

Dielectric and mechanical properties of hot-pressed SiCN/Si₃N₄ composites

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Abstract A series of high temperature radar wave-absorbing materials, SiCN/Si₃N₄ ceramics, were prepared by hot-pressing. The nanometer SiCN powder, used as an absorber in the SiCN/Si₃N₄ ceramic, was synthesized through laser pyrolysis of ((CH₃)₃Si)₂NH and NH₃. The dielectric and mechanical properties of the prepared ceramics were investigated. XRD and SAED were conducted to study the growth of crystals in the ceramics. The results showed that the transformation of Si₃N₄ from α to β was inhibited. The growth of the rod-like β -Si₃N₄ grains in SiCN/Si₃N₄ ceramics was retarded during hot-pressing process due to the existence of the nanometer SiCN particles. The relative density and the strength of the composites both decreased with the increase of the SiCN content in the composites. The dielectric properties of the ceramics prepared at different temperatures were very different. For the samples sintered at 1600°C and 1700°C, both the real and imaginary parts of the complex permittivity of them increased as the content of SiCN powder in the sample obviously. For the sample with same concentration of SiCN, the real and imaginary parts of them varied with the sintering temperature. SAED pattern revealed that structure of the SiCN in SiCN/Si₃N₄ sintered at 1800°C tended to crystallize fully. Its real, imaginary parts and dissipation factor were much lower than those sintered at 1600°C and 1700°C greatly.

Keywords Permittivity · SiCN · Si₃N₄ · Composite

Supported by national natural science foundation of China (No. 50572090)

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Introduction

Stealthiness is now a required specification for modern weapons. The specific absorbing materials may be used to absorb the emitted electromagnetic energy and to minimize the wave reflected in the direction of the enemy radar receiver. Some potential application, such as high velocity missile, require that the materials may undergo high thermo mechanical stress. The most promising class of new materials is ceramic woven fabric reinforced ceramic matrix, which is a kind of excellent materials with high strength, high toughness and oxidation resistance at high temperature [1]. The composites could be prepared by CVI process and hot-pressing methods. But high cost of CVI process prevents the fiber reinforced ceramic matrix composites from being widely used. Silicon nitride ceramics are of great interest for high temperature structural application due to their strength, toughness, creep, oxidation resistance and thermal shock properties. Niihara reported that the dispersion of very fine SiC particles in Si₃N₄ could lead to a remarkable improvement in the mechanical properties of the matrix both at room temperature and high temperatures [2].

In this paper, a new kind of absorbing material which is promising to undergo high thermo mechanical stress, SiCN/Si₃N₄ ceramic, is developed using the Si₃N₄ ceramic as the matrix and the nanometer SiCN powder as the absorber to dissipate microwave. The microstructure, mechanical and dielectric properties of the ceramics were examined.

Experimental procedure

Commercial Si₃N₄ powder (α -Si₃N₄ content >90%; average diameter 0.5 μ m, Si₃N₄ content >99 wt%) and β -SiCN (synthesized by laser pyrolysis of (Me₃Si)₂NH)(Me:CH₃) and

NH_3 , average diameter 45 nm, free carbon content about 5 wt%, with permittivity of $\epsilon_r = 235 - j277$) were used to sinter the ceramics. High purity Y_2O_3 (5 wt%) and MgO (5 wt%) powders were used as sintering aids. These powders, with different SiCN contents (0, 5, 10 and 15 wt%), were mixed by wet ball milling with ethanol in a plastic bottle for 4 h. After ball milling, the slurries were dried and the mixtures were put into a graphite die with inner BN powder coating and then subjected to hot pressing at 1600, 1700 and 1800° under a pressure of 15 MPa for 1 h in a N_2 atmosphere, respectively.

The hot-pressed billets were cut into specimens with dimensions of 3 mm \times 5 mm \times 30 mm for three-point bending strength tests. The cross-head speed was 0.5 mm min^{-1} .

The sintered samples were cut into cuboids of 22.86 mm \times 10.16 mm \times 2.0 mm for permittivity test in a frequency range of 8.2 ~ 12.4 GHz. The permittivity of the specimens was measured by a method, which was based on the measurements of the reflection and transmission module between 8.2 GHz and 12.4 GHz, in the fundamental wave-guide mode TE₁₀, using rectangular samples (10.16 \times 22.86 \times

2.00 mm). After calibration, reflection and transmission coefficients were obtained with the help of an automated measuring system (HP8510B network analyzer). Both the real and imaginary parts of the permittivity and permeability were calculated.

The phase identification of the samples was performed by conventional X-ray diffraction (XRD).

