Original Article

Preparation of porous silicon nitride ceramics by freeze drying

Xiao Chun-fang a,*, Han Bing b

a Changsha Aeronautical Vocational and Technical College, Changsha 410124, China
b Liaoning University of Science and Technology Institute of Mechanical Engineering And Automation, Anshan 114051, China

A R T I C L E   I N F O

Article history:
Received 4 October 2019
Accepted 8 October 2019
Available online 11 November 2019

Keywords:
Freeze drying method
Experimental raw materials and preparation methods
Effect of solid content in slurry
Phase analysis
Microstructure
Dielectric properties

A B S T R A C T

Silicon nitride ceramics have excellent mechanical properties, good thermal and chemical stability, low dielectric constant and dielectric loss. It is an ideal choice for high-speed aircraft electromagnetic wave transmission materials. In this paper, the preparation methods of porous silicon nitride materials with controllable dielectric constant and pore structure were systematically studied. Porous silicon nitride materials with controllable pore structure and directional growth were prepared by freeze-drying process and adjusting the solid content of slurry.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Silicon nitride ceramics have excellent mechanical properties, good thermal and chemical stability, low dielectric constant and dielectric loss. It is an ideal choice for high-speed aircraft electromagnetic wave transmission materials. Porous silicon nitride ceramics have both excellent properties of high strength, high temperature resistance and porous lightweight of silicon nitride. Its dielectric constant can be adjusted in the range of 2–8. Porous silicon nitride ceramics have shown outstanding advantages in high Mach number, broadband and low aiming error radome materials. It has become one of the research hotspots of high temperature transmission materials at home. Low dielectric porous silicon nitride ceramics were prepared by freeze-drying process. In order to further optimize the porous structure of porous silicon nitride ceramics, porous silicon nitride ceramics with directional pore distribution were prepared by freeze-drying process. It was studied that the effects of solid content of SiN slurry on porosity, bulk density, mechanical properties, phase composition, microstructure and dielectric properties of porous SiN material [1–4].

2. Experimental raw materials and preparation methods

2.1. Experimental raw materials

The content of α-Si3N4 is more than 93 wt.% in Si3N4 powder and the median particle size is 0.8 μm. The SEM photograph is shown in Fig. 1.
2.2. Technological process

(1) Slurry preparation

Silicon nitride slurries with different solid content were prepared by planetary ball milling using Si$_3$N$_4$ powder as raw material, high purity Y$_2$O$_3$ powder and Al$_2$O$_3$ powder as composite sintering additives, polyacrylamide as dispersant, PVB solution as binder and deionized water as solvent for freeze-drying.

(2) Vacuum defoaming

The slurry prepared in step (1) is placed in a vacuum defoamer to vacuum and remove the bubbles introduced in the process of ball milling.

(3) Freeze Forming

The vacuum defoaming slurry was frozen by freeze dryer. Firstly, the temperature/pressure parameter of the freeze dryer was set at $-40 \, ^\circ C/13.33 \, Pa$, and the slurry was frozen. Then the pressure is reduced to below 1.33 Pa to $-60 \, ^\circ C$, and the heating system is turned on to continuously supply the heat needed for ice sublimation until the ice existing in the slurry sublimes, thus removing the solvent moisture in the slurry and obtaining porous silicon nitride blanks.

(4) Pressure sintering

Porous silicon nitride ceramics were prepared by sintering the freeze-dried porous silicon nitride body in a gas pressure furnace.

3. Effect of solid content of slurry on pore size distribution of porous silicon nitride

Fig. 2 shows the effect of solid content on pore size distribution of porous silicon nitride. It can be seen from the figure that pore size of porous silicon nitride prepared by freeze-drying method has two main scales, i.e. the pore size presents a bimodal distribution. It can be observed that the size of small pore size is less than 500 nm, and that of large pore size is about 1 \, \mu m. With the increase of solid content, the peak of large pore size gradually moves towards the peak of small pore size. As a result, the pore size decreased by about 0.3 \, \mu m, the bimodal phenomenon gradually weakened, and the difference between large and small pore sizes tended to disappear. The pore size of the porous silicon nitride slurry is almost unchanged, and its content increases with the solid content of the slurry. Finally, when the volume content of the slurry is 40 vol.\%, the pore size of the porous silicon nitride material is basically below 1 \, \mu m. The reason is that when the solid content of slurry is low, the large size pore in the material is mainly formed by the physical accumulation of powder particles. At this time, the amount of solid particles is less, and there are more air holes in the material. With the increase of the solid content of slurry, the formation of silicon nitride grains in the material is due to the accumulation of liquid phase sintered silicon nitride grains. With the increase of solid content of slurry, the amount of small pore will decrease further, and the amount of small pore will increase accordingly. The grains generated by sintering drive overlap with each other to form small pore. The quantitative analysis in Table 1 further reveals the effect of solid content on pore size distribution [8–10].

Table 1 – The influence of solid content on the pore size distribution of Si3N4 ceramics.

