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Synthesis of Si_3N_4–TiN–SiC composites by combustion reaction under high nitrogen pressures

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Abstract

Si_3N_4–TiN–SiC composites were synthesized from $TiSi_2$ and SiC mixtures via the combustion reaction under high nitrogen pressure. The nitridation mechanism of $TiSi_2$ was analyzed. The results show that the nitridation of $TiSi_2$ produced TiN and Si firstly, and Si_3N_4 phase was formed by the further nitriding of Si. The molten eutectic phase and its agglomeration between Si and $TiSi_2$ formed one core-shell structure and affected the nitridation process. Under higher nitrogen pressure, the nitridation reaction was complete and the relatively dense Si_3N_4–TiN–SiC composites obtained. TEM observation revealed inhomogeneous Si_3N_4 grain size, amorphous phase, cavities, microcracks and dislocations, and graphite from the nitridation of SiC in the microstructure. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Combustion synthesis; Composites; Microstructure-final; SHS; SiC; Si_3N_4; TiN

1. Introduction

Material based on silicon nitride is characterized by its high heat resistance, refractoriness, hardness, durability, thermal shock resistance, and chemical resistance, which has a high potential in the practical utilization not only as a structural material but also as a functional material. However, silicon nitride is extremely hard and machining using conventional diamond tools is an inconvenient and expensive routine that contributes considerably to the final cost of the ceramic parts. Therefore, new conductive silicon nitride-based composites were developed for electrical discharge machining (EDM) by adding amounts of TiC, TiN or TiCN particles to the ceramic matrix.[1,2] Wang[3] reported that the Si_3N_4–TiN composite with the critical content of TiN could be machined by low-cost electric spark technique. On the other hand, an energy- and time-saving technique based on combustion synthesis or self-propagating high temperature synthesis (SHS) has been widely investigated for the synthesis of metal nitrides.[4–6] Zhang et al.[7] and Skibska et al.[8] have studied the morphology and formation mechanism of Si_3N_4 by the combustion reaction of silicon powder in a pressurized nitrogen atmosphere. Lei[9] and Bandyopadhyay[10] have examined the nitridation kinetics and microstructure of Si_3N_4-based materials by combustion. Much information on the relationship of microstructure and properties of Si_3N_4 based materials under combustion conditions is not clear. The necessity of continuing studies of the Si–N SHS reaction in a pressurized nitrogen atmosphere is suggested to enable fabrication of materials with the desired microstructure and properties.[8,10]

In the present work, the combustion synthesis of electrically conductive Si_3N_4–TiN–SiC composite has been studied using $TiSi_2$ and SiC powder mixture compact under a nitrogen pressure of 130 MPa. The nitridization mechanism and microstructure formation were analyzed.

2. Experimental

The experimental set-up used for high-pressure investigations of SHS synthesis of nitrides is shown in Fig. 1. It includes a high-pressure vessel equipped with an ignition system, a gas pressure multiplication system, and a control system. A tungsten spiral at the top of

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ignition pellets is applied as an external heat source. W/Re thermocouples are used to measure the combustion temperature and are placed at fixed points on samples.

Experiments on combustion synthesis of Si_3N_4–TiN–SiC composite were conducted under a nitrogen pressure in range 10–130 MPa (nitrogen gas purity –99.9%). $TiSi_2$ and $TiSi_2$/SiC (weight ratio 65:35) powder mixture compacts were used as initial materials. High purity (>99.5%) SiC (7 μm) and SHS $TiSi_2$ (13 μm) were used in compositions for sample compaction. The $TiSi_2$ powder was prepared with silicon (5 μm, 99%) and Ti (45 μm, 99%) powders in accord with a Ti+2Si composition, as shown in Fig. 2. Cold-pressed cylindrical compacts with different initial porosity were putted into the high-pressure vessel and then ignited to synthesis the composites. The as-received compacts were sectioned for microstructure analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM/EPMA) and transmission electron microscopy (TEM), and mechanical property testing.

