Preparation and mechanical properties of carbon nanotube-silicon nitride nano-ceramic matrix composites

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Abstract. Carbon nanotube–silicon nitride nano-ceramic matrix composites were fabricated by hot-pressing nano-sized Si₃N₄ powders and carbon nanotubes. The effect of CNTs on the mechanical properties of silicon nitride was researched. The phase compositions and the microstructure characteristics of the samples as well as the distribution of carbon nanotube in the silicon nitride ceramic were analyzed by X-ray diffraction and scanning electron microscope. The results show that the microstructure of composites consists mainly of α-Si₃N₄, β-Si₃N₄, Si₂N₂O and carbon nanotubes. The addition of proper amount of carbon nanotubes can improve the fracture toughness and the flexural strength, and the optimal amount of carbon nanotube are both 3wt.%. However the Vickers hardness values decrease with the increase of carbon nanotubes content.

1. Introduction

Silicon nitride (Si₃N₄) ceramic has been regarded as one of the promising engineering ceramic materials because of its high strength, high hardness, high corrosion and wear resistance [1, 2]. However, silicon nitride ceramics still have some inadequacy, such as insufficient resistance to brittle fracture, insufficient thermal-shock resistance and fracture toughness. Therefore, improving the mechanical properties and wear behaviour of silicon nitride ceramic is an important object in developing Si₃N₄-based ceramics [3, 4].

In the late 80’s Niihara proposed the nanocomposite concept. Ceramic nanocomposite has attracted a lot of scientific interest because of its high mechanical properties, wear resistance, chemical inertness, and corrosion resistance [5, 6]. It is an effective way to incorporate a secondary phase such as nanoparticles, whisker into Si₃N₄ matrix to improve the mechanical properties [7, 8].

In recent years, carbon nanotubes (CNTs) has been considered as the most promising reinforcement for composite materials because of its exceptional mechanical (E ≈ 1.8TPa) and electrical properties [9, 10]. The potential for nanocomposites reinforced with CNTs which have extraordinary specific stiffness and strength represents tremendous opportunities for application in the 21st century. It is expected that the addition of carbon nanotubes will significantly improve the quality of different matrixes including metal, polymer or ceramic. Therefore there have been several attempts to fabricated CNT/ceramic composites with improved flexural strength and fracture toughness [11, 12]. Zhan et al. fabricated CNT/alumina nanocomposite by spark-plasma-sintering the mixture of single-wall nanotubes and nano-alumina powders, and their experimental results show that the facture toughness of the nanocomposite is three times as much as that of monolithic alumina ceramic [13]. Other research results show that the addition of CNT into alumina results in a rather low increment in fracture toughness, while a significant increase in the contact damage and wear resistance [14]. But
carbon nanotubes reinforced silicon carbide and silicon nitride matrix composites only show modest improvements [15, 16], which may be related to the bonding between CNT and ceramic matrix as well as the distribution of CNT in the ceramic matrix. So it is crucial to achieve a homogeneous distribution of CNT and a good bonding between CNT and ceramic matrix.

Synthesis of dense ceramics based on silicon nitride nano-powders is a promising route towards ceramic engineering materials. An advantage of nano-powders is their ultra-diffusivity and large specific surfaces. In this study, carbon nanotube–silicon nitride nano-ceramic matrix composites were fabricated by hot-pressing nano-sized Si₃N₄ powders and carbon nanotubes. The homogeneous distribution of CNTs on the silicon nitride matrix was studied to achieve a good bonding between CNT and ceramic matrix. The effect of carbon nanotubes on properties of silicon nitride nanoceramics and the strengthening mechanism were researched.

2. Experimental procedure

2.1. Characteristics of the original powders
Nanosized Si₃N₄ and multi-wall carbon nanotubes were used to prepare silicon nitride matrix ceramic composites. The silicon Nitride powders are mixture of amorphous Si₃N₄ and α-phase Si₃N₄, and the amount ratio of amorphous Si₃N₄ to α-phase Si₃N₄ is 4. Nanosized yttrium oxide and alumina powders were used as sintering aids and both of their amounts were 5wt%. Details about composition of the original powder mixtures are shown in table 1.

| Specimen | Si₃N₄ | Al₂O₃ | Y₂O₃ | CNT |
|----------|-------|-------|------|-----|
| A        | 90    | 5     | 5    | 0   |
| B        | 89    | 5     | 5    | 1   |
| C        | 87    | 5     | 5    | 3   |
| D        | 85    | 5     | 5    | 5   |

The morphology of silicon nitride powders and carbon nanotubes is determined by TEM (H–800 Transmission Electron Microscopy) analysis, as shown in Figure 1.

