Study on Preparation and Physical Mechanical Properties of Si₃N₄ Composite Ceramics

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ABSTRACT: In this paper, by using the hot-pressed sintered technology, pure Si_3N_4 ceramics and Si_3N_4 composite ceramics containing different volume fraction(hBN) are prepared with the sintered catalyst of Al_2O_3 and Y_2O_3(total 10vol%) by HIGH MULTI 5000 multi-functional high temperature sintering furnace. And the phase compositions, microstructure and mechanical properties of specimen were studied. The results show that, based on the hot pressing sintering process, the α-Si_3N_4 is all changed into β-Si_3N_4. Addition of hBN into Si_3N_4 inhibits the growth of the crystal grain and makes the ceramic materials generate hBN segregation zone in internal materials, which causes the addition of hBN that cannot improve the physical mechanical properties effectively just because the serious stress concentrates and fatigue break down. In addition, compared with other sintering process, the physical and mechanical properties of Si_3N_4 prepared by hot-pressing sintering are better than other methods. Improvement of sintering temperature and time can refine the crystal grain and be a helpful densification. The changed β-Si_3N_4 grain completely forms an intertwined structure and increases the physical and mechanical properties of Si_3N_4. Meanwhile, Y_2O_3 and Al_2O_3 additives are melted and filled into Si3N4 particles at the high temperature, leading to a significant drop of the porosity and the increase of density.

Keywords: Si₃N₄ Composite Ceramics; hot pressed sintering; Physical Mechanical Properties

1 INTRODUCTION

Si₃N₄ ceramic occupies an important position in engineering ceramic, because it has excellent comprehensive performances such as high strength, high temperature resistance, oxidation resistance, wear resistance, heat shock resistance and so on. Thus it is widely used in mechanical, chemical, oceanographic engineering, aerospace and other important areas. But pure Si₃N₄ ceramic material is limited in engineering because it's very fragile and rigid. In order to improve the physical and mechanical properties of Si₃N₄ ceramic, some scholars adopt additive with stratified structure [1]. By deflection of the crack and bridging of the layer, the main crack growth resistance will increase greatly, and the fracture toughness property and flaw tolerance will be greatly increase, too. In this regard, Saito T et a l[2]and Liu H et al[3] adopt BN as an additive of ceramic material and product Si₃N₄ ceramics matrix layered composites which shows perfect fracture toughness.

Sintering as the end process of ceramic material production which has great influence on the ultimate performance of ceramic material [4]. Therefore, it's important to select the sintering method and control the sintering process strictly. The way to sinter ceramic material can be generally divided into: general sintering, reaction sintering, atmosphere pressure sintering, heat-pressing sintering, heat isostatic pressing sintering, microwave sintering, the discharge plasma sintering and high temperature self-propagating sin-

tering. For polycrystalline materials, the grain boundary condition plays an important role in mechanical properties. Si₃N₄ is high covalent compound because its covalent bond accounts for 70 percentage and the electrovalent bond accounts for 30 percentage. The self-diffusion coefficient of nitrogen-atoms and silicon-atoms is small; the volume diffusion, the grain boundary diffusion velocity, and the sintering driving force of densification are small; only the sintering temperature which is close to Si₃N₄ dispersion temperature (> 1850 ℃) and atomic migration have enough speed. It shows that the heat-pressing sintering is a good method to densifying the ceramic [5-8].

In this paper, the Si₃N₄-hBN composite ceramic material (hBN content gradient change) is obtained by heat-pressing sintering which are added Al₂O₃ and Y₂O₃ as sintering catalysts and Si₃N₄ powder and hexagonal boron nitride powder as raw materials. What's more, the rule of corresponding layered composite materials mechanics performance which is compared with other sintering methods is investigated.

2 EXPERIMENT

2.1 *Preparation*

Pure Si₃N₄ and Si₃N₄-hBN ceramic composite is obtained in HIGH MULTI 5000 Multi-functional high-temperature sintering furnace which is added Si3N4 powder (purity is 99.99%, phase alpha > 94%,

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the average particle size is 0.3 microns) and hBN powder (purity is 99.6%, the average particle size is 0.5 microns) as raw materials, Al_2O_3 and Y_2O_3 powder (purity 99.5%, the average particle size is 1 microns) as sintering catalyst. The hBN content in Si3N4-hBN ceramic composite is 5vol.%, 10vol.%,20vol.% and 30vol.%. Sintered samples are disc samples, the size is Φ44mm*6mm.