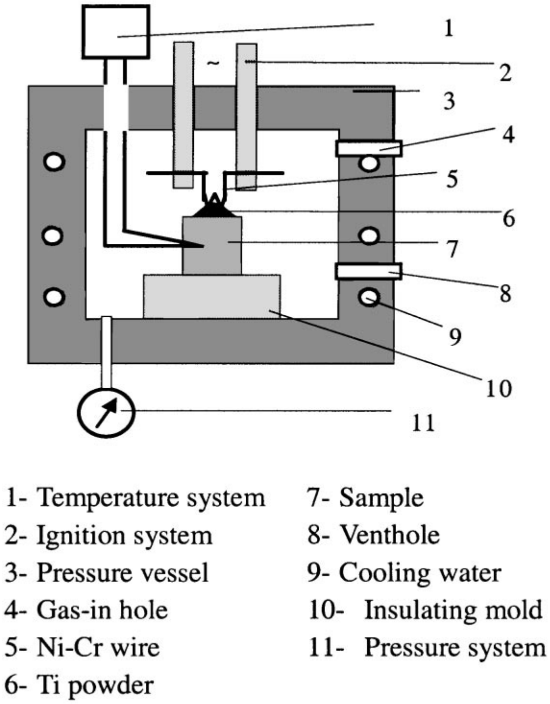


Fig. 1. Schematic diagram of experimental equipment.

3. Results and discussion

X-ray diffraction (XRD) patterns layer-by-layer (Fig. 3) for the nitridation product of $TiSi_2$ green compact with the relative density of 52% under 10 MPa nitrogen pressure

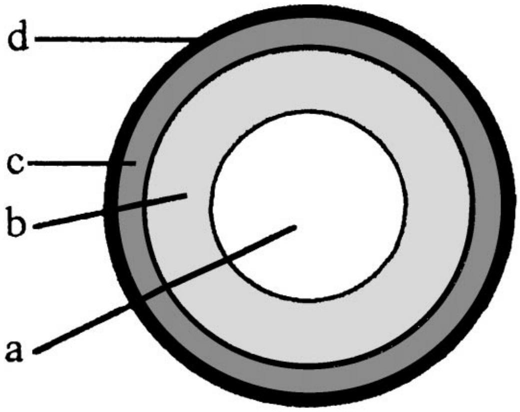
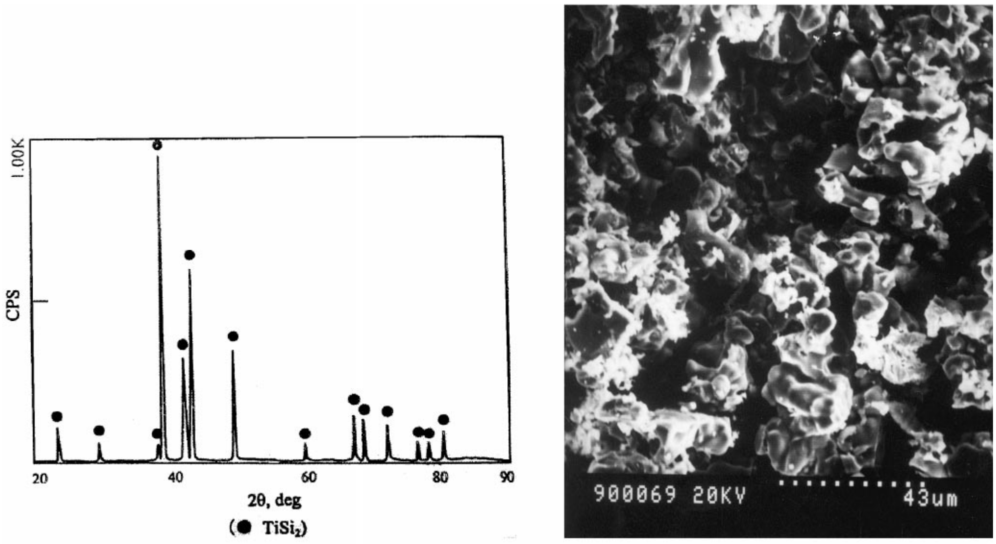


