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Combustion synthesis of Si_3N_4–TiN composite powders

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Abstract

Si_3N_4–TiN composite powders have been prepared by self-propagating high-temperature synthesis (SHS). Y_2O_3 plays a dominant role on the formation of rod-like Si_3N_4 whiskers. Full nitridation occurred of the Si–Ti mixtures. In the SHS process, TiN formation preceeds that of Si_3N_4. The formation of TiN inhibits the grain growth of rod-like Si_3N_4 crystals. Meanwhile some solid solutions between Si_3N_4 and TiN have formed.

Keywords: D. Si_3N_4; SHS; TiN

1. Introduction

Si_3N_4-based materials have been investigated for many years as one of the most promising structural materials due to their high heat resistance, hardness, durability, thermal shock resistance, chemical resistance and good oxidation resistance [1]. However, Si_3N_4 is extremely hard, and its machining using conventional diamond tool is an inconvenient and expensive routine that contributes considerably to the final cost of the ceramic parts. Therefore, new electrical conductive Si_3N_4-based materials have been developed for electrical discharge machining (EDM) by adding certain amounts of TiC, TiN or TiCN particles to the ceramic matrix [2,3].

Among the above-mentioned materials, TiN-reinforced Si_3N_4 composites are proved better due to their high strength, low density and good electric conductivity [4]. The double role of TiN in the Si_3N_4-based materials provides the possibility of improving the fracture toughness and obtaining an electrical conductivity that would make the composite feasible for EDM.

On the other hand, an energy- and time-saving technique based on self-propagating high temperature synthesis (SHS) has been widely used to synthesize metal nitrides [5–7]. SHS is a process that utilizes the heat generated by an exothermic reaction to sustain itself in the form of a combustion wave after external ignition. It has many potential advantages such as low, great energy efficiency and a high production rate.

Preparing of Si_3N_4–TiN composite powders can be an important stage for making electro-conductive Si_3N_4–TiN composite. However, there are limited reports of the synthesis of Si_3N_4–TiN composites powders by SHS technique, in the present study, our aim is to investigate the feasibility of preparing Si_3N_4–TiN composite powders by SHS.

2. Experimental procedure

Purity and size of the raw materials are shown in Table 1. Table 2 shows the compositions of the designed samples. The samples were first ball milled for 24 h in absolute alcohol by using Si_3N_4 balls as the milling media. Then the powder mixtures were dried and passed through 60-mesh sieves.

The experiments were performed in a cold isostatic pressure vessel under 5 MPa nitrogen pressure. The samples packed in a porous graphite crucible were buried by Ti powder on the top. The ignition of the Ti powder was carried out using a tungsten coil. The combustion wave temperature was measured with a W/Re thermocouple (protected by a layer of BN), which was inserted into the center of the powders.

The phase analysis of the combustion products was performed by X-ray diffractometry (XRD). The morphologies

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Table 1
The purity and size of the powders used

	Si	Si_3N_4	Ti	Y_2O_3
Purity (%)	98.92	(α)93	98.9	99.95
Diameter (μm)	6.10	0.52	74	0.52

Table 2
The composition of the samples

Sample	Si (wt.%)	Si_3N_4 (wt.%)	Ti (wt.%)	Y_2O_3 (wt.%) (additional)
A	50	50	–	–
B	50	50	–	5
C	45	45	10	–
D	45	45	10	5
E	40	40	20	–
F	40	40	20	5

of combustion products were studied using scanning electron microscopy (SEM).

