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Mechanical, dielectric properties and thermal shock resistance of porous Si_2N_2O/Si_3N_4 composite ceramics

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Porous Si_2N_2O/Si_3N_4 composite ceramics were fabricated by gas pressure sintering of Si_3N_4 and SiO_2 with Sm_2O_3 as sintering additive under N_2 atmosphere. Porosity and β -Si₃ N_4 phase of the composites are increased with the increasing α -Si₃ N_4 content in starting materials. The composite ceramics show high flexural strength (223 ~ 288 MPa at room temperature) and good thermal shock resistance and the critical thermal shock temperature (ΔT_c) could be up to 1100 °C. The dielectric properties are mainly influenced by the sample porosity and phase composition. The as-prepared Si₂ N_2O / Si₃ N_4 composite ceramics possess both low dielectric constant (ϵ = 4.8-5.2) and loss tangent (tan δ = 0.0014-0.0063), combined with excellent mechanical performance and thermal shock resistance, showing Si₂ N_2O/Si_3N_4 composite ceramics could be promising high-temperature wave transparent materials.

Key words: Si₂N₂O/Si₃N₄ composite ceramics, Mechanical properties, Thermal shock resistance, Dielectric properties.

Introduction

Wave transparent material is a kind of dielectric material which is used to protect radar system of aircraft and integrates multi-functions such as load bearing, wave transparent and heat-proofing. Silicon nitride (Si₃N₄) ceramics is a suitable material for missile radome because of high mechanical strength, good resistance to ablation and good thermomechanical property [1, 2], and have received much attractions in the past decades. However, Si₃N₄ ceramics possess high dielectric constant ($\varepsilon > 7$) and show catastrophic drops in flexural strength after thermal shock above the critical temperature due to larger elastic modulus which can't meet the requirements of high-speed flight of aircraft and limit its application. While silicon oxynitride (Si₂N₂O) ceramics have been considered as a potential material for wave transparent materials due to low dielectric constant, good thermal shock resistance and excellent oxidation resistance [3, 4]. Consequently, Si₃N₄/ Si₂N₂O composite ceramics is being studied to combine desirable properties such as the oxidation and thermal shock resistance of Si₂N₂O and the strength of Si₃N₄.

Generally, compared with dense bodies, porous ceramics exhibit such unique properties as lighter weight, better thermal shock resistance and lower dielectric constant [5-7], thus various process methods have been developed to fabricate porous ceramics. A common technique is adding an organic substance or using organic foam as a template that is carbonized and burned out to form pores such as gelcasting [8,9]. However, residual carbon is generally difficult to remove completely, which seriously restricts the radome applications. Another technique is partial sintering process [10], that is sintering green body to a certain degree of densification by controlling the size of raw materials and sintering process based on chemical reaction and sintering behavior of powders. Gas-pressure sintering is a simple and effective way to realize partial sintering by adjusting sintering process parameters such as sintering temperature, sintering time and gas pressure. Therefore, Si₂N₂O/Si₃N₄ composite ceramics were fabricated by gas pressure sintering using Sm₂O₃ powders as sintering additives in the present work. Mechanical, thermal shock resistance and dielectric properties of Si₂N₂O/Si₃N₄ composite ceramics as well as Si₂N₂O, Si₃N₄ single-phase ceramics were investigated.

Materials and Experimental Procedure

α-Si₃N₄ (purity = 99.99%, D₅₀ ≤ 0.7 μm), SiO₂ (purity = 99.9%, D₅₀ ≤ 1.0 μm) and Sm₂O₃ powders (99.9% pure) were used as starting powders. The molar contents of Si₃N₄, SiO₂ and Sm₂O₃ were modified and listed in Table 1 in order to prepare the Si₂N₂O/Si₃N₄ composites with various β-Si₃N₄ contents. Samples were given brief names, for example, as-prepared samples with SiO₂+ 2 mol%Sm₂O₃ + 60 mol% Si₃N₄ as starting materials were designated as SN60. The above starting powders according to a certain ratio shown in Table 1 were weighed and wet mixed in anhydrous alcohol in a plastic bottle, and then the mixture was milled with high-purity Si₃N₄ balls for 12 hrs. After milling, the