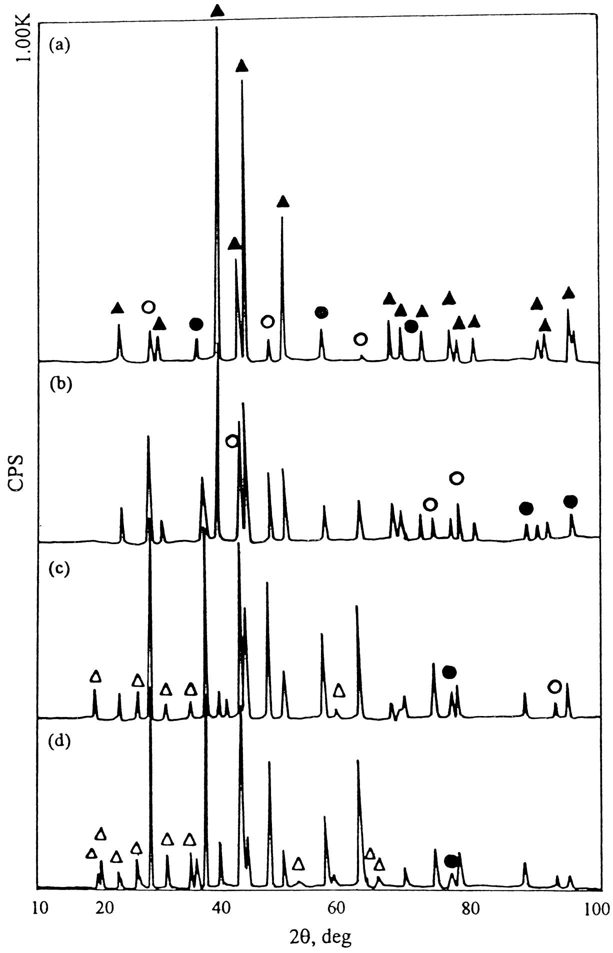
Fig.3. Diagram of infiltration combustion reaction process.



(a) (b)

Fig. 2. (a) XRD pattern and (b) SEM micrograph of $TiSi_2$ powder synthesized by the authors in SHS reactor as the raw material of composite.

are presented in Fig. 4. It can be seen that the phases in the internal layer consist of $TiSi_2$, and the nitridation phases of Si and TiN [Fig. 4(a)]. From the internal layer to outer layer, the nitrogen pressure for the nitridation reaction of $TiSi_2$ increased, the $TiSi_2$ content decreased, and Si and TiN increased [Fig. 4(b)]. The β-Si_3N_4 was first detected in the "c" layer [Fig. 4(c)], and Si content decreased and β-Si_3N_4 increased in the outer layer [Fig. 4(d)] during the infiltration combustion of $TiSi_2$ with high pressure nitrogen gas. The change of relative percents of maximum XRD peak intensity for each phase is summarized in Table 1. It seems that the whole nitridation reaction can be divided into two stages as follows



(● Si, ▲ $TiSi_2$, ○TiN, △ Si_3N_4)

Fig.4. XRD patterns of nitridation products from $TiSi_2$ at high nitrogen pressure layer-by-layer as shown in Fig. 3.