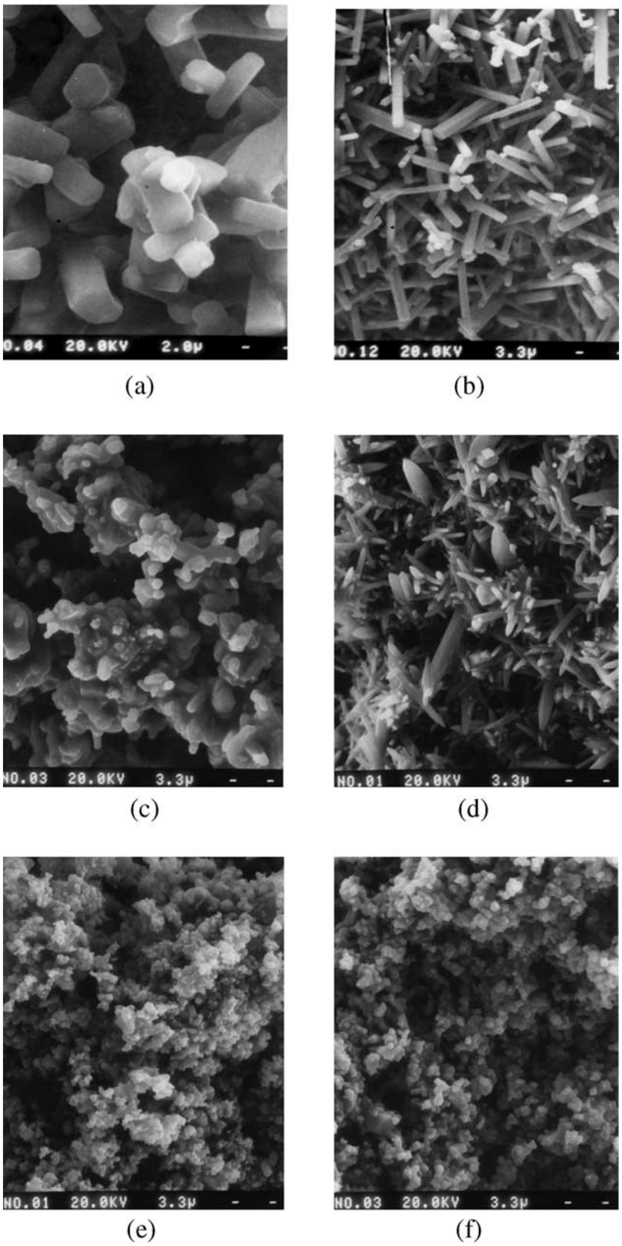
3. Results and discussion

The morphologies of the samples are shown in Fig. 1. In samples A–D, rod-like β-Si_3N_4 is present, but there are clear differences in their microstructures. As compared with the crystals of β-Si_3N_4 in sample A, the β-Si_3N_4 crystals are straight, uniform, and regular in sample B, the average aspect ratio is about 10.

XRD analysis indicates that only β-Si_3N_4 phase is present in sample B (Fig. 2a). This suggests that Si powder has been fully nitrided at the high nitrogen pressure, α-Si_3N_4, added as diluents, has also completely converted to β-Si_3N_4. The combustion wave temperature measured by a W/Re thermocouple was over 2000 °C. There was no evidence of the presence of Y_2O_3. It can be implicated that Y_2O_3 forms a Y–Si–O–N liquid at such a high temperature.

It is well-known that Y_2O_3 acts as a sintering aid for Si_3N_4 to form a liquid phase to accelerate the α–β phase transformation and grain growth via the dissolution–reprecipitation process [8–10]. The formed Y–Si–O–N liquid would be beneficial for the α–β phase transformation and the grain growth of β-Si_3N_4. It has been reported that liquid Si can act as suitable liquid solvent for Si_3N_4 and assist in the α–β phase transformation. In our results the marked increase of the aspect ratio of Si_3N_4 grains suggests that Y–Si–O–N liquid plays the dominant role in the grain growth of β-Si_3N_4.

In samples C and D, the addition of Ti has changed the morphologies of the samples. As compared to that in sample A, the aspect ratio of β-Si_3N_4 in sample C is rather small, and in sample D, simple rod-like morphologies have changed to more complicated morphologies, there are needle-like and rod-like crystals, the microstructure of Si_3N_4 matrix is rather inhomogeneous in grain size and aspect ratio (Fig. 1).