Experimental results

Figure 1 shows the XRD patterns of the Si_3N_4 and SiCN/ Si_3N_4 ceramics sintered at 1700°C. The main phases in them are α - Si_3N_4 and β - Si_3N_4 crystals. The content of β - Si_3N_4 calculated from the results of XRD is about 73%, 66%, 54% and 45% for the samples with 0 wt%, 5 wt%, 10 wt% and 15 wt% SiCN, respectively. It infers that the transformation of Si_3N_4 from α to β is inhibited during hot-pressing process due to the presence of the nanometer SiCN particles and the low sintering temperature 1700°C does not ensure all the α - Si_3N_4 can be transformed into β - Si_3N_4 even in the monolithic Si_3N_4 ceramic.

Scanning electron micrographs of the sample sintered at 1600°C are shown in Fig. 2. It can be found that the grain shape in the monolithic Si_3N_4 is rod-like and the grain size is in a very wide range. But in the SiCN/ Si_3N_4 sample showed in Fig. 2(b), the grain size and shape become smaller and granular after 10 wt% SiCN was introduced into it. Therefore, it implies that rod-like grains of Si_3N_4 are suppressed and growth of the grain size is retarded after addition of the nanometer SiCN into Si_3N_4 .

Figure 3 shows the bulk density of SiCN/ Si_3N_4 samples with different SiCN content sintered under the same pressure but at different temperatures. It can be seen that the bulk density of the SiCN/ Si_3N_4 ceramics with 5 wt%, 10 wt%

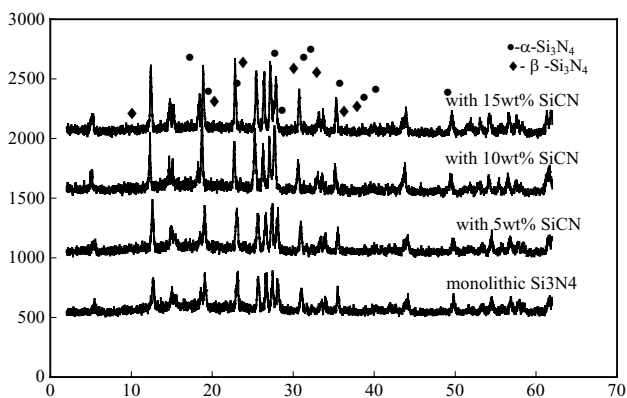


Fig. 1 The XRD patterns of the samples sintered at 1700° for 1 h under pressure of 15 MPa

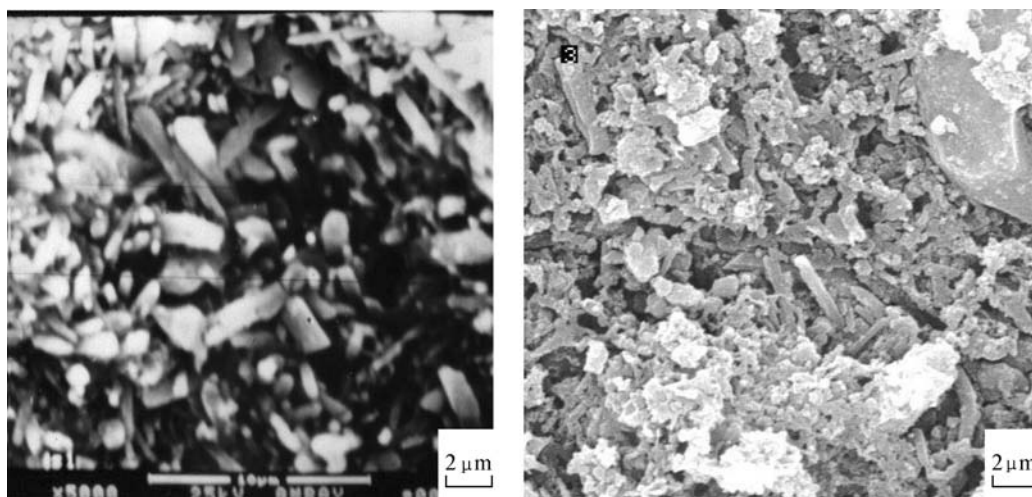


Fig. 2 Micrograph of different samples (a) monolithic Si_3N_4 , (b) SiCN/ Si_3N_4 with 10 wt% SiCN

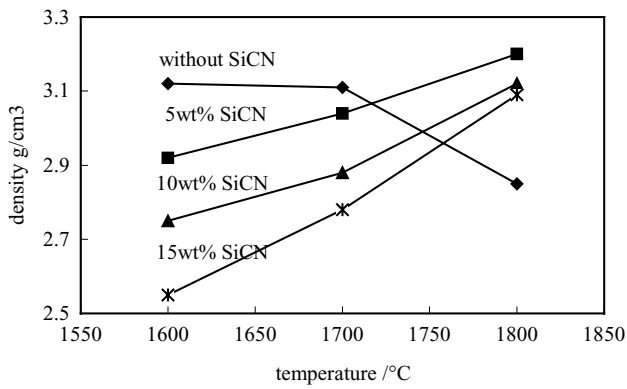


Fig. 3 Effect of hot-pressing temperature on the densification behavior of samples