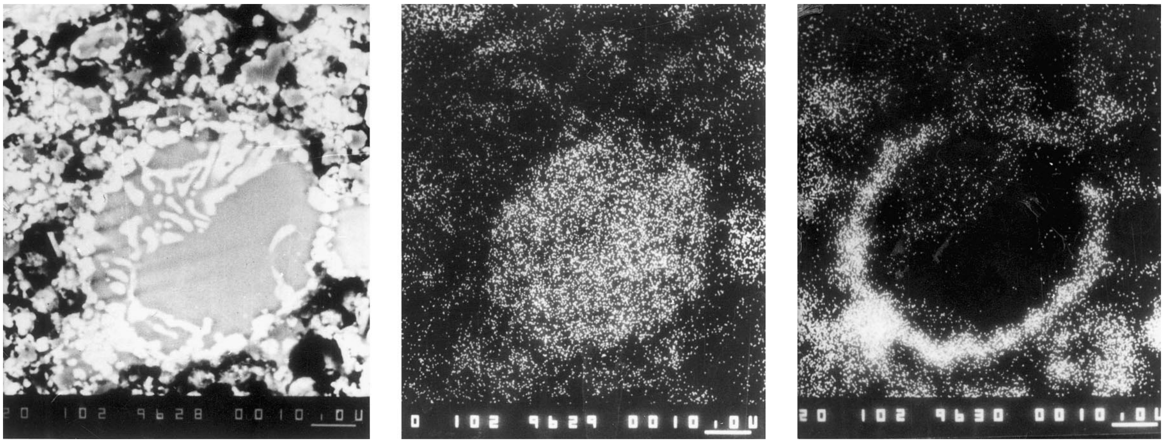
$$TiSi_2 + N_2 = TiN + Si \tag{1}$$

$$Si + N_2 = Si_3N_4 \tag{2}$$

In the second stage, the nitridation of Si–TiN mixtures allows porous electro-conductive composites to be obtained; the TiN phase produced in the first stage as a diluent decreases the combustion temperature of Si under high-pressure nitrogen. This process can be based on the nitridation of Si + Si_3N_4 mixtures. Zhang et al.[7] made an experimental analysis of the combustion reaction of silicon in a pressurized nitrogen atmosphere and concluded that the formation of β-Si_3N_4 was controlled by the kinetic-controlled reaction and diffusion-controlled reaction. The kinetic reaction between Si vapor and N_2 on the surface of Si_3N_4 microcrystals is very fast, but Si vapor diffuses through N_2 to surface of

Table 1
XRD results of nitridation products from $TiSi_2$ layer-by-layer

Layer number	The relative intensity of maximum peak for each phase (%)			
	β-Si_3N_4	TiN	Si	$TiSi_2$
A	0	5.6	9.8	84.6
B	0	23.2	27.5	49.3
C	4.0	41.3	38.9	15.8
D	7.3	47.7	35.8	9.2



(a) (b) (c)

Fig. 5. SEM and EPMA micrograph of nitridation products (a) a large Si particle, (b) dot map of Si and (c) dot map of Ti.

Si_3N_4 microcrystals and reacts with N_2 very slowly. In the present work, Si phase is formed by the nitridation of $TiSi_2$, no devitrification process of silicon film on the Si surface is necessary as shown in Ref. [9].

For the gas-phase combustion synthesis of Si_3N_4 based materials, the degree of conversion depends on the local availability of nitrogen. Larger and more numerous pores in the compact favour higher degrees of conversion and lower dependence on the permeation of the nitrogen gas through the compact. In order to provide a beneficial condition to study the reaction mechanism, the nitridation experiment of loose $TiSi_2$ powder under 100 MPa high nitrogen pressure was carried out. At the first stage of nitridation reaction, the high nitrogen pressure and porosity of powder compact result in the high combustion temperature, great amounts of molten phases are produced and affect the nitridation process of $TiSi_2$. The molten Si from the nitridation of $TiSi_2$ formed the eutectic liquid (1330°C) with residue $TiSi_2$. The large agglomerated molten particle, as shown in Fig. 5(a), slows down the further nitridation of Si and $TiSi_2$. The morphology of a large particle is different from that of $TiSi_2$ powder and like a core-shell structure. The Si core and Ti shell are shown in Fig. 5(b) and (c), respectively. Transmission electron micrograph revealed that many TiN particles dispersed in the grains of β-Si_3N_4 as shown in Fig. 6. This also confirmed that the nitridation of $TiSi_2$ produced TiN first and then β-Si_3N_4, the TiN phase was encircled by β-Si_3N_4.

