Influence of $Y_2O_3$ particle size on the microstructure and corrosion behaviour of porous $Si_3N_4$ ceramics

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Abstract. In this study, porous silicon nitride ceramics were fabricated by pressureless with different particle size of $Y_2O_3$ using as sintering additive. The effects of particle size of $Y_2O_3$ particles on sintering behaviour, microstructure and corrosion behaviour of the $\beta-Si_3N_4$ ceramics were studied in detail. As the $Y_2O_3$ particles size decreasing from 5 μm to 0.5 μm, the linear shrinkage of porous $\beta-Si_3N_4$ ceramics increased from 14.3% to 18.3%, and the sintering porosity decreased from 25.3% to 17.6%. The smaller $Y_2O_3$ particles additions were consisted of finer $\beta-Si_3N_4$ grains and demonstrated more accordant microstructure due to the well-dispersed $Y_2O_3$. The finer microstructure resulted in the improvement of mechanical properties, the sintered sample with 0.5 μm $Y_2O_3$ addition shown flexural strength of 450 MPa. Significant weight loss was observed after corrosion in 1 M HCl solution at 70°C for different time, due to the assumed formation of the grain boundary phase added to the $Y_2O_3$

Keywords: $Y_2O_3$; Particle Size; Corrosion Properties; Porous $Si_3N_4$ Ceramics

1. Introduction

Porous $Si_3N_4$ ceramics are promising structural material because of the excellent mechanical properties and relatively low dielectric constant [1-3]. Especially porous $Si_3N_4$ ceramics composed of finer $\beta-Si_3N_4$ grains with high aspect ratio have excellent mechanical properties, such as high strength and good thermal shock resistance [4-9]. During the sintering process of $Si_3N_4$, the self-diffusion coefficient of Si and N atoms is very low, resulted in the decreasing of volume diffusion and grain boundary diffusion rate. There is not enough driving force to get densification with low temperature, without the temperature rising to the decomposition temperature of $Si_3N_4$. Thus, some metal oxides and rare earth oxide such as $Y_2O_3$, MgO, Al$_2$O$_3$ and Yb$_2$O$_3$ were added as sintering additives during liquid sintering to improve the densification process [10-13]. The oxides formed a low-melting point eutectic liquid with the $SiO_2$ on the $Si_3N_4$ surface layer, promoted the densification and phase transformation of $Si_3N_4$ ceramics. The oxide and $SiO_2$ formed low melting point eutectic liquid and covered $Si_3N_4$ grains surface, which promotes the densification process and phase transformed from $\alpha$ to $\beta-Si_3N_4$.

Many researchers have successfully prepared porous $\beta-Si_3N_4$ ceramics using different sintering additives and studied the influence of the type and content of these additives on the micrograph and...
mechanical properties of porous $\beta$-Si$_3$N$_4$ ceramics. Yang [14] fabricated porous Si$_3$N$_4$ ceramics by using different content of Yb$_2$O$_3$ as sintering additive, the results revealed that the densification and the grain growth of $\beta$-Si$_3$N$_4$ were enhanced as the increasing of sintering additive content. Yang [15] took four types of rare oxides as sintering aids, they found that with the decreasing ionic radii of rare elements, a high viscosity low melting point eutectic liquid was produced. The higher viscosity liquid phase retarded the new nuclear formed and atoms diffusion rate, which yield finer rod-like $\beta$-Si$_3$N$_4$ grains. Cheng [16] fabricated porous Si$_3$N$_4$ ceramics by pressureless sintering and investigated the influence of Yb$_2$O$_3$ or Y$_2$O$_3$ as sintering additive. Both Yb$_2$O$_3$ and Y$_2$O$_3$ could formed high melting crystalline promote the phase transformation of Si$_3$N$_4$. This paper addressed the fabrication of porous Si$_3$N$_4$ ceramics by adding different particle size Y$_2$O$_3$ as sintering additive and investigated the influence of Y$_2$O$_3$ particle size on sintering behavior, microstructure and corrosion behavior of porous $\beta$-Si$_3$N$_4$ ceramics.

2. Experiment

High-purity $\alpha$-Si$_3$N$_4$ was original powder in this investigation, with average grain diameter of 5 $\mu$m, 2 $\mu$m and 0.5 $\mu$m, respectively. Small amounts of Y$_2$O$_3$ were used as additives. The starting powder mixture contained 95wt.% $\alpha$-Si$_3$N$_4$ powder and 5wt.% Y$_2$O$_3$ powder. Powder mixtures were designated by the letters YSN (for Y$_2$O$_3$ and Si$_3$N$_4$) along with the particle size of the Y$_2$O$_3$ powder. For example, the porous Si$_3$N$_4$ ceramics prepared from Si$_3$N$_4$ and 5 $\mu$m Y$_2$O$_3$ was designated by 5YSN. The mixed powder was ball-milled in a polyethylene tank with 12 h, ethanol as solvent, the slurry formed after ball milling was vacuum dried and through a 150$\mu$m sieve. The powder was pressed at 60 MPa to form green bodies with size of 5 mm×5 mm×50 mm. The green blocks were placed in BN-coated graphite crucibles and sintered in a furnace at 1750°C for 2 h at nitrogen pressure of 0.3 MPa. The graphite crucibles coated with BN slurry firstly, and then put the Si$_3$N$_4$ green blocks in, the bodies were sintered at 0.3 MPa N$_2$, 1750°C for 2 h.

