Cold spray and pressureless sintering of zirconium phosphate bonded silicon nitride ceramics with porous gradient structure

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Abstract. In the present study, silicon nitride (Si₃N₄) electromagnetic wave transparent ceramics with high porosity and porous gradient structure are prepared by cold spray and pressureless sintering technique. Zirconium phosphate solution is used as a binder material instead of the traditional organic materials, in order to prevent the residual carbon which is severe to the dielectric properties of the Si₃N₄ porous ceramics. Firstly, Si₃N₄ ceramic slurries with different phosphorus acid and pore-forming agent contents are prepared. Then the Si₃N₄ slurries are cold sprayed layer by layer to achieve a porous gradient structure, and finally the samples are pressurelessly sintered at 1000 °C in a nitrogen atmosphere. The results show that the porosity of the obtained Si₃N₄ ceramics is 20~70 % and the Si₃N₄ ceramics exhibits a good porous graded structure from high to low porosity.

1. Introduction

Functionally graded materials (FGMs) are innovative composite materials which have been intensively studied in recent years. FGMs feature gradual transitions in microstructure and composition that are engineered to meet functional performance requirements that vary with location in a single component and optimize the overall performance of the component [1]. Materials with porous gradient structure are special types of FGMs, and applications of this kind of materials may satisfy particular physical requirements. Silicon nitride (Si₃N₄) ceramics with porous gradient structure are used in numerous applications because of its superior properties, such as high-temperature strength, good oxidation resistance and low thermal expansion coefficient [2-5].

Nowadays, various processing techniques have been developed to prepare ceramic matrix composite with porous gradient structure, such as powder metallurgy, partially sintering, thermal/cold spray, tape casting, in-situ reaction sintering, metal or glass melt infiltration, etc [6-9]. Among these methods, powder metallurgy and partially sintering are considered as the most common methods for the better controlling of each layer’s porosity.
However, cracks may appear in the material because of different sintering shrinkage attributing to the different thermal property of each layer. When using tape casting, the porous structure is hard to control because of the excessive organics. For in-situ reaction sintering, some other materials will be introduced during the reaction process. Therefore, from the existing literatures and patents [10-12], thermal/cold spray is the suitable method to prepare Si₃N₄ ceramics with porous gradient structure. S. Thiele [13] has prepared Si₃N₄ ceramic coating on Si₃N₄ substrate using detonation gun spray, high-velocity oxy-fuel (HVOF) thermal spray and plasma spray. However, thermal spray involves the heating of a source material to form molten droplets and tends to produce a splat-like structure, at which temperatures Si₃N₄ have already decomposed [14,15].

Cold spray uses high speed air to accelerate the particles or directly sprays viscosity slurries, avoiding the high temperature effect on coating and substrate material structure [16,17]. P. Holtappels [18] fabricated YSZ → LSM → LSCo gradient coatings with nine layers on zirconia substrate by cold spray, using (La₀.₈₅Sr₀.₁₅)₀.₉MnO₃ (LSM), La₀.₈₄Sr₀.₁₆CoO₃ (LSCo) and ZrO₂ (YSZ) powders with different contents as the raw materials, adding dispersant and anhydrous ethanol to achieve slurries. This work indicates that cold spray of viscosity slurries combined with heat treatment technology is an effect method to prepare ceramics with gradient structure.

Our previous research [19-21] described a pressureless sintering technique to fabricate α-Si₃N₄ porous ceramics with controlled porosity by using H₃PO₄ as a pore-forming agent and ZrP₂O₇ as a binder. After sintering at 1000~1200 °C, α-Si₃N₄ porous ceramics with controlled porosity of 20–63 %, dielectric properties of 2~5, and bending strengths of more than 100 MPa were obtained. Meantime, Si₃N₄ ceramics with porous gradient structure can be obtained by powder metallurgy and the pressureless sintering. However, it is very difficult to get uniformly mixed power, crack-free material and good adhesion of each layer by using this method.

In this paper, cold spray and pressureless sintering are applied for the preparation of α-Si₃N₄ ceramics with porous gradient structure by using H₃PO₄ as a pore-forming agent and ZrP₂O₇ as a binder. The purpose of this study is to investigate the processing method for preparation of porous α-Si₃N₄ ceramics, and then to explore a proper way to fabricate α-Si₃N₄ ceramics with porous gradient structure.