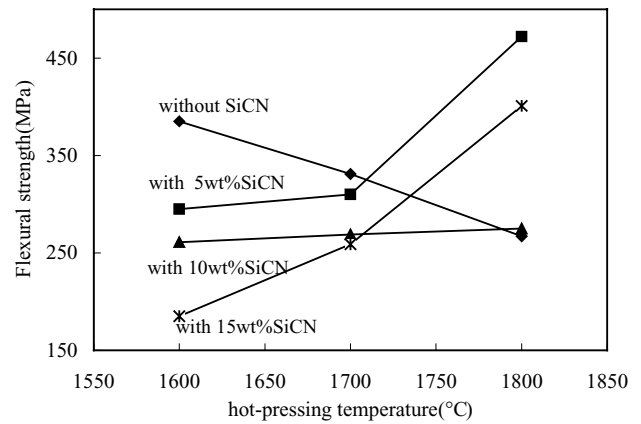


Fig. 4 Effect of hot-pressing temperature on the strength of the samples with 0, 5, 10 and 15 wt% SiCN

and 15 wt% SiCN increases with the sintering temperature, respectively. It is because that more liquid formed from MgO+Y₂O₃ additive and some SiO₂ on the surface of Si₃N₄ particles in higher sintering temperature will promote the densification of the SiCN/Si₃N₄ ceramics. For the ceramics prepared at the same sintering temperature, however, their density decreases with the SiCN content, which means that the introduction of the nanometer SiCN retards the densification of the SiCN/Si₃N₄ ceramics. It is well understood that densification of Si₃N₄ ceramic takes place when β-Si₃N₄ crystallizes and grows in glassy phase formed from the additives, α-Si₃N₄ and SiO₂ on the surface of α-Si₃N₄. For the ceramics with a higher SiCN concentration, more SiCN will remain in the glass phase during the sintering process, which makes the glass more viscous, and therefore, blocks crystallization and growth of β-Si₃N₄ from the glass. It is consistent with the results about the microstructures of ceramics shown in Fig. 2.

The density decrease of the pure Si₃N₄ ceramics with the increase of sintering temperature in Fig. 3 might be attributed to excessive growth of grain or decomposition of β-Si₃N₄ in the temperature 1800°C under a fairly low sintering pressure 15 MPa.

Figure 4 shows the flexural strength of the samples. It can be seen that the flexural strength of the SiCN/Si₃N₄ ceramics with the same SiCN content increases with the sintering temperature. More liquid and more β-Si₃N₄ formed at a higher sintering temperature not only increase the density of the SiCN/Si₃N₄ ceramics, but also strengthen those ceramics. An exception is that the flexural strength of sample with 10% SiCN has very little change as the sintering temperature increase and the reason is unknown till now. The decrease of the flexural strength for the pure Si₃N₄ ceramics with sintering temperature is due to their low bulk densities.

The as-prepared β-SiCN is characterized by high dissipation to electromagnetic wave. Its dissipation factor (tan δ = ε''/ε')

and bulk SiC. Our result reveals that its permittivity, which nearly equals to that of carbon black, is closely related to its microstructure and composition, especially the N concentration in it dominated by the synthesized temperature [5, 6]. Its higher dissipation electromagnetic wave comes from N substitution of C in the nanometer low-crystalline SiC. When the powder is heat-treated over 1750°C for a long time, it tends to crystallize fully; and its real, imaginary parts and the dissipation factor decrease greatly. Figure 5 is the SAED pattern of the β-SiCN synthesized at 1650°C. We can see that the