With the addition of SiC particles, the large agglomerated molten particle was dispersed and the degree of conversion increased during the nitriding of $TiSi_2$, but the decreased combustion temperature made the reactant unignited. For a given gas–solid combustion system, an explicit relationship between the combustion temperature and nitrogen pressure is given by[11]

$$T \approx P/K \text{ in which } K \approx S\frac{(1-\rho)}{\rho}\cdot\frac{RC}{V_m} = \text{constant} \qquad (3)$$

where P is the pressure of N_2 (g), the number of moles of N_2(g) per mol of metal in the reaction, ρ the porosity of the powder compact, R the universal gas constant, V_m the molar volume of metal, T the absolute temperature and C the degree of conversion. The above equation shows that the temperature increases with the rising

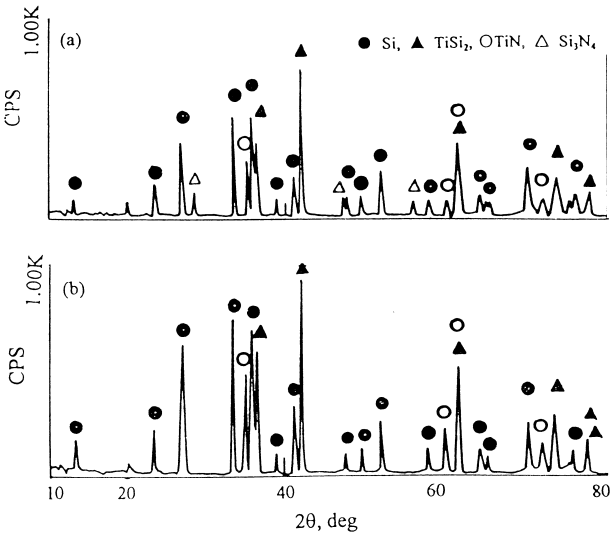
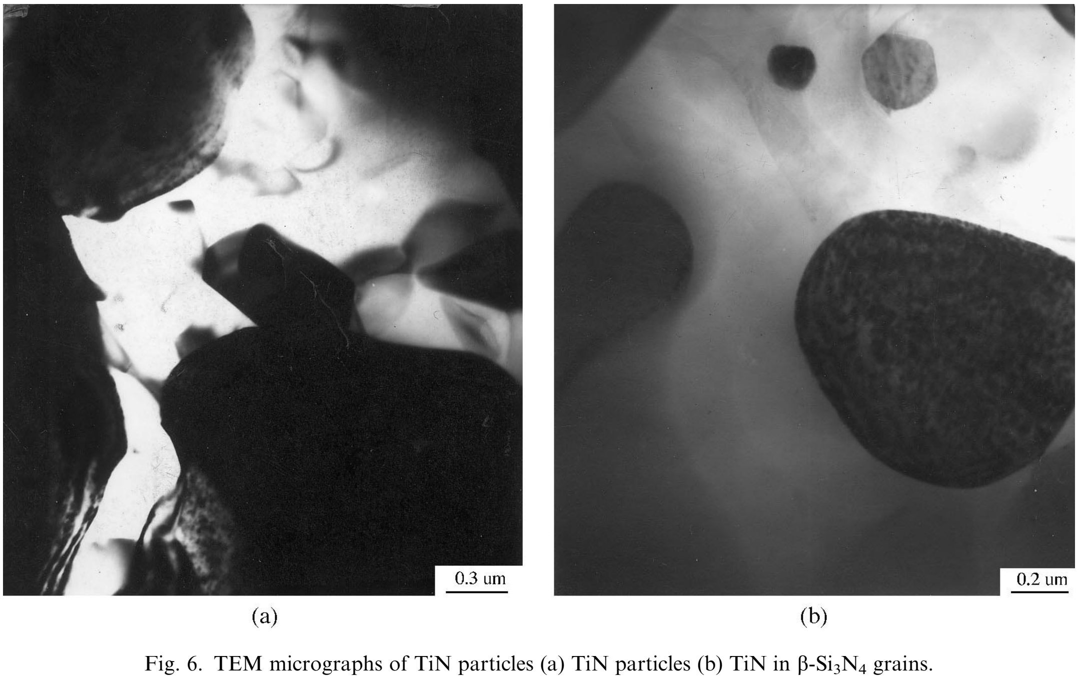