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Materials	The molar ratio of composi- tion in starting materials (mol. %)			The calculated contents of β -Si ₃ N ₄ (mol. %)	
	Sm ₂ O ₃	Si ₃ N ₄	SiO ₂	Theoretical content	True content
SN50	2	49	49	0	0
SN60	2	60	38	37	27
SN70	2	70	28	60	41
SN100	2	98	0	100	100

Table 1. The molar ratio of composition in starting materials and the β -Si₃N₄ contents in as-sintered samples.

slurry was dried, sieved, and bilaterally pressed to form rectangular bars at 100 MPa. Some powders were shaped into f50 mm disks by bilaterally prepressing at 20 MPa in a steel mold and followed with isostatic pressure of 100 MPa.The green bodies of SN50, SN60, SN70 were placed in a graphite crucible and sintered for 2 h at 1750 °C and SN100 for 2 hrs at 1800 °C, respectively.

The porosity of as-prepared samples was measured by the Archimedes method. The three-point bending strength was measured on rectangular bars $(3 \text{ mm} \times 4 \text{ mm} \times 20 \text{ mm})$ at a crosshead speed of 0.5 mm/min by an instrument (Instron 1195, Instron Co., Buckinghamshire, England). Each final value was averaged over five measurements. Young's modulus E were measured by pulse echo overlap method in the frequency range from 2 to 10 MHz with cylindrical specimens (20 mm diameter and 16 mm thick).

$$E = \rho \times \left(C_{L}^{2} - \frac{4}{3} \times C_{s}^{2} \right)$$
(1)

where ρ is density of the sample, C_L and C_s are the speed of transverse wave and longitudinal wave, respectively. Dielectric constant and loss tangent of the specimens with a size of $f50.0 \text{ mm} \times 2.5 \text{ mm}$ were measured in the frequency range of 7-18 GHz at room temperature by a vector network analyzer and a high Q resonant cavity device. Water quenching experiments were to test thermal shock performance of the samples in a Muffle furnace between 400 °C and 1200 °C. When the furnace was heated to the expired temperature, the polished rectangular specimens $(3 \text{ mm} \times 4 \text{ mm} \times 20 \text{ mm})$ were placed in it and kept for 20 min, and then immersed into a bath of ice and water rapidly. The residual strength of the specimens after the thermal shock were measured. Critical temperature difference (ΔT_c) was defined as the temperature difference in the water quench experiment after which the strength of the quenched specimen was below 70% of the original sample [11, 12].

Phase composition was determined by X-ray diffractometry (XRD, Model X'Pert PRO, PANalytical, Ltd., Holland). The quantitative phase analyses were performed by comparing the peak intensity ratios. The microstructures of bulk samples were observed by

scanning electron microscope (SEM, Model JSM-7000F, Jeol, Japan).

Results and Discussion

Phase, microstructure and mechanical performance

SiO₂, 2 mol%Sm₂O₃ and different molar ratio of α -Si₃N₄ and SiO₂ as starting materials were sintered for 2 hrs at 1750 °C under 0.5 MPa nitrogen pressure to prepare Si₂N₂O/Si₃N₄ composites. The XRD patterns of the as-sintered samples are presented in Fig. 1. The diffractograms show that only peaks of Si₂N₂O are detected in sample SN50 and no peak for other crystalline phases are detected, which suggests complete reaction of α -Si₃N₄ and SiO₂ after sintering at 1750 °C with Sm₂O₃ additives. The formation of Si₂N₂O can be illustrated as the following reaction [13].

$$Si_3N_4 + SiO_2 \rightarrow 2Si_2N_2O$$
 (1)

It can be seen that the sample SN60 and SN70 are well crystallized and only β -Si₃N₄ and Si₂N₂O are identified. With the increasing α -Si₃N₄ contents, a portion of α -Si₃N₄ reacts with SiO₂ to form Si₂N₂O. Excess α -Si₃N₄, which does not react with SiO₂, dissolve and precipitate β -Si₃N₄. Quantitative analysis (as shown in Table 1) indicates that the relative content of β -Si₃N₄ increases with the increasing α -Si₃N₄ content in starting materials. The true content of β -Si₃N₄ lower than theoretical content indicates surface oxygen of α -Si₃N₄ involved in the reaction.

