Fabrication and properties of porous boron nitride/silicon oxynitride ceramic composites via gas pressure sintering

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ABSTRACT

Silicon oxynitride (Si_2N_2O) based wave transparent composites with different volumes of hexagonal boron nitride (h-BN) were prepared by gas pressure sintering at 1700 °C with 5.0–10.0 mol% Li_2O as additive. The effects of Li_2O and BN contents on phase, microstructure, mechanical and dielectric properties of the composites were investigated. The decomposition of Si_2N_2O and pore structures was influenced by Li_2O content, while the incorporation of h-BN effectively alleviated Si_2N_2O decomposition. The BN/Si_2N_2O composites could withstand a thermal shock of 1100 °C without strength degradation in N_2, while only the samples with adequate porosity exhibited high thermal shock resistance in air. The high thermal shock resistance was attributed to the crack-healing ability of the composites. The as-sintered BN/Si_2N_2O ceramics showed both low dielectric constant ($\varepsilon < 4.49$) and loss tangent ($\tan\delta < 0.0056$) with good mechanical properties and thermal shock resistance, indicating that the as-sintered BN/Si_2N_2O composites could be used as promising high temperature wave transparent material.

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1. Introduction

Silicon oxynitride (Si_2N_2O) is a promising structural/functional material for high temperature applications due to its high strength, excellent thermal shock resistance, low density and high thermal stability [1–5]. Pure and dense Si_2N_2O ceramic obtained by hot pressing technique exhibited good mechanical and dielectric properties, thus making it a potential wave transparent material [6,7]. However, the as-sintered dense bodies showed poor thermal shock resistance (critical temperature difference $\Delta T_c = 600$ °C), and the dielectric constant ($\varepsilon = 6.17$) is still too high for use in broadband missile antenna shield [8–10]. Our previous work showed that the porous Si_2N_2O ceramics obtained by gas pressure sintering (GPS) possess high strength, excellent thermal shock resistance ($\Delta T_c = 1200$–1300 °C) and improved dielectric properties ($\varepsilon < 4.59$, $\tan\delta < 0.0049$) [11], however, the processability of the as-obtained specimen is not satisfied. For instance, the hardness reached 4.5–6.2 GPa and requires 20–25 min to cut down a rectangular bar (3 mm × 4 mm × 36 mm) using diamond blade. Thus, appropriate ways should be tried to improve the machinability of Si_2N_2O ceramics.

In recent years, based on the weak boundary phase (WBP) concept, plate-liked h-BN particles were adopted as a WBP into ceramic matrix to improve the machinability [12–14]. Besides, h-BN is commonly used as a radar window material because it has a very low dielectric constant of 4.2, a low loss tangent of 1.1×10^{-3}, high sublimation temperature of 3000 °C (no melting point), and good thermal shock resistance

[15–17]. It is therefore expected that the addition of h-BN particles would improve the machinability of the composites and reduce the dielectric constant as well.

Generally, porous ceramics have better thermal shock resistance and are easier to be machined into complex shapes than the dense ceramics [18–20]. Although BN/Si_2N_2O is a proper electro-magnetic wave penetrating material, little work has been done on preparation of porous BN/Si_2N_2O ceramics. In this paper, porous BN/Si_2N_2O ceramics with high performance were fabricated by gas pressure sintering. Effects of Li_2O and BN contents on phase micro-structure, mechanical and dielectric properties of the materials were investigated. The influences of oxidation of Si_2N_2O and h-BN on thermal shock resistance are also discussed.

2. Materials and experimental procedure

α-Si_3N_4 (E10 grade, UBE Industries Ltd., Japan), SiO_2 ($d_{50} = 50$ nm, Rare Metallic Ltd., Japan) and BN ($d_{50} = 10$ μm, purity = 99.9%, UBE Industries Ltd., Japan) were used as starting powders. To obtain an equimolar mixture of Si_3N_4 and SiO_2, the amount of Si_3N_4 was increased to compensate for its surface oxygen content. Li_2O powders (99% pure, Sinopharm Group Chemical Reagent Co., Ltd., China) as sintering aids were added to the equimolar Si_3N_4/SiO_2 mixture at 5.0–10.0 mol%. The mixtures were ball-milled with ethanol medium for 24 h.