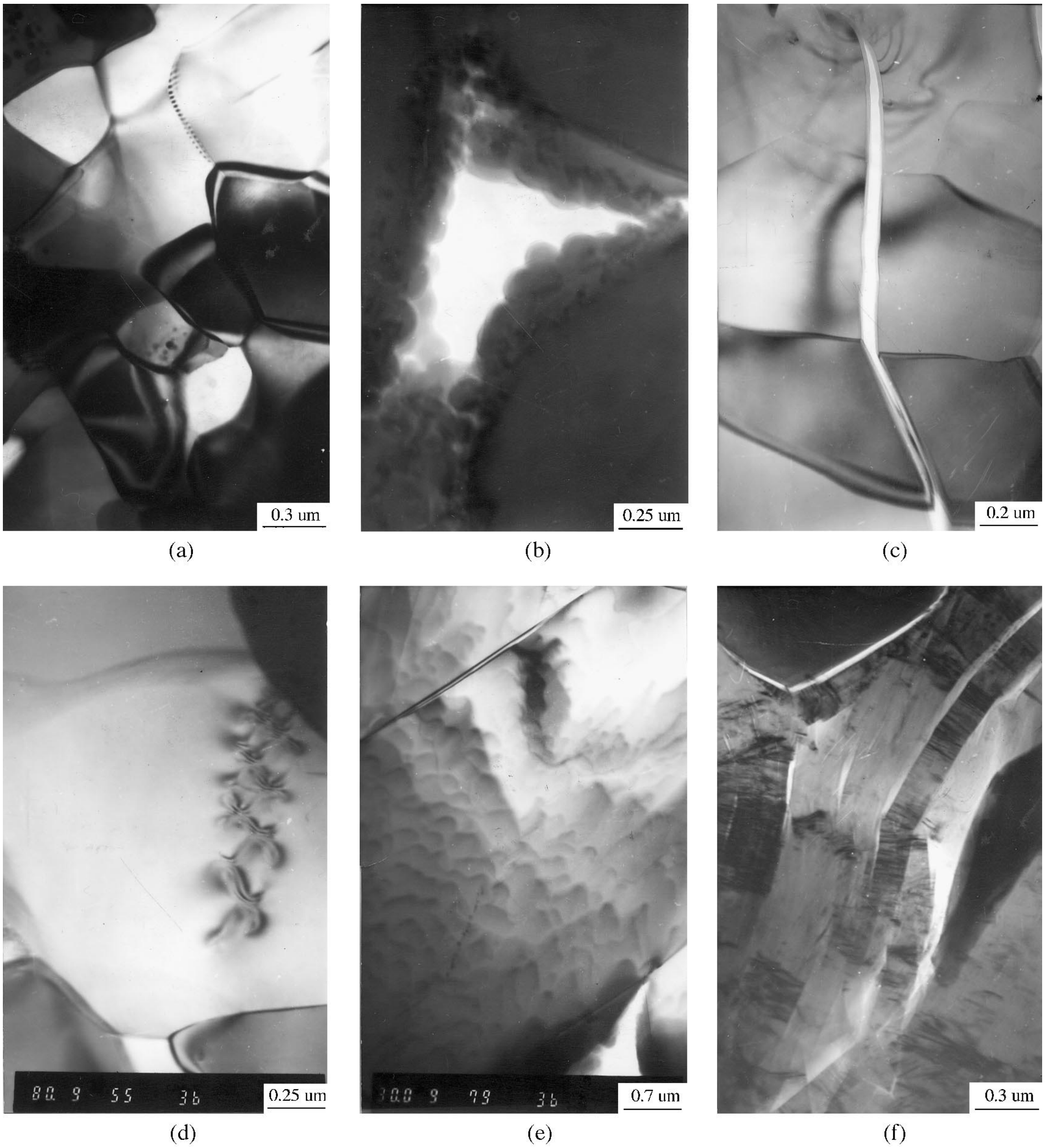
Fig. 7. XRD patterns of Si_3N_4–TiN–SiC composite at different layer (a) internal layer and (b) external layer.