2. Experimental procedures

2.1. Materials
The raw materials used in the present study were as follows: commercial Si₃N₄ powder whose grain size was about 0.5 μm and content of α phase was more than 93 %, β phase was less than 5 %; commercial ZrO₂ powder whose grain size was around 0.5 μm and the purity was up to 99.9 %; phosphorus acid (H₃PO₄) liquid whose concentration was 85 % and the purity was up to 99.9 %.

2.2. Preparation of ceramics
Si₃N₄ slurries were prepared by mixing Si₃N₄ and ZrO₂ in designed content (the final molar ratio of ZrP₂O₇ and Si₃N₄ is 1:3) at room temperature and then adding excess H₃PO₄ (exceed the stoichiometric ratio of ZrO₂ and H₃PO₄ which formed ZrP₂O₇) to this mixture powder. The different porosity and porous gradient structure was
controlled by the different content of excess H$_3$PO$_4$. The mixtures have been rotary ball-milled to get homogeneous. Then, the Si$_3$N$_4$ slurries were sprayed onto the surface of the substrate layer by layer with compressed air to achieve a porous gradient structure. The preparation of the individual layers and their mutual adhesion was controlled by intermediate pre-heat treatment, which was as follows: the samples were slowly heated to 250 °C and held for 2 h so as to obtain a total formation of ZrP$_2$O$_7$ bonded Si$_3$N$_4$ porous structure. Finally, the as-obtained Si$_3$N$_4$ porous gradient structure were sintered at 1000 °C in a furnace protected by a nitrogen (N$_2$) atmosphere and held for 2 h to achieve the Si$_3$N$_4$ porous ceramic. In this work, excess H$_3$PO$_4$ was used as pore-forming agent and ZrP$_2$O$_7$ used as binder with no organic matter, which indicates that the porosity will be better controlled. The preparation of Si$_3$N$_4$ slurries in a liquid condition indicates the more homogeneous mixture than powder metallurgy.

2.3. Characterization

After sintering, the bulk density of the sintered products is measured according to Archimedes displacement method using distilled water. The porosity is obtained from the relative density that is calculated from the bulk density of the products and the theoretical density of the Si$_3$N$_4$ composites. The phase compositions are analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-IIIA diffractometer with Cu radiation at 40 kV and 50 mA. A scan rate of 10 °/min is used to record the diffraction patterns in 2θ range between 10° and 80°. The microstructure of the fractured surface is observed by Scanning Electron Microscopy (SEM).

3. Results and discussion

3.1 Effect of cold spray parameters on the macrostructure of each layer

Thermal expansion plays a key role when two materials are combined and suffer a temperature change. Prior to preparation, a coefficient of thermal expansion (CTE) match should be considered. For both coating and substrate are using silicon nitride as matrix, the CTE of them are very similar, suggesting a good CTE match between the coating and substrate.

It is very clearly seen from Table 1 that with the increasing of slip solid content from 42 wt.% to 60 wt.% (corresponding to excess H$_3$PO$_4$ content decreasing from 95 vol.% to 55 vol.%) and spray time from 8 min to 35 min, coating thickness increases from 56 µm to 82 µm and from 56 µm to 400 µm, respectively. Coating thickness can be well controlled by slip solid content and spray time. Only the thickness of the coating changes, while the microstructure of either the porous coating or dense substrate maintains the same. The thick coating with controlled thickness makes it possible for the preparation of ceramic block materials.

| Table 1. Effect of spray parameters on the coating thickness |
|------------------|---|---|---|---|
| Slip solid content (wt.%) | 42 | 60 | 60 | 60 |
| Excess H$_3$PO$_4$ content (vol.%) | 95 | 55 | 55 | 55 |
| Spray time (min) | 8 | 8 | 15 | 35 |
| Coating thickness (µm) | 56 | 82 | 163 | 405 |
3.2 Phase compositions and porosity of cold sprayed porous Si₃N₄ ceramics