![Figure 1. TEM images of original Si₃N₄ powders and CNTs (a) α-Si₃N₄ particles, (b) amorphous Si₃N₄ particles, (c) CNTs](image-url)

It can be seen from the TEM images that the amorphous Si₃N₄ powders are spherical particles (20–50nm), while the α-Si₃N₄ powders consist of hexagonal particles (50–100nm) as well as some whisker-like particles with diameter of 20nm or so. The original CNTs are not straight and tangle
together, and their diameter is between 20nm–40nm and length is 2–5um. The CNTs used in the experiments were acid treated with nitric acid in order to remove catalysis particles and improve the surface properties, which contributes to a good bonding between CNT and ceramic matrix. In addition, the walls of CNTs become straight and length becomes shorter after the acid treatment that contributes to the homogeneous distribution of CNTs on the silicon nitride matrix.

2.2. Preparation of samples
First, the Si₃N₄, Al₂O₃ and Y₂O₃ powders mixtures were supersonically dispersed for 1h and ball milled with agate balls in anhydrous ethanol for 16h, then the CNTs were added into the powder mixtures. Second, the CNTs and powder mixtures were supersonically dispersed for 1h and ball-milled in ethanol for 2h so as to get a better homogenous dispersion, then dried at 80°C in a vacuum furnace and sieved with 200-mesh sieve. The dried mixtures were sintered at 1700°C in a hot-press furnace which is full of nitride gas, and the applied pressure is 30MPa and holding time is 1h.

Testing specimens with dimension of 3mm × 4mm × 36mm were prepared by diamond cutting from the sintered materials. All surfaces of the samples were finely ground with a diamond wheel and polished with 1um diamond pastes.

2.3. Structure observation and properties testing
The relative density of the sintered samples was measured by the Archimedes method in distilled water. The phase compositions of the sintered samples were identified by X-ray diffractometer (Rigaku, D/max-rB x-ray diffractometer). The microstructure and fracture surface morphology of the samples were observed by a scanning electron microscope (SEM, LEO-1530VP) after coating gold.

The flexural strength was measured on a universal testing machine (MTS tester) using a 3-point bending method, and the span length and cross-head speed were 30mm and 0.2 mm/min respectively. The hardness and the fracture toughness were measured on a HV120 hardness tester by the Vickers indentation technique, with a load of 3kgf and 5kgf respectively.

3. Results and discussion
3.1. Microstructure and phase
X-ray diffraction (XRD) patterns of the samples are shown in figure 2. A phase transformation from α-Si₃N₄ to β-Si₃N₄ takes place during sintering. The crystalline phases of carbon nanotube–silicon nitride nano-ceramic matrix composites are α-Si₃N₄, β-Si₃N₄ and a little amount of Si₂N₂O. No characteristic peak of CNT is observed. The existence of Si₂N₂O can be explained by the following reaction which occurs during sintering process when the temperature reaches 1600 °C [17]:

\[
2\text{Si}_3\text{N}_4 (s) + 1.5\text{O}_2 (g) = 3 \text{Si}_2\text{N}_2\text{O} (s) + \text{N}_2 (g)
\]  

In reaction (1), the exit of O₂ may due to the insufficient vacuum of sintering equipment. In addition, the oxygen may interfuse into the powder mixtures during the dispersing and drying process.

When the temperature is higher than 1650 °C, another reaction happens and the amount of Si₂N₂O gradually decreases:

\[
2\text{Si}_2\text{N}_2\text{O} (s) = \text{Si}_3\text{N}_4 (s) + \text{SiO} (g) + 0.5\text{O}_2 (g)
\]  

The morphology of fracture surface indicates that the CNTs are still present in the structure after sintering, as shown in figure 3. The monolithic silicon nitride nano-ceramic shows an inter-granular fracture mode and there is no obvious β-Si₃N₄ grains pullout phenomenon in the fracture surface, whereas all composites show a different degree of CNTs pullout effect. The most CNTs are vertical to the fracture surface and parallel to the pressed surface which is beneficial to the improvement of mechanical properties. The CNTs homogeneously disperse in silicon nitride matrix when its amount is lower, but the agglomerated CNTs can be seen from the fracture surface when the amount of CNTs is 5wt.%. 

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Figure 2. X-ray diffraction patterns of sample A, B, C and D.