(a) (b)

Fig. 6. TEM micrographs of TiN particles (a) TiN particles (b) TiN in β-Si_3N_4 grains.

pressure of nitrogen gas. In the present study, the higher nitrogen pressure of 130 MPa is applied to ignite and nitride the $TiSi_2$ and SiC (35 wt%) mixture compact with green porosity of 45%. The as-reacted product was characterized by X-ray diffraction. Fig. 7 shows typical X-ray diffraction patterns of the Si_3N_4–TiN–SiC body. In the internal layer, the nitridation was incomplete and β-Si_3N_4, TiN and SiC coexisted as well as a small amount of residual Si phase in Fig. 7(a), but the reaction was complete and only β-Si_3N_4, TiN and SiC were detected in Fig. 7(b). The relative density and hardness of the Si_3N_4–TiN–TiC composite are 83% and 78 HRA, respectively. The densification is suggested to be due to the volume expansion of $TiSi_2$ decomposition and the nitridation of Si and Ti, and hot isostatic pressing under high nitrogen pressure. In the transmission electron micrograph the microstructure of the matrix β-Si_3N_4 was rather inhomogeneous in grain size [Fig. 8(a)]. The cavities and interfacial amorphous phase were found between β-Si_3N_4 grains and at the multi-grain junctions [Fig. 8(b)]. Sometimes the microcrack passed through a few grains and stopped in the β-Si_3N_4 grain as shown in Fig. 8(c), the presence of fault dislocation in β-Si_3N_4 grains [Fig. 8(d)] indicated that the deformation of the β-Si_3N_4 matrix is well accommodated by that of TiN particles. The SiC/Si_3N_4 interface boundaries are clear [Fig. 8(e)] and the observed graphite [Fig. 8(f)] revealed that the nitridation reaction: $SiC + N = Si_3N_4 + C$ was presented during the combustion reaction of $TiSi_2$ and SiC mixtures under high nitrogen pressure.



(a) (b) (c)

(d) (e) (f)

Fig. 8. TEM micrographs of Si_3N_4–TiN–SiC composite (a) β-Si_3N_4 grains (b) cavity and amorphous phase (c) microcracking (d) fault dislocations (e) SiC (f) graphite.

4. Conclusions

The whole nitridation reaction of $TiSi_2$ under high nitrogen pressure can be divided into two stages: $TiSi_2 + N_2 = TiN + Si$ and $Si + N_2 = Si_3N_4$. The TiN phase formed in the first reaction decreased the combustion temperature in the second stage as the diluent phase, pure Si was easy to further nitriding, but the eutectic liquid between Si and $TiSi_2$ formed the core-shell structure and slowed down the nitridation of Si and $TiSi_2$. The relatively dense Si_3N_4–TiN–TiC composite was produced by high gas pressure combustion synthesis. XRD analysis revealed that the reaction was complete and only small amounts of residue Si phases were detected in the internal layer. The microstructure was complex with microcracks and dislocations, but no reaction between Si_3N_4, TiN and SiC was present.

Acknowledgements

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