The heat-pressing sintering process of Si3N4-hBN ceramic composite material is divided into the following seven steps: (1) Burdening: Weighing the Si3N4, hBN, Y_2O_3 and Al_2O_3 powder ingredients in certain proportion by using electronic balance. (2) Ball mill mixing: Put the powder in the ball mill jar and add alcohol (in which the quantity is about 1/2), adjust the fluid viscosity by using the planetary ball mill at the rate of 150 r·min-1until 5 h. (3) Drying: Dry the powder in the oven, stir the powder until the alcohol is lost, however, prevent the powder from changing into block. (4)Selecting: Grind the mixture and select by 160-mesh sieve. (5)Loading: Mat the graphite paper whose thickness is 0.2 mm around the mould in order to demould easily, and preload the powder in the mould. Figure 1 shows the structure diagram of the mould. (6)Heat-pressing: Put the mould loaded powder in the HIGH MULTI 5000 multi-function sintering furnace, sintering after well installed, and the heat-pressing sintering process is using nitrogen atmosphere to protect it. The temperature is 1800°C, the pressure is 30MPA, and the thermal pressure maintaining time is 30 min. (7) Demould: Open the furnace lid until the furnace temperature reaches to room temperature, take out the mould, and take out the sintered sample from the mould, tear off the graphite paper from the sample.
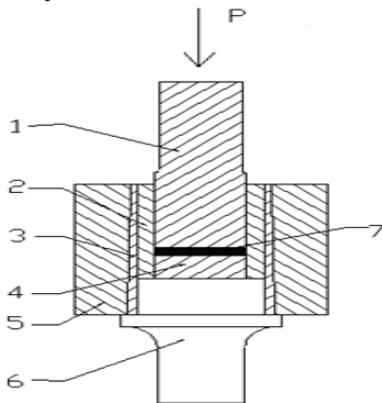

Figure 1. Graphite Mould

1 is the Upper Die; 2 is the Internal Shell; 3is the Mid Sleeve; 4 is the Lower Die; 5 is the Out Sleeve; 6 is the Substrate

The plate was grinded into 5mm×5mm×20mm as mechanics performance test sample by inner circle cutting machine. The ceramic phase was analyzed by X-ray diffraction machine. The fracture morphology was examined by scanning electron microscope.

2.2 *Physical and mechanical performance test methods*

For heat-pressing sintered sample, the density and open porosity are measured by Archimedes principle method; the hardness is measured by Vickers; the bending strength is measured by three point bending test; the fracture toughness is measured by indentation method; the detailed test method is shown as follows:

(1)Density and open porosity

The density and open porosity of the heat-pressing sintered Si_3N_4-hBN sample are measured by Archimedes principle method.

When measure the density and open porosity, first, clean the sample surface; second, boil the sample in distilled water for 1 hour until gas out of sample; third, measure the mass of sample in water, the mass of wet sample and drying mass of the sample in pheatoelectric analytical balance (sensitivity of 1/10000). Calculate the sample density and open porosity according to the formula (1), (2) [9] .The density calculation formula is shown as follows:

$$d_{sample} = \frac{m_{dry}}{V_{displacement}} = \frac{m_{dry}d_{water}}{m_{wet} - m_{water}} \quad (1)$$

In the formula: d_{sample} is the density of the sample/g•cm^{-3};

m_{dry} is the drying mass of sample /g;

$v_{displacement}$ is the displacement of the sample in water;

m_{water} is the mass of the sample in water;

m_{wet} is the mass of the wet sample/g;

d_{water} is the density of water/g•cm-3. Open porosity calculation formula is shown as follows:

$$P = \frac{m_{wet} - m_{dry}}{m_{wet} - m_{water}} \times 100\% \quad (2)$$

In this formula: P is the open porosity of the sample/%.

(2)Bending strength

The bending strength of the heat-pressing sintered Si_3N_4-hBN ceramic composite material can be measured by three point bending test in the electronic universal material testing machine. The sample span is 16mm, the loading speed is 0.5mm·min^{-1}, and take the average of five samples. The calculating formula of bending strength is shown in formula (3) [9] :

$$\sigma_w = \frac{3PL}{2bh^2} \quad (3)$$

In this formula: σ_w is the bending strength/MPa; L is the fulcrum span/mm;P is the breaking load/N; b

is the width of bar sample/mm; h is the height of bar sample/mm.