After being dried and sieved, the powders were shaped into Φ60 mm disks by uniaxial pressing at 20 MPa in a steel mold and followed with isostatic pressure of 200 MPa (LDJ 200/600-300IV, AVIC, China). The green bodies were placed in a graphite crucible in a powder bed of BN

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and Si_3N_4 with the content of 50 vol.% each and sintered for 2 h at 1700 °C. Sintering was conducted at 1.5 MPa nitrogen pressure with a heating rate of 5 °C/min. Samples were given brief names, for instance, mixtures with 5.0 mol% Li_2O and 15 vol.% BN were labeled as $L_{5.0}BN_{15.0}$. Samples without BN were also prepared for comparison and were designated as $L_{5.0}$, $L_{7.5}$ and $L_{10.0}$, respectively.

Flexural strength was tested by the three-point bending method using rectangular bars (3 mm × 4 mm × 36 mm) in a universal testing machine (Istron-5569, Instron Group, USA) with a span of 30 mm. Fracture toughness measurement was performed using single-edge-notch beam (SENB) method. The thermal shock resistance was evaluated by water quenching experiments. To characterize the machinability, the drilling test was performed using a Φ3.5 mm hard metal alloy (WC/Co) drill at a speed of 600 rpm. The constant drilling force is 19.8 N, and the drilling rate is 2.0 mm/min.

Phase analysis was done by X-ray diffraction (XRD; RigakuD/Max 2200VPC, Japan). Quantitative analysis was determined by comparing the peak intensity ratios. The microstructures were examined by scanning electron microscopy (SEM; Quanta 200, FEI Co., USA). Density was calculated according to the Archimedes principle, while porosities were measured by mercury intrusion method (Autopore 9500, Micrometics Co., USA). Dielectric constant and loss tangent of the specimens (Φ18.0 mm × 1.0 mm) were measured in the frequency range of 21 GHz to 38 GHz at room temperature by RF impedance/material analyzer (PNA N5230A, Agilent, USA).

3. Results and discussion

3.1. Phase assemblages

The effects of Li_2O and BN contents on phase evolution of the products were shown in Fig. 1. It could be seen from Fig. 1(a) that the main crystalline phase is Si_2N_2O. Si_2N_2O was formed by chemical reaction of equip-molar mixtures of Si_3N_4 and SiO_2 at temperature above 1450 °C [6]. With the increase of Li_2O in starting materials, the diffraction peak intensities of β-Si_3N_4 increased apparently. β-Si_3N_4 was produced by the decomposition of Si_2N_2O, which was thermaldynamically easier in the liquid rich environment and accelerated by increasing the Li_2O content [11]. The formation and decomposition reactions of Si_2N_2O could be described in the following equations [21,22]:

$$Si_3N_4(s) + SiO_2(s) = 2Si_2N_2O(s) \tag{1}$$

$$Si_2N_2O(s) = \beta-Si_3N_4(s) + SiO(g) + N_2(g). \tag{2}$$
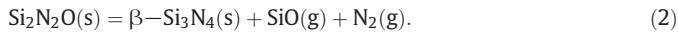
It is reported that Li_2O volatilized easily at high temperatures and theoretically neither Li_2O nor its compound should be existed after

sintering [23,24]. However, small peaks of $Li_2Si_2O_5$ were detected in sample $L_{10.0}BN_{15.0}$. The presence of $Li_2Si_2O_5$ suggested a part of SiO_2 in the starting material reacted with excessive Li_2O (10 mol%). The low porosity of $L_{10.0}BN_{15.0}$ (lack diffusion channel for Li_2O evaporation) is responsible for the formation of $Li_2Si_2O_5$. The porosities of the as-sintered BN/Si_2N_2O ceramic composite were illustrated in Table 1.

