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Mechanical, dielectric properties and thermal shock resistance of porous silicon oxynitride ceramics by gas pressure sintering

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ABSTRACT

Porous silicon oxynitride (Si_2N_2O) ceramics were prepared by gas pressure sintering with 2.5–10.0 mol% Li_2O as additive. The influences of Li_2O content on phase, microstructure, mechanical and dielectric properties of the Si_2N_2O ceramics were investigated. XRD analysis showed that the increase of Li_2O content facilitate both the densification and the decomposition of Si_2N_2O into Si_3N_4. The elongated Si_2N_2O crystals contribute to the high flexural strength (161.3–228.4 MPa at room temperature) of the products. The thermal shock resistance was greatly influenced by the sample porosity, and the highest critical temperature difference (ΔT_c) could be up to 1300 °C. The dielectric properties were mainly affected by the sample porosity. The as-sintered Si_2N_2O ceramics showed both low dielectric constant ($\varepsilon < 4.59$) and loss tangent ($\tan\delta < 0.0049$) with good mechanical properties and excellent thermal shock resistance, indicating the gas pressure sintered Si_2N_2O ceramics could be used as promising high temperature wave transparent material.

1. Introduction

Silicon oxynitride (Si_2N_2O) is a unique compound in the Si_3N_4–SiO_2 binary system and possesses many outstanding properties such as high mechanical properties, excellent oxidation resistance, low density and high thermal stability, thus making it a promising high temperature structural material [1–5]. Tong [6] reported that pure and dense Si_2N_2O ceramic could be prepared at relative low temperatures by hot pressing technique with Li_2O an additive. The obtained material exhibits good mechanical and dielectric properties which makes it suitable for use in the wave transparent application field such as the missile radomes. However, the as-sintered dense product showed poor thermal shock resistance (critical temperature difference of about 600 °C) [7], and the dielectric constant of dense Si_2N_2O ($\varepsilon = 6.17$) is still too high for radome application (for broadband missile radomes, the dielectric constant (ε) and loss tangent ($\tan\delta$) are required to be less than 5 and 0.005, respectively). In addition, hot pressing is not a good option due to the limited size of the products and difficulties in subsequent machining. Thus, appropriate ways should be tried in order to improve thermal shock resistance, reduce the dielectric constant and obtain components with large size.

Generally, porous ceramics possess both lower dielectric constant and better thermal shock resistance than dense bodies [8–10], thus various processing techniques have been developed to prepare porous ceramics. A common method is adding an organic fugitive substance or using sacrificial template that is burned out to form pores. However, it is generally difficult to eliminate the impurity of residual carbon, which severely influences radome applications. Another method is sintering powder compacts to a certain degree of densification, the so-called partial sintering process [11]. Gas-pressure sintering (GPS) is an effective and simple way to realize partial sintering by adjusting gas pressure, sintering temperature, sintering time, and the amount of additives. For instance, Li [12] reported 1 MPa nitrogen pressure sintered arbitrary porous Si_3N_4 ceramics with porosity of 40–54% and flexural strength of 60–226 MPa. Yang [13] also fabricated high performance porous Si_3N_4 ceramics with porosity of 40–60% using 0.6 MPa nitrogen pressure sintering and 2.5–5 wt% of Y_2O_3 as sintering additive. Besides, high N_2 pressure is useful for the prevention of thermal decomposition of Si_2N_2O [14], thus gas pressure sintering technique is chosen in the present work to prepare porous Si_2N_2O ceramics.

Although Si_2N_2O is a proper electro-magnetic wave penetrating material, little work has been done on porous Si_2N_2O obtained by gas pressure sintering. In this paper, porous Si_2N_2O ceramics with high performance were fabricated under a nitrogen pressure of 1.5 MPa. The effect of Li_2O content on phase assemblages, grain morphology, mechanical and dielectric properties of the materials are investigated. The influences of porosity and oxidation on thermal shock resistance are also discussed. An appropriate way to increase the thermal shock properties is proposed.

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2. Materials and experimental procedure

α-Si_3N_4 (E10 grade, UBE Industries Ltd., Japan) and SiO_2 ($d_{50}=50$ nm, purity=99.95%, Chengdu Sinuowei Co, Ltd., China) 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 2.5–10.0 mol%. The mixtures were ball-milled with methanol medium for 24 h.

After being dried and sieved, the powders were shaped into ⌀60 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 and Si_3N_4 with the content of 50 vol% each and sintered for 2 h at 1600, 1650 and 1700 °C, respectively. Sintering was conducted under 1.5 MPa Nitrogen pressure with a heating rate of 5 °C/min. Samples were given brief names, for instance, mixtures sintered at 1650 °C with 5.0 mol% Li_2O was designated as SNO 1650/5.0.

Three-point flexural strength was performed at room temperature using rectangular bars (3 mm × 4 mm × 36 mm) in a universal testing machine (Istron-5969, Instron Group., USA) at a crosshead speed of 0.5 mm/min with a span of 30 mm. Fracture toughness measurement was performed using single-edge-notch beam method (SENB) with a span of 16 mm, and a half-thickness notch was made using a 0.3 mm thick diamond blade. Water quenching experiments were carried out in a Muffle furnace at temperatures between 800 and 1300 °C in air. After the furnace was heated to the desired temperatures, the ground and polished rectangular bars (3 mm × 4 mm × 36 mm) were put into the furnace and kept for 10 min. Then the samples were immersed into a mixture of water and ice immediately. Critical temperature difference (ΔT_c) was defined as the temperature difference in the quench test after which the strength of the quenched specimen was less than 70% of the original specimen [15,16].

