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Formation of SiC whiskers from silicon nitride

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Attempts have been made to produce SiC whiskers through vacuum pyrolysis of Si_3N_4 without any addition of extraneous carbon. Vacuum pyrolysis of Si_3N_4 granules and powder compacts, has been carried out at 1550 and 1700 °C using a graphite resistance furnace. The products of pyrolysis have been identified through XRD and SEM as SiC whiskers and particles. Small amounts of elemental silicon at 1550 °C and free carbon at 1700 °C have been detected through X-ray diffraction. Detection of elemental silicon through X-ray diffraction and solidified silicon droplets at the whisker tips in the SEM provide important clues regarding the mechanism of SiC_w formation, as the one involving the reaction

$$2Si(l) + CO(g) \rightarrow SiC(s) + SiO(g)$$

Silicon carbide whiskers, 3–4 mm long, have been grown from Si_3N_4 compacts at 1550 °C over a short period of 0.5 h. It has been shown in the present study that Si_3N_4 can be completely converted to SiC_w, when a loose bed of Si_3N_4 in the form of granules is pyrolysed in the presence of CO at about 1550 °C.

1. Introduction

Silicon carbide whiskers (SiC_w) are used to obtain stronger and tougher composite ceramics and light metal alloys for structural uses. SiC_w can be produced from several precursors such as potentially inexpensive agricultural waste such as rice husks [1–3], metallic silicon and coal tar pitch mixture [4], through a reaction of SiO_2 and CH_4 [5], by hydrogen reduction of methyl trichlorosilane [6–8] and by vaporization of bulk SiC [9, 10]. SiC_w can also be formed by reaction between Si_3N_4 powder and carbon in the presence of CO, with a high yield [11, 12]. It has been observed that the unreacted carbon existing in the entangled mixture of the reaction product cannot easily be removed by air oxidation and the attempts to eliminate carbon often lead to the oxidation of thin SiC_w [12]. In this report a process for the formation of SiC_w from Si_3N_4 powder without any carbon additions is discussed.

2. Experimental procedure

Si_3N_4 powder, grade SN-E10 with specific surface area of 10.3 $m^2 g^{-1}$ and $(\beta/\alpha + \beta) < 5$ wt % was used in the present investigation (Table I). The Si_3N_4 as-received was in the form of loose granules of about 2 mm diameter and the granules could easily be powdered.

Three sets of samples were subjected to vacuum pyrolysis. The first set consisted of Si_3N_4 granules loosely held in a cylindrical graphite crucible of size, 60 mm outer diameter, 52 mm inner diameter and 125 mm height. The second set was that of Si_3N_4 compacts. The Si_3N_4 granules were ground in a mortar and compacted in a steel die at a pressure of about 200 MPa to obtain pellets of size 10 mm diameter and 20 mm height. The third set was that of compacts of a blend containing Si_3N_4 powder and 40 wt % phenolic resin. The pellets were placed on a graphite block.

TABLE I Composition of Si_3N_4

Nitrogen (wt %)	> 38.00
Oxygen (wt %)	1.39
Chlorine (p.p.m.)	< 100
Iron (p.p.m.)	< 100
Calcium (p.p.m.)	< 50
Aluminium (p.p.m.)	< 50
Crystallinity (wt %)	> 99.50

The graphite crucible containing Si_3N_4 granules or the graphite block with compacts was inserted in separate batches into the heating zone of a graphite resistance ASTRO high-temperature vacuum furnace model 1000A-2560. The furnace was evacuated to 6.66 $\times 10^{-7}$ MPa with the help of a Hind Hivac vacuum system. The temperature was monitored by focusing a Honeywell small target radiation pyrometer on to the compacts and on to the graphite crucible in the case of Si_3N_4 granules. The Si_3N_4 conversion to SiC was carried out at 1550 °C for 0.5 h. In addition, the conversion of Si_3N_4 compacts was carried out at 1700 °C for 0.5 h. After the conversion process, the samples were analysed by Cam Scan DV-2 scanning electron microscope. A Philips X-ray diffractometer model PW1840 with CuK_α radiation was used for X-ray diffraction (XRD) analysis.