The porosities of green bodies were obtained by measuring its weight and size. The sintering porosity were measured by the Archimedes method, five samples were estimated to get the mean value. The microstructure of the $\beta$-Si$_3$N$_4$ ceramics were observed by scanning electron microscopy (SEM, KYKY-2800B, KYKY, China) at an accelerating voltage of 20 kV, the surface of the samples was sputter-coated with gold powder. Y elemental microanalysis was carried out in backscattered electron mode (BSE). The three-point flexural strength was tested using a universal testing machine (CMT5305, MST Co., U.K., with crosshead speed of 0.5 mm/min, span of 16 mm) by highly polished rectangular samples with size of 3 mm×4 mm×30 mm. All experiments were carried out on a series of at least 5 bars to get the mean value. The 0.5YSN, 2YSN and 5YSN samples were exposure in 1 M HCl solution at 70°C in a PTFE container. After corroded with different times, the samples were washed by deionized water, dried at 70°C and calculated the weight loss of the samples.

3. Results and Discussion

3.1 The distribution of Y elemental in Green compacts

Figure 1 presented the Y elemental distribution map of green compacts with different particle size Y$_2$O$_3$ addition by BSE, the white spots were Y$_2$O$_3$ particles. The white spots show homogeneous distributed which indicated a uniform distribution of Y elemental. However, for the 5YSN sample, some large Y$_2$O$_3$ particles could be detected in photomicrograph, as the Y$_2$O$_3$ particles size became smaller, the distribution sites of the Y$_2$O$_3$ particles increased dramatically with 2YSN sample. Some more tiny particles could be observed in 0.5YSN sample, as the Y$_2$O$_3$ particles became finer, the more connection between Y$_2$O$_3$ and Si$_3$N$_4$ particles.
Figure 1. Y elemental distribution map of the Si₃N₄-Y₂O₃ green compacts.

3.2 Microstructure

Figure 2 presents the SEM images of sintered porous Si₃N₄ ceramics microstructure as different size of Y₂O₃ added. In these pictures, a multidirectional interlocked microstructure of numerous rod-like β-Si₃N₄ grains could be clearly seen. The existence of the elongated β-Si₃N₄ grains enhanced the strength of the porous Si₃N₄ ceramics by the crack deflection, bridge and pull-out performance. Besides, the intertwining rod-like β-Si₃N₄ grains developed irregular continuous pores inside the specimens, keeping a high porosity with a high strength. However, a significant effect of Y₂O₃ particle size on microstructure of β-Si₃N₄ grains was observed. The 5YSN sample shows a bimodal microstructure with some elongated β-Si₃N₄ grains was formed in the fine β-Si₃N₄ grains matrix. Decreasing the Y₂O₃ particle size resulted in a tendency to form finer, more uniform microstructure, the β-Si₃N₄ grains with higher aspect ratio and grain widths tend to be finer. It was known that both phase transformation and grain growth of β-Si₃N₄ were influenced by the liquid phase formation at the grain boundaries [17]. When the coarse Y₂O₃ powder was addition, the Y₂O₃ particles and the liquid phase were nonuniform distribution in the specimen. Numerous β-nuclei could be obtained located at the less liquid phase distribution site, resulting in a small β-Si₃N₄ grain size with a low aspect ratio, because the space for the grain growth was inhibited by the other β-Si₃N₄ grains. Meanwhile, some extra-large β-Si₃N₄ grains were obtained in the sufficient liquid phase distribution site [18, 19]. As the particle size of Y₂O₃ was smaller, the Y₂O₃ particles and liquid phase showing a homogeneous distribution in the specimen, the nuclei site was decreased and the grain growth of the β-Si₃N₄ grains were improvement.

