 4.47 of porous Si₃N₄ with addition of Si₂N₂O phase (SN-5N). The two ceramics have almost the same porosities (37.94 and 37.99%) and the Si₂N₂O phase is the only variation, thus the Si₂N₂O phase could reduce dielectric constant of porous Si₃N₄ ceramic. Our research result is consistent with the reported conclusions, the dielectric constant of porous Si₃N₄-O-Si₃N₄ multiphase ceramics reduced with the increase of Si₂N₂O content.

Fig. 3. XRD patterns of porous SN-6P5N and SN-5N composites prepared by pressureless sintering at 1750°C.

Fig. 4. a) Flexural strength and fracture toughness, and b) porosity and dielectric constant of porous SN-5N and SN-6P5N composites prepared by pressureless sintering at 1750°C.
4. Conclusions

SNNWs/Si₃N₄ porous ceramics were prepared by pressureless sintering of micro-sized Si₃N₄ powders with 5 wt% nano-sized Si₃N₄ powders and 6 wt% PSN. The SNNWs enhance the flexural strength and fracture toughness of Si₃N₄ porous ceramics from 263 to 296 MPa, and 5.15 to 6.53 MPa·m⁴/², respectively, and the corresponding dielectric constant reduces from 4.47 to 4.38. Overall, the in-situ formed SNNWs alter the microstructure and promote the mechanical and dielectric properties of Si₃N₄ porous ceramic.

Acknowledgements This work is supported by the National Natural Science Foundation of China under Grant Nos 11572105 and 51772061, the National Fund for Distinguished Young Scholars (No. 51525201), and the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (No. 11421091).

References
1) F. L. Riley, J. Am. Ceram. Soc., 83, 245–265 (2000).
2) Z. Krstic and V. D. Krstic, J. Mater. Sci., 47, 535–552 (2012).
3) R. Zhang, D. Fang, Y. Pei and L. Zhou, Ceram. Int., 38, 4373–4437 (2012).
4) S. Liu, S. Gao, W. Li, P. Chen, Z. Guo, L. Zhang, Y. Zhou and F. Ye, Ceram. Int., 43, 9348–9354 (2017).
5) Y. Inagaki and O. T. Kondon, J. Eur. Ceram. Soc., 22, 2489–2494 (2002).
6) D. Aranzazu and H. Stuart, J. Eur. Ceram. Soc., 24, 413–419 (2004).
7) S. Q. Ding, Y. P. Zeng and D. L. Jiang, Mater. Lett., 61, 2277–2280 (2007).
8) T. Wan, D. Yao, J. Yin, Y. Xia, K. Zuo, H. Liang and Y. Zeng, J. Eur. Ceram. Soc., 37, 3285–3291 (2017).
9) T. Ohji, Mat. Sci. Eng. A-Struct., 498, 5–11 (2008).
10) X. Li, L. Zhang and X. Yin, Scripta Mater., 67, 380–383 (2012).
11) S. J. Lee and S. Baek, Ceram. Int., 42, 9921–9925 (2016).
12) W. Duan, X. Yin, F. Cao, Y. Jia, Y. Xie, P. Greil and N. Travitzky, Mater. Lett., 158, 257–260 (2015).
13) E. Bódis, K. Molnár, A. Mucsi, Z. Károly, J. Möczó, S. Klébert, A. M. Keszlér, P. Fazekas and J. Szépvölgyi, Ceram. Int., 43, 16811–16818 (2017).
14) G. Logesh, M. Rashad, M. Lodhe, U. Sabu, A. Joseph, K. C. James Raju and M. Balasubramanian, J. Alloy. Compd., 787, 1083–1093 (2018).
15) Y. Yang, B. Li, C. Zhang, S. Wang, K. Liu and B. Yang, Mat. Sci. Eng. A-Struct., 644, 90–95 (2015).
16) W. Yang, F. Gao, H. Wang, X. Zheng, Z. Xie and L. An, J. Am. Ceram. Soc., 91, 1312–1315 (2010).
17) Y. Li, W. Han, G. Chen, Y. Cheng and Q. Yang, Ceram. Int., 43, 3435–3438 (2017).
18) X. Li, L. Zhang and X. Yin, Scripta Mater., 66, 33–36 (2012).
19) X. Zhang, N. Li, T. Lan, Y. Lu, K. Gan, J. Wu, W. Huo, J. Xu and J. Yang, Ceram. Int., 43, 4235–4240 (2017).