Gas pressure sintering of BN/Si$_3$N$_4$ wave-transparent material with Y$_2$O$_3$–MgO nanopowders addition

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Received 6 March 2014; received in revised form 7 May 2014; accepted 8 May 2014
Available online 29 May 2014

Abstract

BN/Si$_3$N$_4$ ceramics performed as wave-transparent material in spacecraft were fabricated with boron nitride powders, silicon nitride powders and Y$_2$O$_3$–MgO nanopowders by gas pressure sintering at 1700 °C under 6 MPa in N$_2$ atmosphere. The effects of Y$_2$O$_3$–MgO nanopowders on densification, phase evolution, microstructure and mechanical properties of BN/Si$_3$N$_4$ material were investigated. The addition of Y$_2$O$_3$–MgO nanopowders was found beneficial to the mechanical properties of BN/Si$_3$N$_4$ composites. The BN/Si$_3$N$_4$ ceramics with 8 wt% Y$_2$O$_3$–MgO nanopowders showed a relative density of 80.2%, combining a fracture toughness of 4.6 MPa m$^{1/2}$ with an acceptable flexural strength of 396.5 MPa.

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Keywords: C. Mechanical properties; BN/Si$_3$N$_4$ wave-transparent material; Gas pressure sintering; Y$_2$O$_3$–MgO nanopowders

1. Introduction

Si$_3$N$_4$ was one of the most promising ceramics for the application of microwave-transparent materials which protected the spacecraft from the influences of harsh environment [1,2] due to its high mechanical strength, good thermal shock resistance and excellent rain erosion resistance [3–5]. However, the relatively high dielectric constant and dielectric loss tangent limited its wider application in spaceflight [6,7]. In order to improve dielectric properties of Si$_3$N$_4$ ceramics, BN nanoparticles with low dielectric constant and low thermal expansion coefficient were introduced into Si$_3$N$_4$ matrix to fabricate BN/Si$_3$N$_4$ composites by gas pressure sintering [8,9]. Therefore BN/Si$_3$N$_4$ composites have low dielectric constant and outstanding mechanical properties.

However, a sintered body with high density of BN/Si$_3$N$_4$ composites was difficult to be obtained due to strong covalent bonds between Si–N and B–N [10]. Some metal oxides such as MgO, Al$_2$O$_3$, Y$_2$O$_3$ and Re$_2$O$_3$ have been used as sintering additives for the densification of Si$_3$N$_4$ [11–14]. The liquid formed via the chemical reactions between the additives and SiO$_2$ in Si$_3$N$_4$ could enhance the diffusivity of atoms to reduce the sintering temperature. Finally we can fabricate the most promising BN/Si$_3$N$_4$ materials because of their excellent strength and toughness at elevated temperatures, good thermal shock resistance and dielectric properties, and low coefficient of thermal expansion [15–16].

Y$_2$O$_3$ has been a promising sintering additive for both pressureless and gas-pressure sintered Si$_3$N$_4$ [11,12,17–20]. Although the microstructure and mechanical properties of sintered Si$_3$N$_4$ containing Y$_2$O$_3$, Re$_2$O$_3$, Al$_2$O$_3$, MgO have been previously reported [11–14], the effects of Y$_2$O$_3$–MgO nanopowders on the developed microstructure and elevated-temperature properties need further research. Nevertheless, few reports were devoted to the effect of Y$_2$O$_3$–MgO composite nanopowders or its precursors as sintering aids over the mechanical and microstructure of BN/Si$_3$N$_4$ wave-transparent material. So in the present work, the effect of Y$_2$O$_3$–MgO composite nanopowders on the densification and mechanical properties of BN/Si$_3$N$_4$ wave-transparent materials...
properties of BN/Si₃N₄ wave-transparent material was investigated. In addition, microstructural development and phase evolution of sintered samples were investigated with the help of SEM and XRD.