Figure 1 presents the phase compositions of porous Si₃N₄ ceramics with different excess H₃PO₄ content sintered at 1000 °C and the raw Si₃N₄ powder. Owing to the solid state sintering of ZrP₂O₇ binder around the Si₃N₄ grains, sintering of the whole composite is finished at 1000 °C according to the main sintering mechanism. The XRD spectra shows that α-Si₃N₄ is the main matrix phase which maintains the character of Si₃N₄ raw material with just a little amount of β-Si₃N₄ and no apparent phase transformation from α-Si₃N₄ to β-Si₃N₄ is detected. The phases of ZrP₂O₇ and SiP₂O₇ are identified from the XRD spectra. H₃PO₄ has reacted with SiO₂ presenting on the surface of the silicon nitride particles [22]. It is believed that the amount of silicon phosphate is not obvious identified by XRD because the majority of silicon phosphate was amorphous [23].

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**Figure 1.** XRD patterns of ZrP₂O₇ bonded Si₃N₄ porous ceramics with different excess H₃PO₄ content sintered at 1000 °C (the final molar ratio of ZrP₂O₇ and Si₃N₄ is 1:3)

**Figure 2.** Effect of excess H₃PO₄ content on the porosities of the sintered ZrP₂O₇ bonded Si₃N₄ porous ceramics (the final molar ratio of ZrP₂O₇ and Si₃N₄ is 1:3)
Silicon nitride porous ceramics with various porosity and good processing were prepared by cold spray and pressureless sintering technique. Figure 2 shows the effect of excess H$_3$PO$_4$ content on the porosities of the sintered specimens. In general, porosity alters from 40 % to 70 % while the content of excess H$_3$PO$_4$ changes from 55 vol% to 95 vol.%. As can be seen clearly, the porosity is increased with increasing content of excess H$_3$PO$_4$ and shows almost linear variation with the content of excess H$_3$PO$_4$, indicating that the porosity can be well controlled by adjusting the amount of excess H$_3$PO$_4$, without changing sintering conditions.

3.3 Microstructure of Si$_3$N$_4$ ceramics with porous graded structure

Figure 3 shows the SEM images of fracture surface of the coated specimens. Although their porosities have great or some difference, the interface between the coating and substrate both is well bonded, without microcracks, indicating a good thermal physical match between layers. So the interface between the coating and substrate can be well bonded when their porosities are in the range which is from 20 % to 70 %.

Figure 3. SEM images of fracture surface of the coated specimens (the porosities of coating and substrate are 50 % and 40 %)

Figure 4. SEM images of fracture surface of the coated specimens (the porosities of coating and substrate are 70 % and 20 %).

For radome material applications, the porous gradient Si$_3$N$_4$ ceramics with various porosity were designed. From the top layer to the down layer, the porosity of each layer whose thickness is equal is from 20 % to 70 %, respectively. The pore structure and phase compositions of porous Si$_3$N$_4$ structures maintained the characteristic especially sintered at 1000 °C. Moreover, the structure of each layer including thickness and pore structure can be well controlled by cold spray parameters and pressureless sintering technique. So it is by using cold spray and pressureless sintering technique, porous gradient Si$_3$N$_4$ ceramics could be obtained, which could be used as radome material.

4. Conclusion

Silicon nitride (Si$_3$N$_4$) electromagnetic wave transparent ceramics with high porosity and porous gradient structure are prepared by cold spray and pressureless sintering technique. The results are as follows:
1) The porosity of ZrP₂O₇ bonded α-Si₃N₄ matrix porous ceramics could be well controlled by using H₃PO₄ as pore-forming agents and ZrP₂O₇ as binder. Porosity ranged from 40 % to 70 % while the excess H₃PO₄ pore-forming agent content alters from 55 vol.% to 95 vol.% and ZrP₂O₇ binder content maintains 25 wt.%.

2) Coating thickness could be well controlled by varying the spray parameters, including the slip solid content and spray time. Only the thickness of the coating changes, while the microstructure of either the porous coating or substrate maintains the same.

3) By using cold spray and pressureless sintering technique at 1000°C in a nitrogen atmosphere, porous gradient Si₃N₄ ceramics can be obtained with the interface between layers clear and well combined.

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