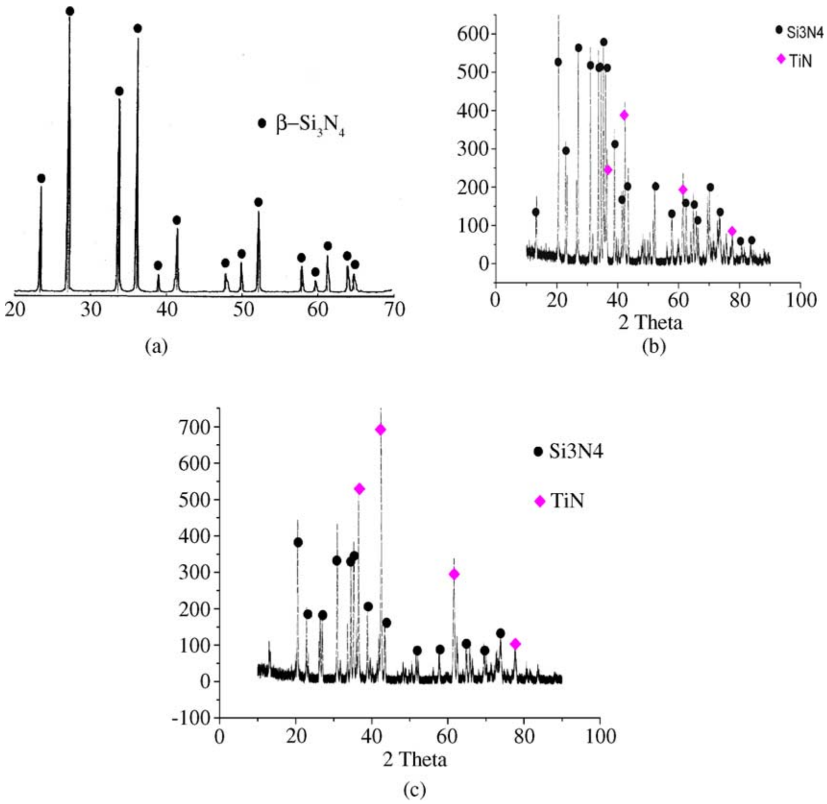


(a) (b) (c) (d) (e) (f)

Fig. 1. The SEM morphologies of samples A (a), B (b), C (c), D (d), E (e) and F (f).

In samples C and D, the grain sizes of Si_3N_4 have considerably reduced. The proportions of large β-Si_3N_4 grains have decreased, whereas the proportion of small β-Si_3N_4 grains increase due to the addition of Ti (Fig. 1d). The results indicate that both sizes and aspect ratios of Si_3N_4 grains decrease largely when the TiN content increases. This suggests that the grain growth of rod-like Si_3N_4 has been inhibited by TiN particles. This is in accordance with the results of the reference [11].

As to sample E and sample F, the microstructures are similar. The aspect ratios of crystals are small, the grain growth has been inhibited. Both the samples have a structure of aggregation of fine crystals. The morphologies have changed from rod-like via needle- and rod-like to round-shape.



(a) (b) (c)

Fig. 2. The XRD patterns of samples B (a), D (b) and F (c).

Table 3
The percentage increases of the corresponding *d* values in samples D and F

	The percentage increases of the corresponding *d* values					
	The corresponding percentage increases of Si_3N_4			The corresponding percentage increases of TiN		
	(2|0|0)	(1|0|1)	(2|1|0)	(1|1|1)	(2|0|0)	(2|2|0)
Sample D (10% Ti)	0.20	0.13	0.14	0.54	0.61	0.54
Sample F (20% Ti)	0.20	0.13	0.15	0.38	0.39	0.25

The simple principle of reactions in the SHS process is shown in the following:

$Ti(s) + 0.5N_2 = TiN(s)$ $\Delta G = -159.29$ kJ/mol 1898 K
$3Si(s) + 2N_2 = Si_3N_4(s,\alpha)$ $\Delta G = -105.81$ kJ/mol 1898 K
$\Delta G_{TiN} < \Delta G_{Si3N4}$ so TiN should form earlier than Si_3N_4.

The formation of TiN is earlier indeed than that of Si_3N_4. The formation of TiN in the first stage also decreases the combustion temperature of Si under high-pressure nitrogen, and the formed TiN has inhibited the grain growth of rod-like Si_3N_4.

XRD patterns show that there are no residue Si and Ti phase in all the samples, powder mixtures have been completely nitrided (Fig. 2). The XRD patterns also show that there are only Si_3N_4 and TiN in samples D and F. This indicates that the stability of TiN in Si_3N_4 is well and there is no obvious reaction between each other. However, the lattice parameters of them have deviated from the standard XRD spectrum. The corresponding *d* values have all augmented. Table 3 shows the details of the deviation from the corresponding standard *d* values. It can be implicated that Si_3N_4 and TiN have formed solid solutions between each other. This is in accordance with the published data that up to 7 wt.% Si_3N_4 can be dissolved in TiN at 1650 °C [12] and up to 30 at.% Ti can be dissolved in Si_3N_4 at 1725 °C [13]. The variation percents of *d* values are small: this indicates that the solubility between Si_3N_4 and TiN in the SHS process is small.

4. Conclusions

Si_3N_4/TiN composite powders have been prepared by the SHS technique. Y_2O_3 is very important in the formation of long aspect ratio rod-like Si_3N_4 crystals. In the SHS process, the formation of TiN occurs before that of Si_3N_4. The formation of TiN inhibits grain growth of rod-like Si_3N_4. Si_3N_4 and TiN have been observed to form some solid solution between each other.

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