

Effect of different preparation methods on the microstructure and mechanical properties of Si₃N₄ ceramic composites



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ABSTRACT

In this study, Si₃N₄ ceramic composites were fabricated by using ball-milling, titration preparation and urea preparation methods, respectively. The effect of different preparation methods on microstructure and mechanical properties of the Si₃N₄ ceramic composites was investigated. Obviously, the Si₃N₄ ceramic composite prepared by the urea preparation method (U-SN sample) showed better sintering behavior and higher mechanical properties than that prepared by the other two methods. Compared with the Si₃N₄ ceramic composite by the titration preparation method (T-SN sample), we could avoid the complex titration process or uncontrollable pH value during the preparation process of the U-SN sample. Meanwhile, the coated Y-Al precursor layer in thickness of nanometers was more homogeneous than that prepared by the traditional titration method. B-SN represented the Si₃N₄ ceramic composite prepared by the ball-milling method. These samples were all sintered from room temperature to 1750 °C via hot-pressing sintering. The U-SN specimen showed the optimal flexural strength and fracture toughness of being 817 MPa and 6.90 MPa/m², respectively, which could be attributed to its smallest grain size (0.46 μm) among these three samples.

1. Introduction

Silicon nitride (Si₃N₄) ceramics have excellent thermal conductivity and mechanical properties, such as heat dissipation substrates, good resistance to erosion, high toughness and hardness, which can be applied to the high-temperature industrial, automotive and aerospace application [1–5]. Due to the covalent nature of Si₃N₄, it is difficult to obtain pure Si₃N₄ with high densification and good mechanical properties without sintering additives. In recent studies, the liquid phase sintering technology is a fairly ideal preparation method of the Si₃N₄ ceramic composites. In general, the metal oxides (Al₂O₃, MgO) and rare-earth oxides (Y₂O₃, Yb₂O₃) were used as sintering additives to improve the hardness, fracture toughness and relative density of the Si₃N₄ ceramic composites.

Mechanical mixing method is the main conventional method for the preparation of Si₃N₄ or boride ceramic materials with oxide additions. For example, Xu et al. [6] successfully prepared ZrB₂-based composites using Y₂O₃ and Al₂O₃ as sintering additives through mechanical ball-milling method. However, there are still some problems need to be solved on distribution inhomogeneity of the grain size and sintering additives in the ball-mixing preparation process of the Si₃N₄ ceramic composites. For example, using mechanical mixing method to prepare

Si₃N₄-Y₂O₃-Al₂O₃ composites, the grain size was not easy to be controlled in the ball-mixing process due to the inhomogeneous distribution of additives. Furthermore, the induced impurities and the lattice defect could also be caused by the long time ball-milling [7–9].

With the development of the mixing technology, Si₃N₄ powders coated with Y₂O₃-Al₂O₃ via wet chemical methods such as precipitation [10–14], hydrothermal synthesis [15–19] and sol-gel [20–27], have been widely used as raw-materials to prepare the Si₃N₄ ceramic composites. In the past decade, the main wet chemical method was titration preparation method via NH₃-H₂O or CH₄HCO₃. For example, Zhou [28] reported that the Zr-Al precursor composites were prepared in the CH₄HCO₃ solution via titration preparation method. The ZrOCl₂ and CH₄HCO₃ were dissolved into deionized water, and stirred until the solution became clear. And then, the Al(NO₃)₃ solution was added into the previous solution dropwise. According to the wet chemical mixing in the atom level, the Zr-Al precursor composites were obtained. However, due to the uncontrollable titration speed, the experimental results of the titration preparation method were usually difficult to be reproduced.

In addition, a urea preparation method (UPM) was an advanced method because of its low cost and controllable process. A precise control of pH value in the separation of metals by precipitation as

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hydroxides, hydrous oxides from their aqueous solution was necessary. Qin described the accurate synthesis of yttrium aluminum garnet (YAG) by UPM [29]. In the recent studies, the UPM has become an important method for the synthesis of precipitate from metal ions in aqueous solution. Zhuang et al. [30] used the Al/Y oxide-coated boron nitride (BN) powders by the UPM coating technology as starting powders to fabricate BN/Si₃N₄ composites. And compared with that using raw BN powders, the BN/Si₃N₄ composites by the UPM technology had a better sintering behavior because of the formation of fine and homogeneous Al-Y oxide layer. Especially, density and flexural strength of the composite with BN coated by Y-Al oxide layer were significantly improved. Considering these advantages of controllable pH value and fine oxide layer using UPM in the preparation of the Si₃N₄ ceramic composites, we want to modify the properties of the Si₃N₄ ceramic composite and to make a comparison with that of samples using original Si₃N₄ and conventional Al/Y oxide-coated Si₃N₄ as raw powders.

The effect of the sintering additives on the densification of the Si₃N₄ ceramic composites was extensively studied, while few reports were focused on the effect of mixing process on the properties of the Si₃N₄ ceramic composites. In the present study, we fabricated the Si₃N₄ ceramic composites by hot-pressing method via different mixing process (ball-milling, titration and urea co-precipitation methods). The effect of the different preparation methods on phase composition, microstructure and mechanical properties of the Si₃N₄ ceramic composites were investigated in detail.

2. Experimental procedure

2.1. Raw materials

The α-Si₃N₄ powders (purity > 95%, approximate mean size of 0.5–1.0 μm, Mei shi bang industry, Fujian, China) were used as raw materials. The addition was the Al₂O₃ (purity 99.5%) powder and Y₂O₃ powder (purity 99.5%) with average grain size of 0.5 μm, respectively. NH₃·H₂O and urea were used as precipitant. Al(NO₃)₃·9H₂O (purity 99.9%) and Y(NO₃)₃·6H₂O (purity 99.9%) were used as yttrium and aluminum source, respectively. CO(NH₂)₂ (purity 99.9%), Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O were all purchased from Sinopharm Chemical Reagent Co., Ltd, Specpure.

