

## Formation of SiC whiskers from rice husk silica–carbon black mixture: effect of preheat treatment

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At present most SiC whiskers are produced by carbothermal reduction of silica [1]. There are several reports [2–11] on the formation of SiC whiskers from rice husks which contain amorphous silica and carbon. Four competitive processes, viz. crystallization of silica, crystallization of carbon, formation of SiC whiskers and formation of SiC particles, are simultaneously advancing during thermal decomposition of rice husks [10]. The size, shape and arrangement of crystallites could affect the properties of carbon [12]. The reactivity of the silica and carbon decreases with increasing crystallinity [13]. The formation of SiC whiskers from rice husk silica–carbon black mixtures has been reported previously [14]. In this work rice husk silica and carbon black were separately preheated and the effect of pretreatment on the formation of SiC whiskers is described.

The raw rice husks used in this work consisted of 85 wt% carbonaceous material and 15 wt% silica with trace elements. Carbon black of grade N220 (ISAF), supplied by Philips Carbon Black Ltd, Durgapur, W.B., India, was used. An alumina tubular furnace (model CTF 16/75; Carbolite Furnace Ltd, Sheffield, UK) was used for all experiments. Carbon black was taken in a cylindrical graphite crucible of 50 mm outer diameter and 4 mm wall thickness and the crucible was closed with a graphite lid. Graphitization heat treatment of carbon black was carried out at 1600 °C for 1 h. The heating rate was 15 °C min<sup>-1</sup> from room temperature to 1000 °C and 5 °C min<sup>-1</sup> from 1000 to 1600 °C. Raw rice husks in a quartz tube were inserted into the furnace maintained at 700 °C. The rice husks were allowed to burn at 700 °C for 3 h. The white ash (rice husk silica) obtained was taken in a plastic container and ball-milled for 4 h using alumina balls. Equal quantities of pulverized white ash and graphitized carbon black were taken in a plastic container, and dry mixing by ball-milling was carried out for 4 h. The mixture of white ash and graphitized carbon black was designated as (WA + GC).

Crystalline rice husk silica was obtained by heating the raw rice husks in the furnace. The heating schedule was 15 °C min<sup>-1</sup> from room temperature to 700 °C, holding for 3 h, followed by heating at a rate of 15 °C min<sup>-1</sup> to 1200 °C, holding for 1 h. The crystalline white ash was ground for 4 h by ball-milling. Dry mixing of a mixture containing equal

quantities of crystalline white ash and carbon black was carried out by ball-milling for 4 h. The mixture of crystalline white ash and carbon black was designated as (CWA + C).

The (WA + GC) samples were pyrolysed for 1 h at different temperatures: 1200, 1300, 1400, 1500, 1550 and 1600 °C. The heating rates were 15 °C min<sup>-1</sup> from room temperature to 1000 °C and 5 °C min<sup>-1</sup> from 1000 °C to the pyrolysis temperature. A sample of (WA + GC) and a sample of (CWA + C) were also pyrolysed at 1600 °C for 1 h by heating at a rate of 20 °C min<sup>-1</sup>.

After pyrolysis, phase analysis of samples was carried out using a Philips X-ray diffractometer (model PW 1940) with CuK<sub>α</sub> radiation. A Cam Scan DV-2 (Cambridge, UK) scanning electron microscope (SEM) was used for microstructural evaluation.

The X-ray diffraction (XRD) patterns of carbon black are shown in Fig. 1. The initial carbon black was characterized by diffuse peaks of (002) and (10). A sharpening of these peaks and the appearance of other peaks upon heat treatment could be observed. The average diameter of the crystallites and the average number of layers in the crystallite can be calculated from the width of the (10) and (002) reflections [15]. Several workers have investigated the effect of heat treatment on the properties of carbon [16–20]. The surface area and adsorption capacity of carbon diminishes upon heat treatment [18, 21].