Table 2. Properties of as-sintered samples with different contents of $\beta\text{-}Si_3N_4\!.$

Sample	Porosity/%	Flexural strength/MPa	Young's modulus /GPa
SN50	14.7	357 ± 11	215 ± 4
SN60	19	288 ± 10	192 ±5
SN70	28.7	223 ± 22	175 ± 7
SN100	20.3	354 ± 20	287 ± 3



Fig. 1. X-ray diffraction of as-sintered samples (a) SN50 (b) SN60 (c) SN70 (d) SN100.



Fig. 2. SEM for the as-sintered samples (a) SN50 (b) SN60 (c) SN70 (d) SN100.



Fig. 3. Retained strength of samples with different contents of Si_3N_4 as a function of quenching temperature difference.

The microstructure of Si_2N_2O/Si_3N_4 composite is presented in Fig. 2. Lath-like silicon oxynitride grains and a mass of intergranular glassy phase are developed in SN50 samples. Sample SN60 exhibits plate-like grains overlapped with rod-like grains. Increasing Si_3N_4 content results in more rod-like grains in the morphology which are not sufficiently developed because of high-viscosity liquid phase formed during liquid-phase sintering as shown in Fig. 2(c). Sample SN100 shows well-developed rod crystals.

Properties of the obtained samples are listed in Table 2. Porosity of the samples increases with increasing α -Si₃N₄ content, because excess α -Si₃N₄ tends to develop into rod-shaped grains, among which reciprocal overlap joint results in high porosity. As indicated, the strength and Young's modulus decrease with the increasing porosity of the samples. Besides, the composite ceramics (SN60) have lower flexural strength and elastic modulus than Si₃N₄ (SN100) with the similar porosity.

Thermal shock resistance

Residual strength of specimens after water quenching



Fig. 4. SEM photograph of the SN60 cross-section after quenched at (a) $1000 \,^{\circ}$ C (b) $1100 \,^{\circ}$ C.



Fig. 5. The frequency dependence of (a) dielectric constant (b) loss tangent of Si_2N_2O/Si_3N_4 composites with various α -Si₃N₄ contents.

and critical temperature difference (ΔT_c) are two important parameters to evaluate thermal shock resistance of materials. Fig. 3 shows residual strength of samples with different contents of β -Si₃N₄ as a function of quenching temperature difference. The four samples all show the feature of an extension of the original short crack, that is, once the critical temperature difference ΔT_c is reached, the strength drops suddenly and then into the crack quasi-static expansion stage.

Sample SN50 exhibits poor thermal shock resistance, the residual strength showed a sharp decline when quenched from 600 °C and its residual strength was less than 100 MPa. The poor thermal shock resistance of sample SN50 could be attributed to the phase composition and microstructure morphology. As illustrated in Fig. 2(a), SN50 contains a large number of glass phase which prone to micro-cracks in the process of thermal shock, thus greatly affecting the thermal shock resistance.

Sample SN60 and SN70 exhibit better thermal shock resistance than SN100 (Si₃N₄). After quenched from 800-1000 °C, the strength was reduced slightly, and when temperature difference reached 1100 °C, the strength decreases catastrophically, showing that porous composite ceramics possess excellent thermal shock resistance and the critical thermal shock temperature is up to 1100 °C. Fig. 4 shows the microstructure of the SN60 sample after thermal shock at 1000 °C and 1100 °C. There was no major crack after quenched at 1000 °C and obvious cracks generated after quenched at 1100 °C, which induced the different residual strength.

The critical temperature difference (ΔT_c) for crack initiation by thermal shock can be estimated from [14]:

$$R = \Delta T_{c} = \frac{(1 - v)\sigma_{f}}{E\alpha}$$
(2)

where σ_f is the fracture strength, v is the Poisson's ratio (suppose 0.26 for all the samples) [15], E is the Young's modulus, α is the thermal expansion coefficient. It can be seen from the above formula that the material with higher strength and lower elastic modulus exhibits better thermal shock resistance. As shown in Table 2, compared with Si₃N₄ (SN100), flexural strength of composite ceramics (SN60) is reduced by 1/5, while the elastic modulus is reduced by 1/3. Therefore, Si₂N₂O/Si₃N₄ composite materials exhibit better thermal shock resistance than Si₃N₄.