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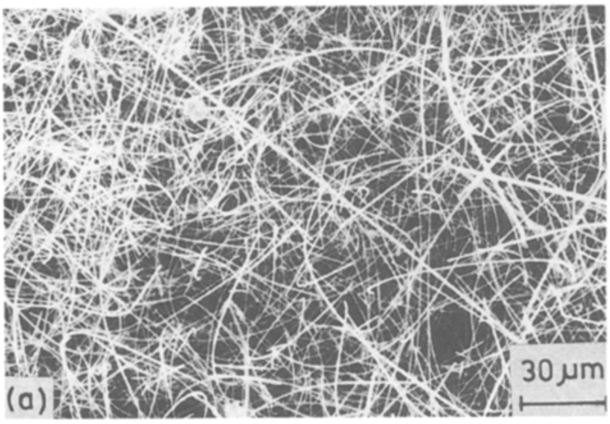
3. Results

3.1. Pyrolysis at 1550 °C

The outer surfaces of the Si_3N_4 and (Si_3N_4 plus phenol) compacts after the pyrolysis at 1550 °C for 0.5 h were found to be covered with SiC whiskers (Fig. 1a and b). Some of the whiskers were as large as 2–3 mm long. The compacts were then sectioned and observed under an optical microscope. The pyrolysed Si_3N_4 compact had a 2 mm thick greenish shell of SiC and the core of the compact was unreacted (Fig. 2) as confirmed by XRD analysis. The (Si_3N_4 plus phenol) compact was greenish over the entire cross-section and SiC_w were also seen to have grown inside the compact. Under the SEM it was observed that the SiC_w were formed at selective places in voids in the Si_3N_4 compacts (Fig. 3a and b).



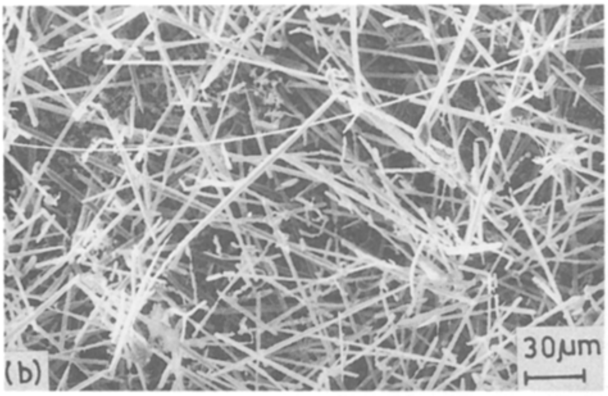


Figure 1 SiC_w grown at 1550 °C (a) on Si_3N_4 compact, (b) on (Si_3N_4 plus phenol) compact.

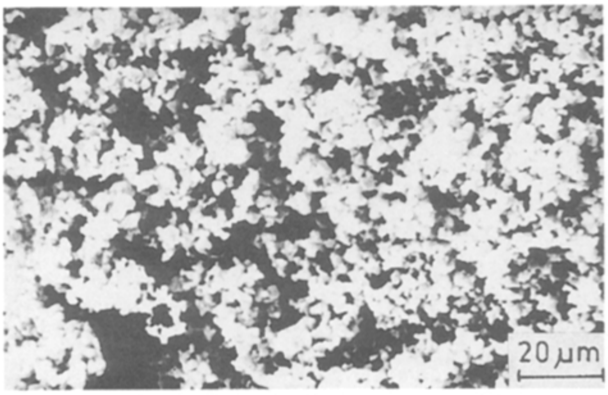


Figure 2 Scanning electron micrographs of Si_3N_4 compact (core) treated at 1550 °C for 0.5 h.