Fig. 5 SAED pattern of the as-formed SiCN

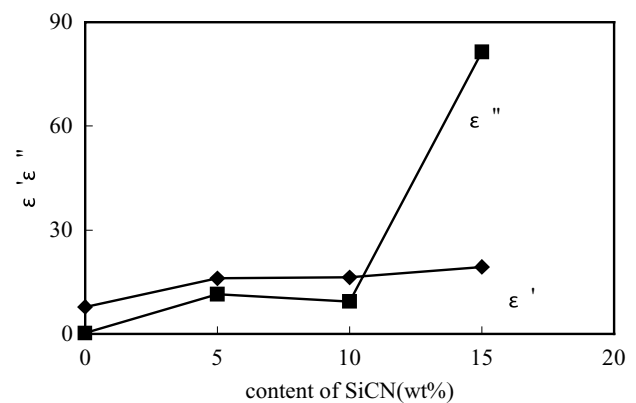


Fig. 6 Relationship between the permittivity of SiCN/Si₃N₄ sintered at 1600°C

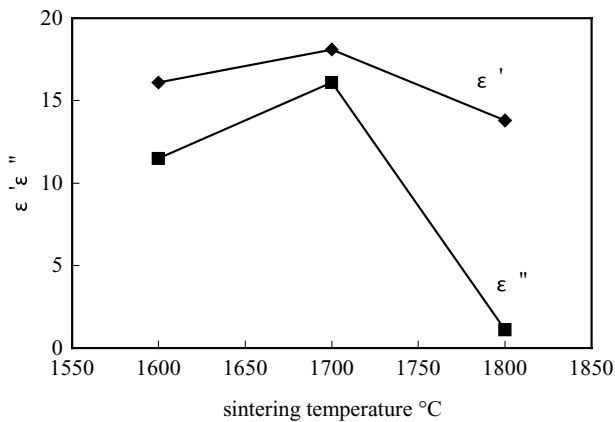


Fig. 7 Relationship between the permittivity of the SiCN/Si₃N₄ ceramics with 10 wt% SiCN

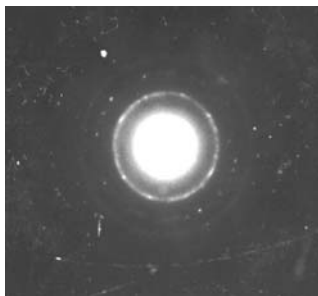


Fig. 8 SAED pattern of SiCN in the SiCN/Si₃N₄ with 10 wt% SiCN sintered at 1800°C

as-prepared SiCN does not fully crystallize. Its permittivity is $\epsilon r = \epsilon r' - j\epsilon r'' = 235 - j277$ at 9.375 GHz [3–5].

Figure 6 shows the relationship between the permittivity of the SiCN/Si₃N₄ sintered at 1600°C and the content of SiCN. It can be found that the real and imaginary parts of the SiCN/Si₃N₄ ceramics increase with the SiCN content, which is in consistence with the mixture rule of permittivity and other mixture equations [6]. But the much higher imaginary part of the SiCN/Si₃N₄ ceramic with 15 wt% SiCN is not expected and could not be explained. The aggregation or formation of mutually connected network of the nanometer SiCN particles in the higher content may be the possible reason.

Figure 7 gives the relationship between the permittivity and their sintering temperature for the SiCN/Si₃N₄ ceramics with 10 wt% SiCN. It is obvious that the real and imaginary parts of the SiCN/Si₃N₄ ceramic sintered at 1700°C are higher than those of the SiCN/Si₃N₄ ceramic sintered at 1600°C, which may be attributed to the higher density of the samples sintered in the higher temperature (1700°C). The imaginary part of the SiCN/Si₃N₄ ceramic sintered at 1800°C is the lowest. The lowest density of the SiCN/Si₃N₄ sintered at 1800°C and the change of structure of the SiCN attribute to the case. Figure 8 exhibits the SAED pattern of the SiCN in the SiCN/Si₃N₄ sintered at 1800°C. It shows that the structure of the SiCN tends to be perfect and its permittivity turns to be low [5, 6]. Thus, the permittivity of the SiCN/Si₃N₄ ceramic sintered at 1800°C is lower than those of SiCN/Si₃N₄ sintered at 1600°C and 1700°C.

Conclusions

The instruction of the nanometer SiCN into Si₃N₄ inhibits the transformation of α -Si₃N₄ to β -Si₃N₄ during hot-pressing process. The flexural strength of the SiCN/Si₃N₄ ceramics, therefore, decreases with the SiCN content. The unexpected low permittivity of the SiCN/Si₃N₄ ceramic sintered at 1800°C is due to the density decrease and the minimization of permittivity of SiCN because of the grain growth, the higher crystalline degree of SiCN and the N loss in SiCN.

References

1. E. Mouchon, P.H. Colmban, *J. Mater. Sci.*, **31**, 323 (1996).
2. L. Tian, *J. Mater. Sci.*, **33**, 797 (1998).
3. H. Jiao, W. Zhou, and F. Luo, *Fuhe Cailliao Xuebao/Acta Materiae Compositae Sinica*, **20**(4), 34 (2003).
4. D. Zhao and W. Zhou, *Physica E: Low-Dimensional Systems and Nanostructures*, **9**(4), 679 (2001).
5. F. Luo, W. Zhou, D. Zhao, and H. Jiao, *Airop. mater. & Technol.*, **1**, 8 (2002).
6. H. Musal, J. Hahn, and G. Bush, *J. Appl. Phys.*, **63**(8), 3678 (1988).