<table>
<thead>
<tr>
<th>Solid content (vol.%)</th>
<th>D &lt; 1000 nm</th>
<th>D &gt; 1000 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>17%</td>
<td>83%</td>
</tr>
<tr>
<td>20</td>
<td>26%</td>
<td>74%</td>
</tr>
<tr>
<td>25</td>
<td>28.5%</td>
<td>71.5%</td>
</tr>
<tr>
<td>30</td>
<td>31%</td>
<td>69%</td>
</tr>
<tr>
<td>35</td>
<td>54%</td>
<td>46%</td>
</tr>
<tr>
<td>40</td>
<td>64.5%</td>
<td>35.5%</td>
</tr>
<tr>
<td>50</td>
<td>79%</td>
<td>21%</td>
</tr>
</tbody>
</table>

Fig. 1 – Scanning electron microscope of Silicon nitride raw materials (a) × 20,000; (b) × 50,000.
500 nm to the pore size at less than 500 nm. The pore volume at more than 500 nm decreases from 69% to 35.5%, while the pore size at less than 500 nm decreases from 31%. It increased sharply to 64.5%.

4. Phase analysis of porous silicon nitride prepared by freeze-drying method

Fig. 3 is the XRD results of porous silicon nitride prepared under 1700 °C/2 h, 0.3 MPa experimental parameters. It can be seen from the figure that under the sintering conditions of 1700 °C/2 h and 0.3 MPa, the α phase in porous silicon nitride has completely transformed into β phase, and the peak value of the diffraction of β-Si3N4 has a positive correlation with the proportion of solid matter. If the proportion of solid is smaller, the sample is looser, the pore size is larger, and the spacing of particles is larger, it is difficult to bond the grains together when the liquid phase produced by high temperature sintering is less or the liquid phase produced by high temperature sintering. Thus, the sintering driving force formed by the surface tension of liquid phase is relatively weak, while when the solid content of ceramic slurry is high, the sintering driving force formed by the surface tension of liquid phase is relatively weak. The smaller particle spacing, the easier diffusion of liquid phase produced by high temperature sintering, the greater driving force of sintering, and the easier sintering process and phase transition make the growth and development of β-Si3N4 better, so the diffraction peak intensity of β-Si3N4 is stronger [11–14].

5. Microstructure of porous silicon nitride prepared by freeze-drying method

Fig. 4 is the SEM photograph of the green body after freeze-drying with different slurry solid content. According to the SEM results, when the slurry solid content is 15 vol.% in volume, the dendritic ice crystal structure can be clearly seen. At this time, there is a clear distinction between large-sized and small-sized pore, and small-sized pore with silicon nitride particles gathering in the ice crystal Structurally. With the increase of solid content, the micro-morphology of special dendritic ice crystals produced by ice sublimation becomes less and less obvious, the details of ice crystal structure disappear gradually, and the morphology is gradually composed of ice crystal structure-ice crystal dendrite main structure-layered structure-uniform porous structure morphology, which is due to the lower proportion of solid content. The smaller the volume content of ceramic particles, the smaller the driving force of dendrite formation during freeze-drying, and the better the cold-frozen structure of dendrite can be replicated. The higher the proportion of solid phase
content, the more ceramic components, which leads to the increase of driving force for ice crystal formation. It is difficult to generate the details at the end of ice crystal structure. Only the layered structure can be developed, and the increase of solid phase content will make the layered structure blurred. When the solid phase content of slurry is 40 vol.%, the ice crystal structure is almost completely swallowed up. In the micro-morphology, only relatively uniform porous structure was observed, and almost all of the pore forms were nanoporous, which was consistent with the quantitative analysis results of pore volume content and pore size.

Fig. 5 is the SEM image of sintered green bodies with different slurry solid content. It can be seen that when slurry solid content is 15 vol.%, the small size pore in the green body is interlaced with the dendritic ice crystal structure of $\beta$-Si$_3$N$_4$, and the large size pore forms directional channels between the main structure of ice crystal and between layers. The interlaced porous microstructures are oriented growth. With the increase of solid content, the morphology changes from ice crystal structure to paracrystalline dendrite structure, and then ice crystal structure gradually disappears to layered structure. Finally, with the increase of solid content of slurry, the morphology changes to uniform porous structure. This provides a very effective method for optimizing the pore structure of porous silicon nitride, which can adjust the pore structure and growth direction according to the need of structural design [11–14].

6. Effect of solid content of slurry on physical properties of porous silicon nitride

Fig. 6 shows the relationship between volume density, linear shrinkage and porosity of porous silicon nitride slurry and solid content of porous silicon nitride slurry. As shown in Fig. 6, with the volume solid content of Si$_3$N$_4$ slurry increasing from 15 vol.% to 40 Vol.%, the volume density of porous Si$_3$N$_4$ and the linear shrinkage of the material increase accordingly. The density of the material increases to 1.32 g/cm$^3$, the linear shrinkage of the material is 0.12%, and the porosity
Fig. 5 – Magnification of SEM micrographs of the porous Si$_3$N$_4$ ceramics with different solid contents.