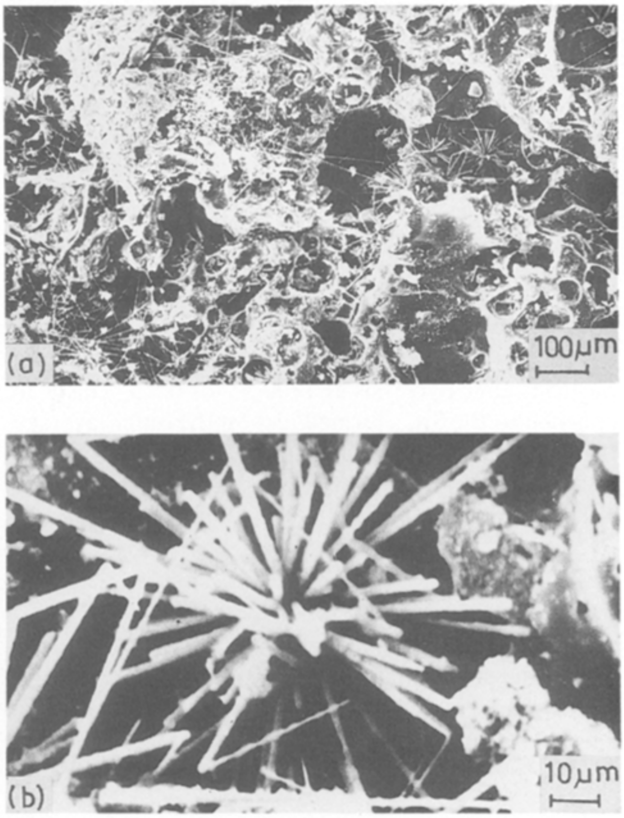


Figure 3 Scanning electron micrographs of (Si_3N_4 plus phenol) compact (core) treated at 1550 °C for 0.5 h. (a) SiC_w formed in voids; (b) higher magnification of (a).

When several (four) Si_3N_4 compacts were treated simultaneously at 1550 °C/0.5 h, SiC_w were also seen to grow on the graphite pedestal at a distance of about 5 cm from the highest temperature zone. SiC_w about 3–4 mm long were seen to have grown in this deposition and the whiskers were mostly triangular in cross-section and showed bamboo-like structure. Branching from growth defects has also been observed (Fig. 4).

When silicon nitride granules in a graphite crucible were heated to 1550 °C, they turned bluish and stuck to each other. Each granule had the appearance of a mass of wool. In the XRD pattern of these granules

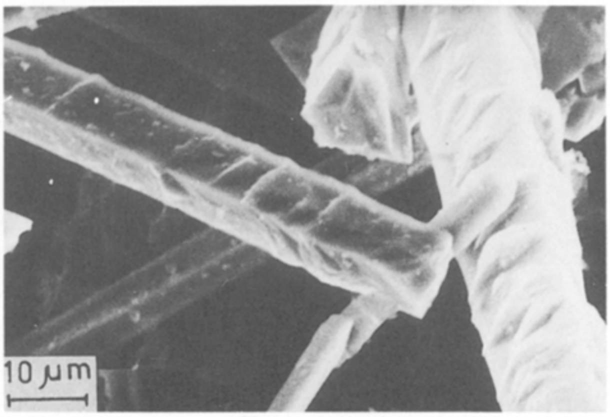


Figure 4 SiC_w grown on a graphite pedestal. Bamboo structure and branching from a growth defect can be observed.

(Fig. 5b), various peaks of SiC and a minor peak of elemental silicon have been identified. Under the SEM the granules were found to contain considerable amounts of SiC whiskers (Fig. 6a and b). At higher magnifications several distinct types of single crystals could also be observed, some with a hexagonal cross-section, some with conical cross-sections (carrot or bomb-shell shaped) in these granules (Fig. 7).

3.2. Pyrolysis at 1700 °C

The Si_3N_4 compact was dominantly consisted of SiC particles after pyrolysis at 1700 °C for 0.5 h. This is in contrast to the SiC_w formed just on the outer layers of the compacts when treated at 1550 °C. A peak corresponding to graphitic carbon was also observed in the XRD pattern (Fig. 5c).

4. Discussion

Although the C–Si–N–O system is of great technological interest for fabrication and high-temperature applications of SiC and Si_3N_4 materials, very few experimental data are available regarding the phase equilibrium. A detailed computer calculation of the heterogeneous phase equilibria in the C–Si–N–O system has been presented by Weiss *et al.* [13]. Lorenz *et al.* [14] have given the equilibrium phase variation as a function of temperature and nitrogen partial pressure (Fig. 8).