(3) Vickers hardness

Polish the sample on mirror, the hardness can be measured in Hv Vickers. Using the diamond indenter of 136° apex Angle, and the load is 5 kg. Taking at least five areas of each sample, the average of the two diagonals is taken in each area, and the error of two diagonals is not greater than 10%.Calculation formula as shown in formula (4) [10] :

$$H_v = 1.8544 \frac{p}{d^2} \qquad (4)$$

In this formula: H_v is the Vickers hardness/GPa; P is the load/N;d is the diagonal length / μ m.

(4) Fracture toughness

The fracture toughness can be calculated by measuring the diagonal crack length through using indentation method, the calculation formula is shown in (5) [10] as follows:

$$K_{IC} = 0.075Pc^{-1.5} \qquad (5)$$

In the formula: K_{IC} is the fracture toughness/MPa•m1/2; P is the load/N; c— is the half length of crack/μm.

3 RESULTS AND DISCUSSION

3.1 *Phase composition*

The phase composition of heat-pressing sinter sample is analyzed by XRD. The diffraction pattern is shown in Figure 2. It's easy to see that α-Si_3N_4 is translated into β-Si_3N_4 after heat-pressing sintering. Due to the α-Si_3N_4 is graininess and β-Si_3N_4 is rod-like, the symmetry of β-Si_3N_4 phase is higher than α phase in two types of crystal. At the same time, the mismatch displacement between the α-Si_3N_4 layer changes the length of Si-N bond. The α-Si_3N_4 tetrahedron crystal structure is easy to tilt and distort. The interlayer displacement will cause the lattice distortion, and α phase will have higher entropy. As a result, the β-Si_3N_4 has higher thermal stability than α-Si_3N_4 phase.
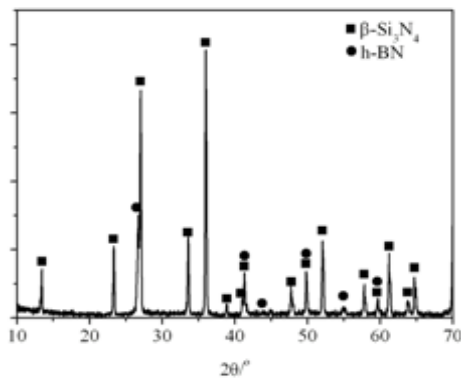

Figure 2. 2 XRD spectra of heat-pressing sintering Si_3N_4-20% hBN sample

Structure of Si_3N_4-20% hBN sample is shown in Figure 3, Figure "1" is a rod-like β- Si_3N_4, and Figure "2" is the flake layer hBN. The "1" and "2" point are analyzed by EDS in Figure 3. The results are shown in Table 1, the Si content in"1" area is significantly higher than "2" area, and the content B in "2" area is significantly higher than "1" area, which further confirmed that the "1" area is Si_3N_4 area, "2" Si_3N_4 is hBN area.
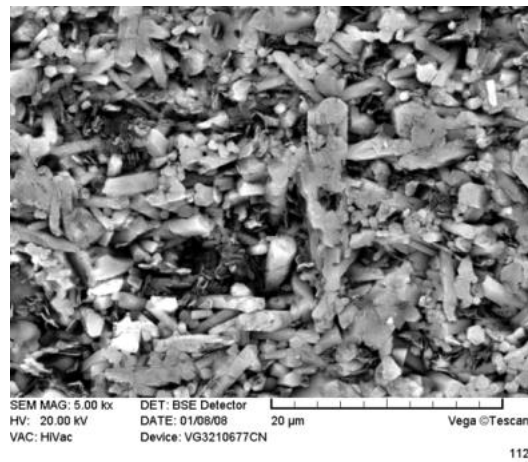

Figure 3. Corrosion surface topography of heat-pressing sintering Si_3N_4-20% hBN (SEM)

Table 1. Energy spectrum analysis of surface composition in Si_3N_4-20% hBN sample (EDS)

	1region Atomic%	2region Atomic%
B K	—	47.66
N K	59.91	43.55
O K	6.76	4.32
Si K	31.6	4.01
Al K	1.72	—
Y K	—	0.46