Phase identification was conducted using X-ray diffraction (XRD). Quantitative analysis was determined by comparing the peak intensity ratios. The microstructures were characterized by scanning electron microscopy (SEM, FEI, Quanta 200). Density and porosity were calculated according to Archimedes principle [17,18]. Mass change before and after oxidation was measured to evaluate the oxidation degree. Dielectric constant and loss tangent of the specimens with a size of ⌀18.0 mm × 1.0 mm were measured in the frequency range of 21–38 GHz at room temperature by RF impedance/material analyzer (Model 4291B, Agilent, USA).

3. Results and discussion

3.1. Phase, microstructure and mechanical properties

The effect of Li_2O content on phase assemblages of the products is shown in Fig. 1. It can be seen that the major phase is Si_2N_2O, while minor α-Si_3N_4 and β-Si_3N_4 could still be detected. The formation of Si_2N_2O can be described as the following reaction [19]:

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

It is known that the formation of Si_2N_2O proceeds in a liquid phase [5–7]. The residual α-Si_3N_4 peaks observed in Fig. 1(a) indicated that the above reaction is not sufficient in sample SNO 1650/2.5 due to the relative low amount of liquid provided by eutectic melts of Li_2O/SiO_2. The α-Si_3N_4 peaks disappeared when Li_2O content is higher than 2.5 mol%, and β-Si_3N_4 peaks were detected. The appearance of β-Si_3N_4 without detectable SiO_2 proved that the decomposition of Si_2N_2O took place, and the increasing β-Si_3N_4 peak intensities found on the samples with higher Li_2O contents suggested that the decomposition of Si_2N_2O is thermodynamically easier in the liquid rich environment. The decomposition reaction of Si_2N_2O could be described as the following equation [20]:

$$3Si_2N_2O_{(s)}\rightarrow 2Si_3N_{4(s)}+3SiO_{(g)}+N_{2(g)} \quad (2)$$

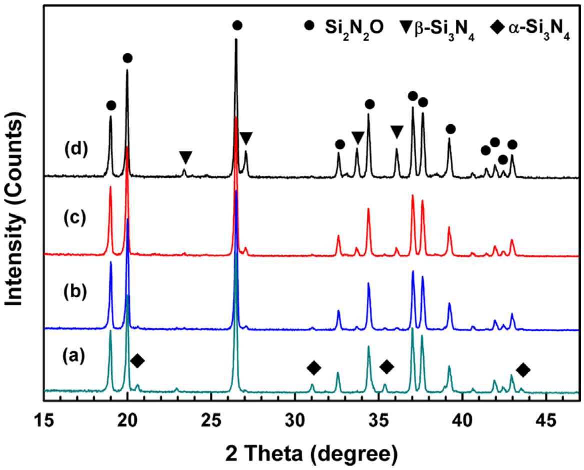

Fig. 1. X-Ray diffraction patterns of the Si_2N_2O ceramics sintered at 1650 °C for 2 h as a function of different Li_2O contents (a) 2.5 mol%; (b) 5.0 mol%; (c) 7.5 mol%; (d) 10.0 mol%.

Shown in Fig. 2(a)–(c), Si_2N_2O grains exhibit elongated lath-like morphology. Increasing Li_2O content resulted in obvious densification in the samples. Due to the severe decomposition of Si_2N_2O into gaseous SiO and N_2, the pore structures of SNO 1650/10.0 were apparently different from the samples doped with 2.5–7.5 mol% Li_2O, and typical elongated β-Si_3N_4 grains were visible, as shown in Fig. 2(d). Properties of the obtained samples were listed in Table 1. The porosity of SNO 1650/10.0 is very close to that of SNO 1650/7.5, indicating that decomposition of Si_2N_2O has negative effect on densification. Quantitative analysis showed that the fraction of Si_2N_2O reaches maximum when the amount of Li_2O is 5.0 mol%.

Samples doped with 5.0 mol% Li_2O were selected to examine the influence of temperature on phase, and the related properties were summarized in Table 2. At relative low temperature of 1600 °C, only 87.8 wt% Si_2N_2O was formed. At 1650 °C, the fraction of Si_2N_2O reaches maximum. Sample SNO 1700/5.0 has almost the same fraction of Si_2N_2O with SNO 1650/5.0 but much lower porosity, indicating that the temperature difference between 1650 and 1700 °C has significant influence on densification but little impact on phase assemblage.

3.2. Thermal shock resistance

Thermal shock resistance of SNO 1700/5.0 and SNO 1650/5.0 were shown in Fig. 3. For SNO 1700/5.0, the residual strength showed little change from room temperature to 800 °C. When quenched from 900–1100 °C, the compacts exhibits abnormal thermal shock resistance and its retained strength is even higher than the strength of unquenched samples. High retained strength was maintained (193.4 MPa) even when temperature difference reached 1200 °C. However, for sample SNO 1650/5.0, a catastrophic decrease in residual strength was observed when temperature is above 900 °C.

The different thermal shock resistance of the above 2 samples could be attributed to the different porosity and oxidation degree.