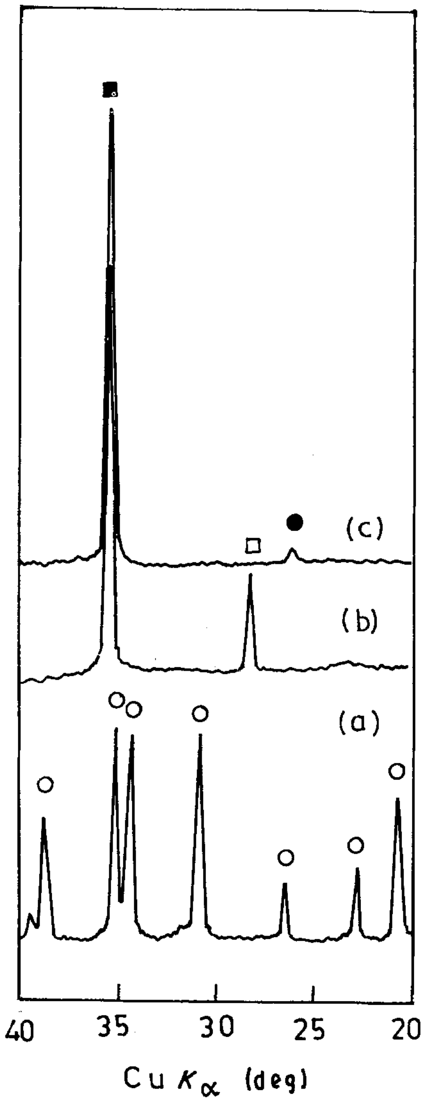


Figure 5 XRD patterns of (a) as-received Si_3N_4, (b) Si_3N_4 granules after pyrolysis at 1550 °C for 0.5 h, (c) Si_3N_4 compact after pyrolysis at 1700 °C for 0.5 h. (○) α-Si_3N_4, (□) silicon, (●) graphite, (■) β-SiC.

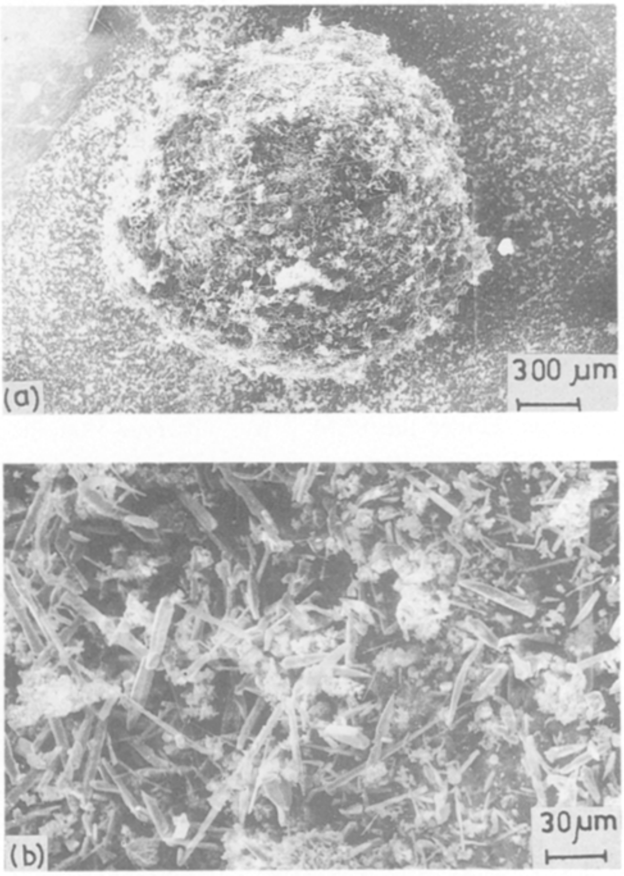


Figure 6 (a) SiC_w formed in a Si_3N_4 granule treated in a graphite crucible at 1550 °C for 0.5 h. (b) Higher magnification of (a).