2. Experimental procedures

α-Si₃N₄ powders (α-Si₃N₄ > 93%, D50 < 0.5 μm; UNISCERA, Beijing, China) and BN nanoparticles (purity > 99.5 wt%, D50 < 100 nm; NNT CO., Taiwan, China) were used as starting materials. The additives used in this work were Y₂O₃ (Hang Zhou Wan Jing New Material Co., Ltd. P.R. China) with the average grain size of 50 nm and 100 nm and MgO (Hang Zhou Wan Jing New Material Co., Ltd. P.R. China) with the average grain size of 50 nm. Y₂O₃–MgO composites were prepared in our laboratory with particle size of less than 80 nm via an esterification sol–gel processing [21] using the following reagents: magnesium nitrate (Mg(NO₃)₂·6H₂O) (AR, Sinopharm Chemical Reagent Co., Ltd), yttrium nitrate (Y(NO₃)₃·6H₂O) (AR, Sinopharm Chemical Reagent Co., Ltd), citric acid (AR, Sinopharm Chemical Reagent Co., Ltd) and ethylene glycol (AR, Sinopharm Chemical Reagent Co., Ltd). The XRD pattern and SEM micrographs of the Y₂O₃–MgO nanopowders are shown in Fig. 1. The results from X-ray diffraction (Fig. 1(a)) indicated that Y₂O₃–MgO nanopowder was a two-phase material consisting of cubic Y₂O₃ and cubic MgO phase. The average particle size of the powders was normally below 80 nm (Fig. 1(b)). The BN nanoparticles were previously washed with methanol to remove little B₂O₃ contamination. The compositions of different samples are referred in Table 1.

100 nm-Y₂O₃+50 nm-MgO, 50 nm-Y₂O₃+50 nm-MgO, Y₂O₃–MgO precursor and Y₂O₃–MgO nanopowders were added to the starting powders as the sintering aids. The starting powders and sintering aids were mixed in anhydrous ethanol by a vertical ball mill, followed by drying at 60 °C for 24 h under vacuum. The mixture was then passed through 200 μm vibrating sieve. This precursor powder was compacted by uniaxial processing to produce square green body with unilateral length of 55 mm. The green body was molded by an isostatic pressing method with rubber mold under 120 MPa.

The BN/Si₃N₄ green body was sintered in BN-coated graphite dyes at 1700 °C for 120 min under a steady pressure of 6 MPa in N₂ atmosphere. The compacted samples were heated to 1700 °C in N₂ atmosphere with a heating/cooling rate of 5 °C/min in gas pressure sintering furnace. The apparent porosity was determined by Archimedes' method using deionized water as a medium. The bending strength was measured by three-point bending test and the fracture toughness was determined by a single edge pre-cracked beam method. The fracture surface of specimens was coated with Au for SEM (Hitachi S-520, Hitachi Ltd., Tokyo, Japan) observation.

3. Results and discussion

3.1. Densification behavior

Fig. 2 plots the apparent porosity and relative density of the BN/Si₃N₄ ceramics with different sintering aids such as 100 nm-Y₂O₃+50 nm-MgO, 50 nm-Y₂O₃+50 nm-MgO, Y₂O₃–MgO precursor and Y₂O₃–MgO nanopowders. The addition of the sintering aids decreases the apparent porosity and therefore increases the relative density of BN/Si₃N₄ ceramics. Compared with the other three sintering aids, Y₂O₃–MgO composite nanopowders are more beneficial to the densification of BN/Si₃N₄ ceramics and the relative density and apparent porosity reach 80.2% and 9.6%

<table>
<thead>
<tr>
<th>Sample’s label</th>
<th>Composition of samples</th>
<th>Amount of Y₂O₃/MgO composite additives (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBY100M50</td>
<td>Si₃N₄+10 wt%BN+100 nm-Y₂O₃+50 nm-MgO</td>
<td>8</td>
</tr>
<tr>
<td>SBY50M50</td>
<td>Si₃N₄+10 wt%BN+50 nm-Y₂O₃+50 nm-MgO</td>
<td>8</td>
</tr>
<tr>
<td>SBY1M1</td>
<td>Si₃N₄+10 wt%BN+Y₂O₃–MgO precursor</td>
<td>8</td>
</tr>
<tr>
<td>SBY0M0</td>
<td>Si₃N₄+10 wt%BN+Y₂O₃–MgO nanopowders</td>
<td>8</td>
</tr>
</tbody>
</table>

The molar ratio of the Y₂O₃/MgO was fixed at Y₂O₃:MgO = 1:1
respectively. Owing to the formation of ample liquid phase at lower temperature which assists mass transport and rearrangement [22], the densification of BN/Si$_3$N$_4$ ceramics proceeds quickly with the addition of Y$_2$O$_3$–MgO composite nanopowders [23–25], whereas the BN/Si$_3$N$_4$ material using Y$_2$O$_3$–MgO precursor as sintering aids shows the minimal relative density and maximum apparent porosity, reaching 55.5% and 35.88% respectively. The possible reason is that big pores appear with the decomposition or evaporation of the organic chemicals in Y$_2$O$_3$–MgO precursor in the sintering process.