3.2 *Microstructure*

Observing the morphology of fracture in Si_3N_4-hBN ceramic composite which volume fraction of hBN were 0%, 10%, 20% and 30%, as shown in Figure 4 (a), (b), (c) and (d), Si_3N_4 grain size become smaller as the increase of the content of hBN. At the same time, the fracture morphology of Si_3N_4 gradually translates from mainly transgranular fracture morphology (flat fracture) to main intergranular fracture morphology (pit). It can be clearly observed that the pits when grain comes out from fracture morphology of Si_3N_4-30% hBN ceramic composite (Figure 4 d). Indicate that as

Table 2. Physical properties of heat-pressing sintering Si_3N_4 and Si_3N_4- hBN sample

Sample No.	hBN Content /vol.%	Density /g·cm^{-3}	Vickers Hardness /GPa	Porosity /%
SN0	0	3.31	19.9	0.84
SN5	5	3.17	19.6	0.90
SN10	10	3.10	15.3	0.91
SN20	20	2.97	9.3	1.04
SN30	30	2.94	6.7	1.05

Table 3. Mechanics performance of Si_3N_4 ceramics made by different sintering by contrast

Material type	Heat-pressing sintering Si_3N_4	Reaction sintering Si_3N_4	Pressureless sintering Si_3N_4	Post-sintering Si_3N_4
Density/g·cm^3	3.2-3.4	2.7-2.8	3.2-3.26	3.2-3.3
hardness/HRA	92-93	83-85	91-92	90-92
Bending strength/MPa	900-1200	250-400	600-800	600-670
Elastic Modulus/GPa	300-320	160-200	290-320	271-286
Apparent porosity/%	<0.1	10-20	0.01	<0.2
Coefficient of thermal expansion/×10^{-6}	2.6	3.2	3.4	3.55-3.6
Thermal conductivity/W·m^{-1}·K^{-1}	30	17	20-25	--

the hBN join, on one hand, hBN hinders the growth of Si_3N_4 grain, refines the grain; on the other hand, hBN reduces the grain boundary bonding strength of ceramic composite, and affects its mechanical performance.
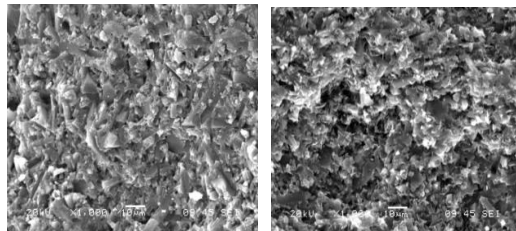
(a)Si_3N_4

(b)Si_3N_4-10％hBN
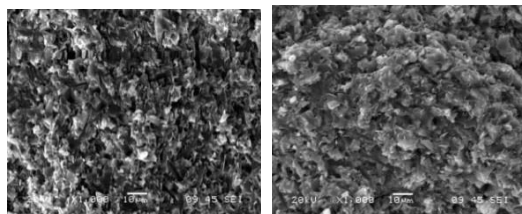
(c)Si_3N_4-20％hBN

(d)Si_3N_4-30％hBN

Figure 4. Fracture morphology of Si_3N_4- hBN ceramic composite

3.3 Physical and mechanical properties

Table 2 shows the change of the physical properties of the Si_3N_4 composite ceramic after adding different hBN. The table denotes that, as the hBN content increases, the density and vickers hardness of sample are gradually decreasing; while porosity is gradually increasing, the physical properties of ceramic materials are gradually reducing.

As shown in Figure 5, mechanical properties of Si_3N_4-hBN ceramic composite are significantly changed with the content of hBN. Bending strength and fracture toughness are increased with the decreasing volume fraction of hBN. The bending strength of pure Si_3N_4 is reduced from 812 MPa to 465 MPa of Si_3N_4-30% hBN. And the fracture toughness of pure Si_3N_4 is reduced from 8.01 MPa·m$^{1/2}$ to 5.50 MPa·m$^{1/2}$ of the Si_3N_4-30%hBN.
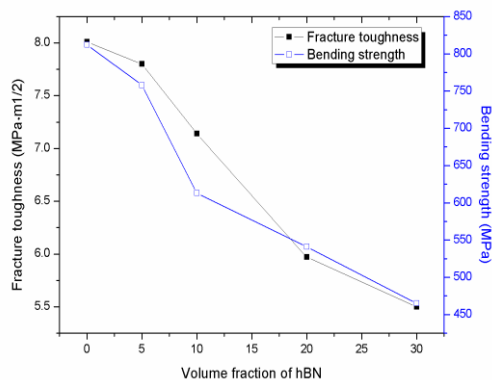
Figure 5. Physical and mechanical properties of Si$_3$N$_4$- hBN ceramic composite