2.2. Preparation processes of Al₂O₃-Y₂O₃-Si₃N₄ powders and composites

We used three methods of ball-milling, titration and urea preparation to prepare Al₂O₃-Y₂O₃-Si₃N₄ powders. Table 1 showed the compositions of the samples for the different preparation methods. Firstly, for the ball-milling method in Fig. 1(a), raw powders were all put into the polyurethane pot using silicon nitride balls and absolute ethyl alcohol as milling media. The mixing time was 24 h. And the mixtures were dried and sieved for further use.

Secondly, for the titration preparation method, the Si₃N₄ powders were coated with Al-Y precursors by the co-precipitation method as shown in Fig. 1(b). Two types of composites (Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O) were simultaneously added into 100 ml deionized water, and the concentration of Al and Y was fixed in a molar ratio of 5:3. Next, the acid-cleaned Si₃N₄ powders were put into 600 ml deionized water and stirred by agitator. The further, the Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O solution were added into Si₃N₄ powders solution drop by

Table 1
Ratios of the starting powders (mol).

Specimen	Si ₃ N ₄	Al ₂ O ₃	Y ₂ O ₃	Al(NO ₃) ₃ ·9H ₂ O	Y(NO ₃) ₃ ·6H ₂ O
B-SN	0.28	0.019	0.011	/	/
T-SN	0.28			0.037	0.022
U-SN	0.28	/	/	0.037	0.022

drop. Meanwhile, the titration speed of Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O solution was controlled at 1 ml/min, while the pH value of mixture solution was maintained at 9 by the 25 wt% NH₃·H₂O solution. The byproducts of the reaction were washed three times with deionized water, then two times with ethanol, and finally dried at 80 °C for 24 h. At last, the prepared powders were crushed with an agate pestle and mortar for further use.

Thirdly, as shown in Fig. 1(c), a suspension of α-Si₃N₄ powders was added into deionized water. Then the CO(NH₂)₂, Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O (the mole ratio of C:(Y:Al = 3:5) = 20:1) were dissolved into distilled water and stirred. This solution was also put into the Si₃N₄ suspension and the slurry mixture was stirred slowly. And then the temperature of the homogeneous solution was increased to 95 °C holding for 4 h. After the solution was returned to room temperature, the washing process was the same as that of the T-SN samples. All the three samples of Si₃N₄ composites were heated from room temperature to 1450 °C holding for 1.5 h with heating rate of 15 °C/min, and then the temperature was elevated to 1750 °C holding for 1.5 h with heating rate of 10 °C/min by hot-pressing sintering, followed by cooling down to room temperature in the graphite furnace.

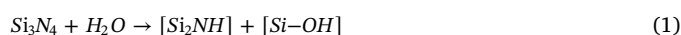
2.3. Characterizations

Phase identification was characterized via the X-ray diffraction (Model PW3040/60; Panalytical B.V, CuK_{α1} radiation, λ = 1.54056 Å, 40 kV/40 mA). The 2θ angle was measured from 10° to 90° with 0.02° step size. The microstructure of the specimens was observed by the scanning electron microscopy (FE-SEM, Model JSM-7001; JEOL, Tokyo, Japan). The surfaces of Si₃N₄ ceramic composites with different preparation methods were etched by molten NaOH for 1 min. At least the short edge length of 300 rod-like grains for each specimen were measured via an image analyzer (Nano Measurer software) based on the etched SEM micrographs of different areas of the specimens at the same magnification.

Density and porosity of Si₃N₄ ceramic composites were measured by the Archimedes method. Fracture toughness and flexural strength were measured using a single-edge notched beam method and a three point bending method by a DSC 5000 Universal Testing Machine at room temperature, respectively. The dimension, span length and cross-head speed were 20 mm × 5 mm × 3 mm, 20 mm and 0.05 mm/min, respectively. Hardness was measured by the Vickers indentation technique using 1 kg for 15 s.

3. Result and discussion

Fig. 2 shows the formation process of Si₃N₄ precursor coating. In the solution, due to the dissociation of Si-N group, we can find that the surface of Si₃N₄ powders consisted of the functional group such as silanol group (Si-OH) based on Eq. (1). When the pH value of solution was higher than 7, the surface of Si₃N₄ powders showed negative charge which could accelerate the dissociation of silanol group according to Eq. (2). In the titration system, Li [31] reported that Al³⁺ and Y³⁺ were released by Y(NO₃)₃ and Al(NO₃)₃ ionization, which would gradually react with the OH⁻ by dissociation of NH₃·H₂O solution as shown in Eqs. (3) and (4). Thus the Al-Y precursor coating of Al(OH)₃ and Y(OH)₃ was formed on the surface of the Si₃N₄ powders. Compared with the titration system, the reaction process of urea coating system was complex relatively. Owing to the generation of OH⁻ and CO₃²⁻ by the urea hydrolysis, Al(OH)₃ and Y₂(CO₃)₃ could be produced according to Eqs. (3) and (5). The prior precipitation of Y₂(CO₃)₃ and YOHC₃ suspension could be resulted from that the solubility of Y₂(CO₃)₃ (K_{sp} = 2.5 × 10⁻³¹) and YOHC₃ were both far less than Y(OH)₃ (K_{sp} = 8.0 × 10⁻²³) in Eqs. (4) and (6). All the main reactions happened during the Si₃N₄ coating process were listed as follows:



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