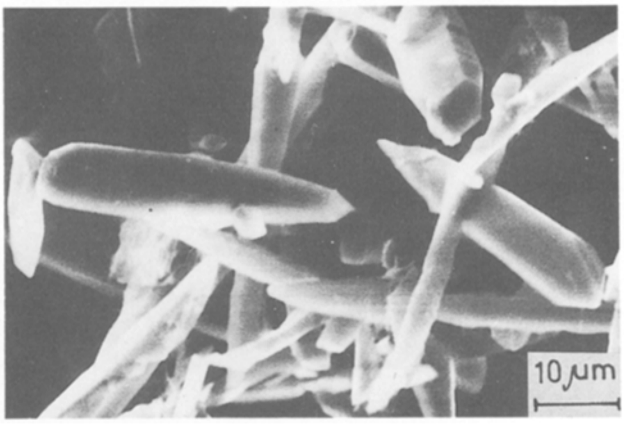


Figure 7 As Fig. 6a, showing bomb-shell-type and hexagonal cross-sectioned SiC crystals.

Under the experimental conditions of vacuum of 6.66×10^{-7} MPa (equal to 5.33×10^{-7} MPa nitrogen partial pressure), and a temperature of 1550 °C, the silicon released on decomposition of Si_3N_4 (Reaction 1) would be in the vapour phase. As the Si_3N_4 compact without carbon was heated from room temperature, silicon liquid would form first at 1450 °C (Region III in Fig. 8).

$$Si_3N_4 \rightarrow 3Si + 2N_2 \qquad (1)$$

The silicon droplets could react with CO present in the furnace atmosphere to form SiC according to Reactions 2–4

$$2Si(l) + CO(g) \rightarrow SiC(s) + SiO(g) \qquad (2)$$

$$SiO + 2C \rightarrow SiC + CO \qquad (3)$$

$$Si + C \rightarrow SiC \qquad (4)$$

As the silicon liquid droplet becomes supersaturated with carbon and SiC, crystal growth would occur by precipitation. Upon heating to 1550 °C (Region IV, Fig. 8), the silicon liquid droplet continuously receives silicon vapour from Si_3N_4 decomposition and CO from the furnace atmosphere. As the precipitation continues, SiC_w grows, lifting the silicon liquid droplet. The solidified silicon-rich spheres could be observed at the tips of SiC_w grown on Si_3N_4 compacts (Fig. 9a and b). When several Si_3N_4 compacts were heated simultaneously at 1550 °C, a large quantity of silicon vapour would be released and would be deposited on the graphite pedestal where 3–4 mm long SiC_w could grow. However, no SiC_w were formed within the Si_3N_4 compact because the Si_3N_4 powder was pressed at a pressure of 200 MPa. Because the compact was so dense, CO probably could not penetrate into the core to form SiC_w. Similarly, as Si_3N_4 is a poor conductor of heat, the temperature at the core of the Si_3N_4 compact could not have been high enough for it to decompose. On the other hand, when phenol was added to Si_3N_4, SiC_w also grew inside the compact. This could be due to the porosity and carbon formed in the compact by the decomposition of phenol, which could facilitate whisker growth. The above results indicate that long SiC_w can be grown from Si_3N_4 compacts by further prolonging the pyrolysis at 1550 °C.

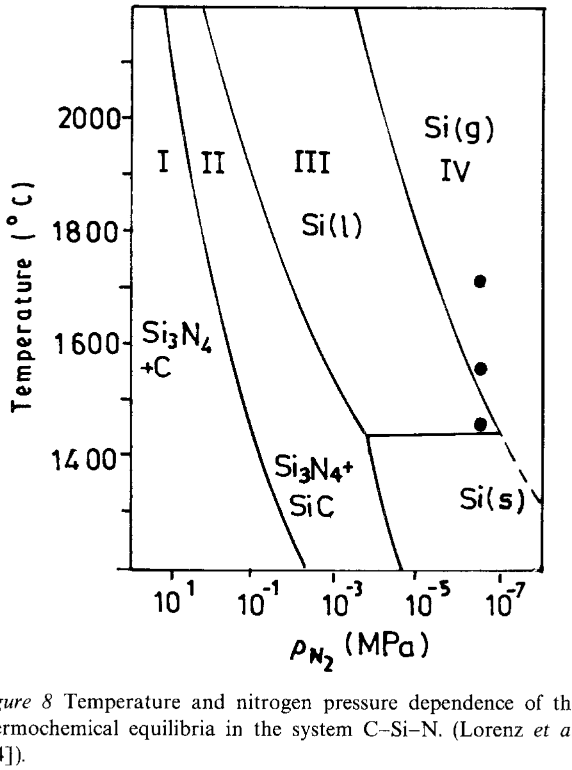


Figure 8 Temperature and nitrogen pressure dependence of the thermochemical equilibria in the system C–Si–N. (Lorenz *et al.* [14]).