Figure 3. SEM micrographs of fracture surfaces at low magnification (a) sample A, (b) sample B, (c) sample C, (d) sample D

Figure 4 shows the fracture surface micrograph of sample C at high magnification and EDX spectrum of selected areas. The CNTs are mainly located at grain boundaries of silicon nitride matrix.
and they are well attached to the silicon nitride grains. Obvious pullout of CNTs and short outcrops of CNTs can be seen clearly on the fracture surface, which indicates that the CNTs bear significant stress by shearing a portion of the load and toughen the matrix by a bridge effect. Moreover, the degradation of CNTs also can be observed, which may be due to the defects on the microstructure of CNTs. These defects make the CNTs break down easily in their sites when the stress is applied.

![Figure 4. SEM micrograph of fractured surface of sample C at large magnification and EDX spectrum of selected areas. (a) fractured surface micrograph of sample D (b) EDX spectrum of carbon nanotube, (c) EDX spectrum of silicon nitride matrix](image)

The microstructures of monolithic silicon nitride ceramic and the composite added 5wt.% CNTs are shown in figure 5. The addition of CNTs has no effect on the morphology of the Si$_3$N$_4$ grains, and the microstructures of the monolithic silicon nitride ceramic consist of spherical grains with 100nm or so, as shown in figure 5(a). The microstructure is lack of the typical elongated β-Si$_3$N$_4$ grains because the shaping of performs within the confined volume of a press-mold prevented the removal of monoxide from the starting powders [18]. From figure 5(b) it can be seen that there are agglomerated CNTs, separated CNTs and micro-pores in the microstructure of the composite besides the spherical grains.
3.2. Mechanical properties

Flexural strength, Vickers hardness and fracture toughness of the samples were tested and the effects of CNTs amount on the mechanical properties were researched, as shown in figure 6. The flexural strength and fracture toughness of carbon nanotube-silicon nitride nano-ceramic matrix composites both increase initially and then decrease with the increase in CNTs amount. The flexural strength and fracture toughness both reach a maximum when CNTs content is 3wt.%.

![Figure 5. SEM microstructure micrographs of sample A and sample D](image)

(a) sample A  (b) sample D.

![Figure 6. Effect of CNT amount (wt.%) on mechanical properties.](image)

(a) Effect of CNT amount on flexural strength, (b) Effect of CNT amount on fracture toughness, (c) Effect of CNT amount on Vickers hardness.
The increase in strength is mainly related to the strengthening effect caused by the CNTs which can bear significant stress by shearing a portion of the load though pullout on the fracture surface. In fiber reinforced composites, a principal source of increased fracture toughness is crack deflection caused by reinforcing fiber ahead of a propagating crack [19]. The crack deflection caused by CNTs prolonged the propagation path of the crack and more energy will be dissipated, which increase the fracture toughness of silicon nitride nanocomposites. In addition, because of the different thermal expansion coefficients between the Si$_3$N$_4$ and CNTs, the internal residual stress generated during cooling process will induce the crack to propagate toward the CNTs and diverge, which is also contributed to the increase of the fracture toughness. But when the CNTs content is high, the agglomeration of CNTs causes the decrease in relative density and the micro-pores in microstructure that lead to the decrease in the flexural strength and fracture toughness. So it can be concluded that the homogenous distribution of CNTs within the matrix as well as the strong interfacial bonding between CNTs and the matrix are important factors affecting the strengthening effect of the CNTs. The Vickers hardness initially has little change, but it start to gradually decrease when the CNTs content is above 1 wt.%. This is mainly due to the decrease in the relative density and the agglomeration of CNTs.

4. Conclusion

Carbon nanotube–silicon nitride nano-ceramic matrix composites were fabricated by hot-pressing nano-sized Si$_3$N$_4$ powders and carbon nanotubes at 1700°C. The optimal manufacturing process has been performed to homogenously disperse the carbon nanotubes in the silicon nitride matrix. The phase composition, microstructure and mechanical properties of the sintered materials are investigated. The microstructure of sintered composites is mainly constituted of α-Si$_3$N$_4$, β-Si$_3$N$_4$, Si$_2$N$_2$O and carbon nanotubes. The CNTs are mainly located at grain boundaries of silicon nitride matrix.

The flexural strength and fracture toughness both increase initially then decrease with the increase of CNTs amount. The maximum values of flexural strength and fracture toughness are both obtained in silicon nitride nano-ceramics added 3 wt.% CNTs. The strengthening and toughening mechanisms are CNTs pullout and crack deflection caused by the CNTs. The Vickers hardness values of the composites start to decrease when the CNTs content is above 1 wt. %.

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