According to above analysis, it can be concluded that hBN does not improve the physical and mechanical properties of Si$_3$N$_4$ ceramics when heat-pressing sintering. Consulting relevant literature, the strength of Si$_3$N$_4$ ceramic is closely related to the size, morphology, and distribution of β-Si$_3$N$_4$ grain. The study of Heinrich [11] shows that the material strength and the grain size have following equation:

$$\sigma_f = (\text{cons tan} t)(a / d^{1/2}) \qquad (6)$$

Among them, "a" is the length to diameter ratio of β-Si$_3$N$_4$, "d" is the diameter. Rod-like β-Si$_3$N$_4$ grain constitutes the mixed microstructure, suppresses the trend of crack propagation, and helps to improve the strength of materials. From material fracture morphology SEM in Figure 4, it can be seen that the grain size will be smaller with the increase of the hBN content. According to the formula (6), it is concluded that the strength of the pure Si$_3$N$_4$ value should be higher than Si$_3$N$_4$-hBN composite ceramic, which is corresponded to the experimental results. In the diagram, β-Si$_3$N$_4$ grain in pure Si$_3$N$_4$ is mixed and disorderly distributed, it shows the crisscross network structure in space, prompts the crack deflected in three-dimensional directions. Its mechanical performance is better than Si$_3$N$_4$-hBN composite ceramic. In addition, ceramic material will produce hBN cluster with the hBN join in, it's easy to cause stress concentration and brittle failure in this area which result in a decline in bending strength. These are the reasons that the mechanical performance of pure Si$_3$N$_4$ is better than Si$_3$N$_4$-hBN.

Compared the mechanical properties with the Si$_3$N$_4$ made by heat-pressing sintering, reaction sintering, pressureless sintering, and post-sintering, the result is shown in Table 3. This table shows that the comprehensive mechanical performance of the heat-pressing sintering Si$_3$N$_4$ is more superior than other sintering methods [12-18]. This is because the covalent bond polarity of Si$_3$N$_4$ is very strong, the diffusion coefficient is very small. It's hard to achieve densification in the general sintering process. But the sintering temperature is higher and the sintering time is longer in heat-pressing sintering process, which makes the β-Si$_3$N$_4$ grain can grow up and achieve densification. At the same time, the heat-pressing sintering process uses Y$_2$O$_3$ and Al$_2$O$_3$ as additive [15], Y, Al, Si, O, and N complex liquid phase will be generated in the sintering, they melt Si$_3$N$_4$ grain at about 1550 ℃ and fill between the grains. With the aid of the surface tension, grains are rearranged, the bulk density is increased, while porosity is decreased. With the increasing temperature, the liquid viscosity is decreased, the dissolving-precipitation process is significant, and the α-Si$_3$N$_4$ phase is translated into β-Si$_3$N$_4$ phase and keeps heat for a period of time which makes it changed completely. At the same time, grain growth, and β-Si$_3$N$_4$ phase grain are formed into intertwined structure as β-Si$_3$N$_4$ phase growth which improves the mechanical properties of Si$_3$N$_4$ ceramic.

4 CONCLUSION

(1) Based on the hot pressing sintering process, addition of hBN into Si$_3$N$_4$ inhibits the growth of the crystal grain and makes the ceramic materials generating hBN segregation zone in materials internal, which causes the addition of hBN cannot effectively improve the physical mechanical properties just because of serious stress concentrates and fatigue break down. The hBN has not made effects on improving the physical mechanical properties.

(2) Compared with other sintering process, the physical and mechanical properties of Si$_3$N$_4$ prepared by hot-pressing sintering are better than other methods. Improvement of sintering temperature and time can refine the crystal grain and be helpful densification. The changed β-Si$_3$N$_4$ grain completely forms an intertwined structure and increases the physical and mechanical properties of Si$_3$N$_4$. Meanwhile, Y$_2$O$_3$ and Al$_2$O$_3$ additives are melted and filled into Si$_3$N$_4$ particles at high temperature, leading to a significant drop of the porosity and the increase of density.

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