Figure 2. SEM micrographs of porous Si₃N₄ ceramics

3.3 Porosity and Flexural strength

Variations in the green porosity, linear shrinkage and sintering porosity with different Y₂O₃ particles size are shown in Table 1. The green porosities were calculated by measuring samples weight and size. As shown in Table 1, the porosities of the green bodies were distinguished with different particle size Y₂O₃ addition. Comparing with the 5YSN and 2YSN samples, 0.5YSN samples exhibited a higher porosity due to the smaller Y₂O₃ particle size. On the other hand, linear shrinkage of ceramics was enhanced visibly by the decreasing Y₂O₃ particle size. During liquid phase sintering, the Si₃N₄ particle rearrangement improved the densification process, especially at the grain boundary sites. The Y₂O₃ reaction with SiO₂ existed on the surface layer of the Si₃N₄ particles and formed liquid phase at high
temperature. Then the liquid phase coated on the α-Si₃N₄ particles and promoted the densification. For the 5YSN samples, the coarse Y₂O₃ particles distribution sites were less than the 2YSN and 0.5YSN samples, so the liquid phase spreading and coating were difficult, which retarded the rearrangement of the α-Si₃N₄ particles and densification. The sintering porosity of the ceramics was determined from the green porosity and the linear shrinkage. The green blocks were composed of a large number of single solid particles before sintering, and green porosity indicated the number of pores, the linear shrinkage indicated the rearrangement of the α-Si₃N₄ particles and densification, as the densification prolonged, the linear shrinkage increased and sintering porosity decreased. The sintering porosities of the 5YSN, 2YSN and 0.5YSN samples were 25.3%, 19.3% and 17.6%, respectively. These results revealed that the finer Y₂O₃ particle size improved the particle rearrangement and had a beneficial effect on the densification of porous Si₃N₄ ceramics.

Table 1 shows the three-point strength with different Y₂O₃ particles added in porous Si₃N₄ ceramics. The strength of the 2YSN samples was higher than that for the 5YSN, but still slightly lower than the 0.5YSN samples. For the 0.5YSN samples, the strength attained to 450MPa at porosity of 17.6%. The microstructure characteristics of the specimen affected the flexural strength directly. The elongated coarse β-Si₃N₄ grains and a loose skeleton structure are the main reason for the low strength of 5YSN sample figure 2(a). As the Y₂O₃ particles were refined, a finer microstructure was dominated. 0.5YSN sample is composed of finer β-Si₃N₄ grains, and the high aspect ratio of grains improved mechanical properties dramatically. Consequently, the strength of 0.5YSN samples was higher than that for 5YSN and 2YSN sample and attained to the highest value with porosity of 17.6%.

As known, the porosity affects the strength of the porous ceramics directly. The relationship of porosity and strength can be expressed as: \( \sigma = \sigma_0 \exp (-\beta P) \) [19], where \( \sigma_0 \) is the strength of nonporous samples, \( \sigma \) is the strength of ceramics with porosity \( P \), and \( \beta \) is the structure factor. We can see that the porosities of the 0.5YSN sample and 2YSN sample were lower than 5YSN sample. However, the strength was 200% higher when the Y₂O₃ particle size reduced to 0.5μm. It is clear that the porosity has little effect on 0.5YSN sample, but the refine elongated β-Si₃N₄ microstructure figure 2(c) obtained the excellent mechanical properties.

| Sample | Green Porosity/% | Linear shrinkage/% | Sintering Porosity/% | Flexural Strength/MPa |
|--------|------------------|--------------------|----------------------|-----------------------|
| 5YSN   | 53.0             | 14.3               | 25.3                 | 205                   |
| 2YSN   | 53.4             | 14.0               | 19.3                 | 429                   |
| 0.5YSN | 55.0             | 18.3               | 17.6                 | 450                   |

### 3.4 Corrosion properties

The corrosion behaviour of Si₃N₄ containing different grain size of Y₂O₃ was studied in 1M HCl aqueous solutions at 70°C. The weight loss rate of the sample increased with the increase of corrosion time. After 12 days of etching, the weight loss rate reached the maximum 9%, which was close to the oxide content of the sample, considering 5% Y₂O₃ and 2% oxygen on the surface of Si₃N₄ powder (corresponding to about 4% SiO₂). It means that the 1M HCl solution nearly has no effects of Si₃N₄ but the grain boundary phase. As can be seen that figure 3 the different Y₂O₃ particle size added as sintering additive results the different corrosion behaviours of porous Si₃N₄ ceramics. With decreasing Y₂O₃ particle size, the weight loss rate increased dramatically and get 5.3%, 6.7% and 6.9% after 12h respectively. Yoshio [20] investigated the dissolution of Y ions in HCl solution by surface chemical reaction control and shrinkage core model. As the surface area of grain boundary phase increases, the dissolution rate of Y ions increases. The Y₂O₃ particles of 0.5YSN sample has a finer particle size and higher surface area which in favour of the dissolution of Y ions and results the high weight loss rate of porous Si₃N₄ ceramics.
Figure 3. Time dependence of the mass loss of porous Si$_3$N$_4$ ceramics corroded in 1M HCl solution at 70°C.

4. Conclusion
The effects of particle size of Y$_2$O$_3$ powder on the porosity, microstructure evolution and corrosion behaviours of porous Si$_3$N$_4$ ceramics were analysed. The linear shrinkage increased from 14.3% to 18.3% and the porosity decreased from 25.3% to 17.6% with the Y$_2$O$_3$ particle size decreased from 5μm to 0.5μm. The finer Y$_2$O$_3$ particles resulted in a finer microstructure consist of finer β-Si$_3$N$_4$ grains results excellent flexural strength, the highest value of flexural strength was obtained in 0.5YSN samples reaching to 450MPa. Due to the surface chemical reaction controlled of dissolution of Y ions in HCl solutions, the finer Y$_2$O$_3$ particles added samples has dramatically weight loss rate but no damage of Si$_3$N$_4$ grains.

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