Dielectric properties of Si₂N₂O/Si₃N₄ composites

For wave transparent materials, besides mechanical properties, dielectric constant and loss tangent of the products are extremely vital performance parameters. Fig. 5 shows dielectric constant (ϵ) and loss tangent (tan δ) of the as-prepared ceramics with increasing α -Si₃N₄ content in the starting powers, respectively. All the Si₂N₂O/Si₃N₄ composites samples exhibit both lower dielectric constant (ϵ = 4.8-5.2) and loss tangent(tan δ = 0.0014-0.0063) than Si₃N₄(SN100) of the similar porosity in the frequency range of 7GHz to 18GHz, which is ideal for radome application.

Porosity and phase composition are two key factors affecting the dielectric constant of the composite [9]. The relationship between porosity and dielectric constant is consistent with the empirical relation that dielectric constant increases with density. The other factor is different relative content of β -Si₃N₄ and Si₂N₂O in the final composition. From sample SN50 to SN70, porosity and the content of β -Si₃N₄ phase increase with the increasing content of α -Si₃N₄ in the starting materials. The increasing porosity would decrease dielectric constant and the increasing amount of β -Si₃N₄ would increase dielectric constant. As a result of the combination of the two factors, the SN60 (ϵ = 4.8) exhibits the best dielectric properties.

Conclusions

In this study, Si_2N_2O / Si_3N_4 composite ceramics were prepared by gas pressure sintering. Phase composition and porosity of the composites can be tailored in a certain range by adjusting α -Si₃N₄ content in starting materials. The high flexural strength (at room temperature) are attributed to overlapping of the plate grains and the rod-shaped grains. The critical temperature difference (ΔT_c) could reach 1100 °C. The dielectric properties of the composites are excellent ($\epsilon = 4.8-5.2$, tan $\delta = 0.0014-0.0063$). So, by this simple process, we can get Si₃N₄/Si₂N₂O composite ceramics with excellent overall performance of strength, thermal shock resistance and dielectric properties and allow it to be used in military and aviation.

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References

- 1. F.L. Riley, J. Am. Ceram. Soc. 83 (2000) 245-265.
- K.S. Mazdiyasni, R. Ruh, J. Am. Ceram. Soc. 64 (1981) 415-419.
- M. Radwan, T. Kashiwagi, Y. Miyamoto, J. Eur. Ceram. Soc. 23 (2003) 2337-2341.
- X. Rong-Jun, M. Mamoru, X. Fang-Fang, Z. Guo-Dong, B. Yoshio, J. Eur. Ceram. Soc. 22 (2002) 963-971.
- V. Inagaki, T. Ohji, S. Kanzaki, Y. Shigegaki, J. Am. Ceram. Soc. 83 (2000) 1807-1809.
- E.S. Reddy, J. Noudem, C. Goupil, Energy Convers. Manag. 48 (2007) 1251-1254.
- J. She, J.F. Yang, D.D. Jayaseelan, N. Kondo, T. Ohji, S. Kanzaki, Y. Inagaki, J. Am. Ceram. Soc. 86 (2003) 738-740.
- Y.C. Pei, S.Q. Li, C.Q. Yu , Z.Y. Huang , J.T. Ma , J.L. Li, Ceram. Int. 35, 3365-3369(2009).
- D.C. Jia, Y.F. Shao, B.Y. Liu, Y. Zhou, Mater. Chem. Phys. 124 (2010) 97-101.
- C. Zou, C. Zhang, B. Li, S. Wang, F. Cao, Mater. Des. 44 (2013) 114-118.
- 11. F. Monteverde, L. Scatteia, J. Am. Ceram. Soc. 90 (2007) 1130-1138.
- 12. D. Jia, Y. Zhou, T. Lei, Ceram. Int. 22 (1996) 107-112.
- M. Ohashi, K. Nakamura, K. Hirao, M. Toriyama, S. Kanzaki, Ceram. Int. (1997) 2327-37.
- 14. W.D. Kingery, J. Am. Ceram. Soc. 38 (1955) 3-15.
- J.H. She, J.F. Yang, D.D. Jayaseelan, N. Kondo, T. Ohji, S. Kanzaki, J. Am. Ceram. Soc. 86 (2003) 738-740.