The low sinterability of h-BN often resulted in porosity increase of the composites [12], and it could be seen from Table 1 that the porosity of the composites increased with increasing BN volume fraction. The increased porosity provided more channels for Li_2O volatilization and accordingly less Li_2O/SiO_2 liquid was formed during sintering. The reduced amount of liquid resulted in lower degree of Si_2N_2O decomposition, and less β-Si_3N_4 was formed because Reaction (2) was retarded by decreasing the amount of liquid. Evidenced by Fig. 1(b), the peak intensities of β-Si_3N_4 decreased slightly when the BN content increased. However, the effect of BN volume change on phase is not very significant. All the composites were composed of Si_2N_2O, h-BN and β-Si_3N_4.

3.2. Microstructure evolution

The influence of Li_2O on microstructure of monolithic Si_2N_2O ceramics was shown in Fig. 2(a) to (c). Si_2N_2O grains exhibited typical elongated lath-like morphology [1]. Generally, the densification process was facilitated by increasing the amount of sintering additive [19,20]. However, in the present research, the density reached its maximum when Li_2O increased from 5.0 mol% to 7.5 mol%. Further increase of Li_2O to 10.0 mol% resulted in an abnormal increase of porosity, indicating that decomposition of Si_2N_2O has a negative effect on densification. Meanwhile, the pore structures changed gradually. In sample $L_{5.0}$, the pores were edged and no elongated β-Si_3N_4 grains were visible. In samples $L_{7.5}$ and $L_{10.0}$, the gas produced by the Si_2N_2O decomposition led to the formation of round pores and many elongated β-Si_3N_4 grains were found around the pores. Severe decomposition of Si_2N_2O in sample $L_{10.0}$ is the reason why it has higher porosity than sample $L_{7.5}$.

The influence of the 15 vol.% BN on the microstructure evolution of the composites was presented from Fig. 2(d) to (f). It is apparent that the density of the composites increased with increasing Li_2O content. As discussed above, severe decomposition of Si_2N_2O would lead to abnormal porosity increase when Li_2O was 10.0 mol% (without adding BN). However, the addition of 15 vol.% h-BN effectively alleviated the decomposition of Si_2N_2O because it reduces the amount of SiO_2 in the starting material and less Li_2O/SiO_2 liquid was formed during sintering. As a result, the density of $L_{10.0}BN_{15.0}$ is higher than that of $L_{10.0}$, even though adding h-BN is often reported to increase the porosity of the composites [14,16].

The typical inhibition effect of h-BN particles on anisotropic grain growth of the matrix was also observed in the present study, as
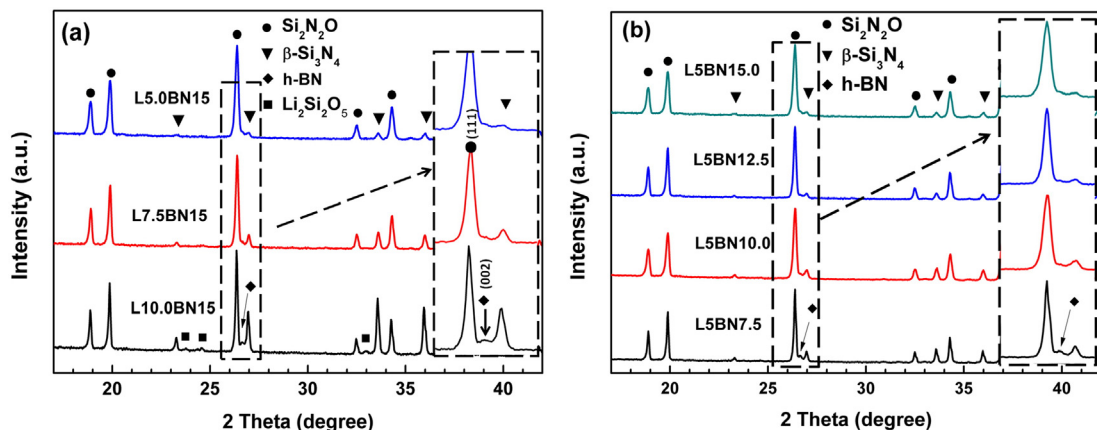

Fig. 1. Phase evolution of BN/Si_2N_2O composites as a function of Li_2O and BN contents. (a) Li_2O varies from 5.0–10.0 mol% and (b) h-BN varies from 7.5–15 vol.%.