Fig. 6 – The bulk density, porosity and shrinkage of porous Si$_3$N$_4$ ceramics fabricated with different solid contents.

decreases from 93.9% to 40.58%. When the solid content of slurry is 25 vol.%, the three curves in the figure intersect. This shows that when the solid content of slurry is 25 vol.%, it is the critical point for the transformation of material physical properties. When the solid content of slurry is less than 25 vol.%, the density of material is less than 1 g/cm$^3$. In practical application, silicon nitride slurry should be controlled. The solid content is 25 vol.%, which is lower than this point. The density of the material is lower, the strength of the green billet and the strength of the sintered billet are lower, so there is no practical application value.

Fig. 7 The effect of solid content of slurry on the mechanical properties of porous silicon nitride. With the increase of solid content of slurry, the mechanical properties of materials show an increasing trend. Especially when the volume solid content of slurry is more than 25 vol.%, the mechanical properties of materials increase rapidly. Therefore, the form of pore is related to the mechanical properties of materials. The bonding effect is due to the formation of nano-pore
formed by interlacing and stacking of silicon nitride grains, which gradually increases the flexural strength of porous silicon nitride. The flexural strength of porous silicon nitride reaches 94.7 MPa when the volume solid content of slurry is 40 vol.% and the compressive strength reaches 314 MPa. Fig. 7 shows the effect of solid content of slurry on the mechanical properties of porous silicon nitride. With the increase of solid content of slurry, the mechanical properties of materials show an increasing trend. Especially when the volume solid content of slurry is more than 25 vol.%, the mechanical properties of materials increase rapidly. Therefore, the amount of pore affects the mechanical properties of materials. It plays a key role. It is the nano-pore formed by interlacing and stacking of silicon nitride grains that gradually increases the flexural strength of porous silicon nitride. The flexural strength of porous silicon nitride reaches 94.7 MPa and the compressive strength reaches 314 MPa when the volume solid content of slurry is 40 vol.%.

7. Dielectric properties of porous silicon nitride prepared by freeze-drying method

From the dielectric properties of porous silicon nitride ceramics prepared by freeze-drying method in Fig. 8, the dielectric constant curves of different solid content with different solid content are gentle, indicating that the dielectric constant values are basically stable in the whole frequency range, and the solid-phase ratio in silicon nitride ceramics is stable. The dielectric constant of porous silicon nitride sample decreases with the decrease of the dielectric constant, which is consistent with the trend of theoretical calculation. The intrinsic dielectric constant of silicon nitride is close to 8, while the dielectric constant of air is 1. Therefore, the higher the porosity of the material, the smaller the dielectric constant. When the solid phase content of silicon nitride slurry is reduced from 40 vol.% to 10 vol.%, the dielectric constant of porous silicon nitride ceramics decreases from 3.2 to 1.4, which is consistent with the theoretical calculation results. The preparation of porous silicon nitride materials with controllable dielectric constant also provides material basis for the subsequent preparation of sandwich structure [10–14].

Summary

In this paper, the preparation methods of porous silicon nitride materials with controllable dielectric constant and pore structure were systematically studied. Porous silicon nitride materials with controllable pore structure and directional growth were prepared by freeze-drying process and adjusting the solid content of slurry. The conclusions are as follows:

(1) With Sm2O3 as sintering additive, the bending strength of the material reaches 300 MPa when the content of Sm2O3 is 1.2 wt.% and the first nitriding temperature is 1200 °C and the second nitriding temperature is 1350 °C. With the increase of nitriding temperature, the weight gain rate of nitriding increases gradually. When the temperature is 1350 °C, the final weight gain rate of nitriding is close to 66% of the theoretical weight gain rate.

(2) The addition of diluent effectively reduces the reaction temperature, and the grain size is fine and uniform. When the diluent content is 30 wt.%, the grain size is relatively uniform.

(3) When the total porosity is less than 60%, the bending strength decreases slightly with the increase of porosity, and the bending strength is about 50 MPa. With the increase of the total porosity, the flexural strength increases obviously. When the porosity is 78%, the flexural strength reaches 300 MPa. When the total porosity is about 80%, the bending strength decreases again. The bending strength of porous silicon nitride material is closely related to the closed porosity, which varies with the change of the closed porosity.

(4) Porous silicon nitride structure with controllable pore structure and macro-directional growth was prepared by freeze-drying process using water as solvent. The dielec-
tric constant of the prepared material can be controlled between 1.4 and 4.0.

(5) The volume solid content of slurry has a significant effect on the properties of the material. When the solid content of slurry increases from 15 vol.% to 40 vol.%, the porosity of porous silicon nitride decreases from 83.9% to 40.58%. The flexural and compressive properties of the material increase, and its strength increases from 0.1 MPa to 94.7 MPa, and from 1.3 MPa to 314 MPa, respectively.

(6) Under 1700 °C/2 h and 0.3 MPa conditions, the α phase in porous silicon nitride has been completely transformed into beta phase. The intensity of the diffraction peak of β-Si3N4 increases with the increase of solid content. When the solid content of slurry is 40 vol.%, almost all the pores in the material are about 500 nm nanoporous.

Conflicts of interest

The author declares no conflicts of interest.

References