3.2. Mechanical properties

Fig. 3 presents the mechanical properties of BN/Si$_3$N$_4$ ceramics with different sintering aids. It can be seen that the BN/Si$_3$N$_4$ material with the sintering aid of Y$_2$O$_3$–MgO nanopowders exhibits the maximum bending strength and fracture toughness, reaching 396.5 MPa and 4.6 MPa m$^{1/2}$ respectively, whereas the BN/Si$_3$N$_4$ material using Y$_2$O$_3$–MgO precursor as sintering aids shows the minimal bending strength and fracture toughness, reaching 137 MPa and 2.73 MPa m$^{1/2}$ respectively. The possible reason is that big pores appear with the decomposition or evaporation of the organic chemicals in the Y$_2$O$_3$–MgO precursor in the sintering process. Compared with SBY100M50, SBY50M50, SBY1M1 and SBY0M0 are more effective in improving the mechanical properties, especially the fracture toughness of BN/Si$_3$N$_4$ composites. The possible reason is that Y$_2$O$_3$ promotes the formation of rod-like Si$_3$N$_4$ particles and MgO promotes the densification of BN/Si$_3$N$_4$ wave-transparent material [26]. In addition, compared with the other three sintering aids, the higher temperature activity and homogeneity of Y$_2$O$_3$–MgO nanopowders are more beneficial to the mechanical properties and fracture toughness [27].

3.3. Phase evolution

Fig. 4 shows the XRD pattern of BN/Si$_3$N$_4$ wave-transparent materials with different sintering aids. The XRD pattern shows that the main crystal phase of the composites is $\beta$-Si$_3$N$_4$, and no $\alpha$-Si$_3$N$_4$ is detected. The existence of Si$_2$N$_2$O can be explained by the following reaction which occurs during the sintering process when the temperature reaches 1600 °C [28]:

$$2\text{Si}_3\text{N}_4(s) + 1.5\text{O}_2(g) \rightarrow 3\text{Si}_2\text{N}_2\text{O}(s) + \text{N}_2(g)$$  \hspace{1cm} (1)

When the temperature is higher than 1650 °C, the following reaction occurs and the amount of Si$_3$N$_2$O decreases [28]:

$$2\text{Si}_2\text{N}_2\text{O}(s) \rightarrow \text{Si}_3\text{N}_4(s) + \text{SiO}(g) + 0.5\text{O}_2(g)$$  \hspace{1cm} (2)

Based on thermodynamic calculations, MgSiO$_3$ is formed readily by a reaction between MgO and SiO$_2$ at $\alpha$-Si$_3$N$_4$ surface as a silicate liquid phase during sintering and then transformed into its glassy phase after cooling down [29]. Maybe it is the reason why no diffraction peaks of MgO are observed. These results supported the $\alpha$-Si$_3$N$_4$–$\beta$-Si$_3$N$_4$ transformation with the help of
sintering additives after the solution of α-Si₃N₄ fine grains and the subsequent reprecipitation as β-Si₃N₄ phase [30]. Distinct reflections of h-BN and Y₂O₃ are observed in the XRD pattern at 26.5° and 31°.

### 3.4. Microstructure

The fracture microstructures of BN/Si₃N₄ wave-transparent composites with different sintering aids can be seen in Fig. 5. It can be clearly seen that more amount of rod-like β-Si₃N₄ particles with higher mean aspect ratio and narrower grain size distribution form in the BN/Si₃N₄ composites with Y₂O₃–MgO nanopowders as sintering aids than the other three sintering aids (Fig. 5(A)–(D)). It is possibly due to the fact that Y₂O₃–MgO nanopowders are formed in molecular level and have higher activation energy and homogeneity than Y₂O₃ or MgO powder [27]. The high temperature activity of Y₂O₃–MgO nanopowders may improve the α→β transformation of Si₃N₄ at 1700°C. The rod-like β phase grains lead to improvement in the fracture toughness of the material, and the toughening mechanism is similar to that in whisker reinforced composite materials, i.e. grain bridging by elongated grains and grain pullout [31].

### 4. Conclusions

The sintering aids promoted the densification of BN/Si₃N₄ wave-transparent materials and increased their mechanical properties. The BN/Si₃N₄ composites using Y₂O₃–MgO nanopowders as sintering aids exhibited the maximum densification, bending strength and fracture toughness, reaching 2.75 g/cm³, 396.5 MPa and 4.6 MPa m¹/² respectively. In addition, when the sintering aids were added to the BN/Si₃N₄ wave-transparent material, all α-Si₃N₄ particles transformed to rod-like β-Si₃N₄ after sintering. When using Y₂O₃–MgO nanopowders as sintering aids, more elongated...
and interlocked rod-like $\beta$-Si$_3$N$_4$ grains and higher mean aspect ratio formed in BN/Si$_3$N$_4$ wave-transparent material, which led to the improvement of mechanical properties of BN/Si$_3$N$_4$ wave-transparent materials.

References

[27] Y. Zhao et al. / Ceramics International 40 (2014) 13537–13541