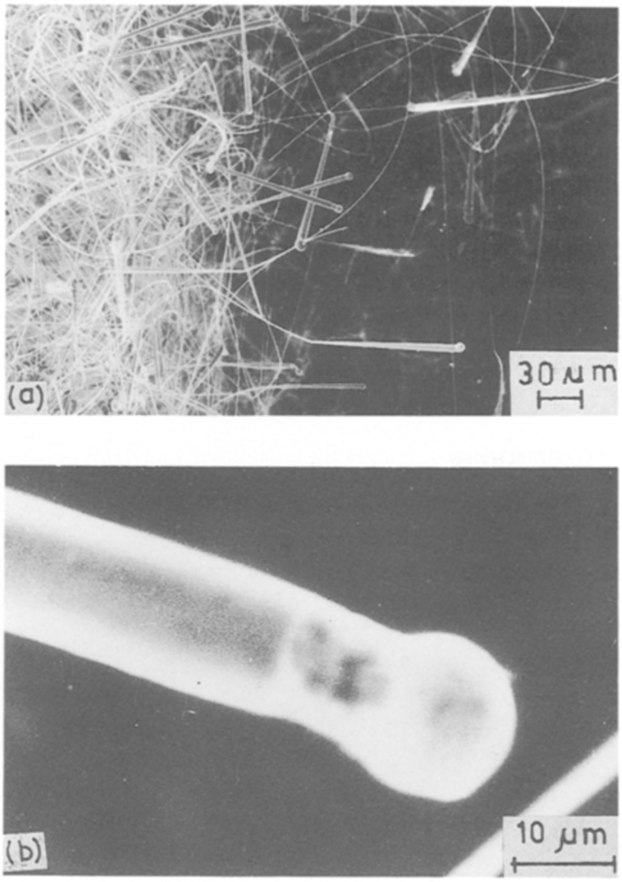


Figure 9 (a) SiC_w grown on Si_3N_4 compact at 1550 °C. Solidified silicon droplets on whiskers can be noticed. (b) Higher magnification of (a).

When the as-received Si_3N_4 granules were heated to 1550 °C in a 4 mm thick walled graphite crucible, the actual temperature of the granules would be lower than 1550 °C. Hence silicon liquid could be present (Region III, Fig. 8). The reaction of silicon liquid with CO would lead to the growth of SiC single crystals of various shapes. The elemental silicon peak detected from the XRD pattern (Fig. 5b) is evidence of the existence of silicon liquid during crystal growth.

At 1700 °C the Si_3N_4 decomposition Reaction 1 and the formation of SiC according to Reactions 2–3 proceed rapidly, giving rise to the formation of SiC and CO. Under the same experimental conditions the SiC formed would also partially decompose (reverse Reaction 4) resulting in an observable carbon peak in the XRD pattern (Fig. 5c).

5. Conclusions

1. Vacuum pyrolysis of Si_3N_4 in the presence of CO leads to its conversion to SiC without the need for the addition of extraneous carbon.
2. Silicon carbide whiskers, 3–4 mm long, can be grown from Si_3N_4 over a short period of 0.5 h.
3. The mechanism of formation of SiC_w from Si_3N_4 in the presence of CO, has been identified as the

reaction between a silicon liquid droplet and CO:

$$\begin{aligned} Si_3N_4 &\rightarrow 3Si + 2N_2 \\ 2Si(l) + CO(g) &\rightarrow SiC(s) + SiO(g) \\ SiO + 2C &\rightarrow SiC + CO \\ Si + C &\rightarrow SiC \end{aligned}$$

4. Complete conversion of Si_3N_4 to SiC_w can be achieved through vacuum pyrolysis of loose Si_3N_4 granules at 1550 °C in the presence of CO.

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