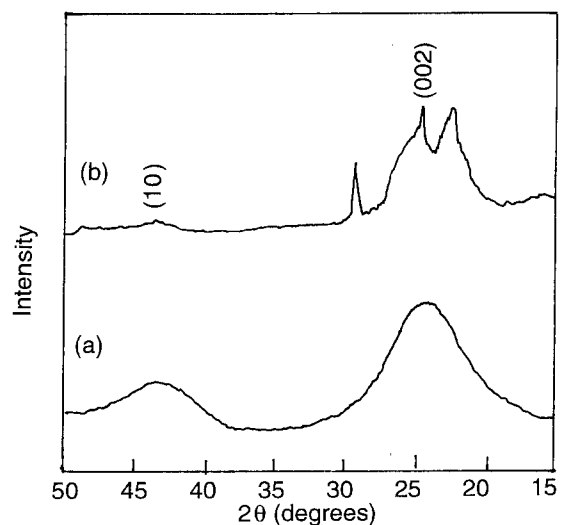


Figure 1 XRD patterns (CuK<sub>α</sub> radiation) of (a) carbon black and (b) heat-treated carbon black.

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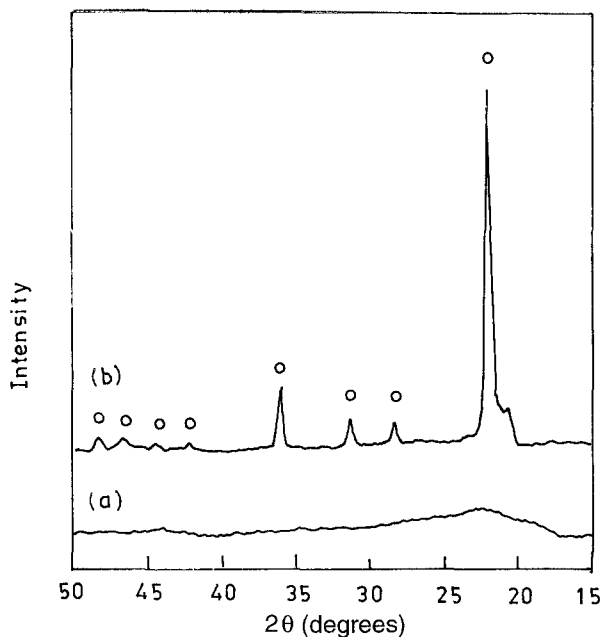


Figure 2 XRD patterns of (a) rice husk silica and (b) heat-treated rice husk silica. (○) Cristobalite.

In Fig. 2 the XRD patterns of rice husk silica and heat-treated rice husk silica are shown. The rice husk silica yielded a diffuse peak. Upon heat treatment all of the peaks of cristobalite were observed, due to the crystallization of amorphous silica. The change in morphology of rice husk silica due to heat treatment can be seen in Fig. 3. After heat treatment the size of the rice husk ash de-

creased and its surface appeared smooth (Fig. 3b and c). This could be due to potassium which causes surface melting and acceleration of the crystallization of amorphous silica to cristobalite [22].

After pyrolysis (WA + GC) samples yielded peaks of cristobalite and graphitic carbon (Fig. 4). The intensity of the cristobalite peak increased up to 1400 °C and decreased from 1500 °C with the appearance of the SiC peak. At 1550 °C some tridymite peaks were also seen. At 1600 °C SiC and graphitic carbon only were seen. Upon rapid heating ( $20\text{ °C min}^{-1}$ ) to 1600 °C the intensity of the SiC peak in (WA + GC) was decreased (Fig. 5b). The (CWA + C) sample upon rapid heating yielded an SiC peak with maximum intensity. The intensity of the graphitic carbon peak was very small (Fig. 5c).

Through SEM, formation of spherical particles was observed up to 1550 °C (Fig. 6a and b). The formation of few SiC whiskers was observed at 1500 °C. Their number increased up to 1600 °C (Fig. 7a). The rapidly heated (WA + GC) sample yielded a greater quantity of SiC whiskers (Fig. 7b). The formation of whiskers in the (CWA + C) sample was higher than that formed in the (WA + GC) samples (Fig. 7c).

During the carbothermal reduction of silica to form SiC, the SiO formation reaction is the rate-controlling step. Silica and carbon react as long as they remain in contact (Equation 1). Further SiO formation occurs by reaction of silica with CO (Equation 4). The  $\text{CO}_2$  then reacts with C and forms CO according to Equation 5.

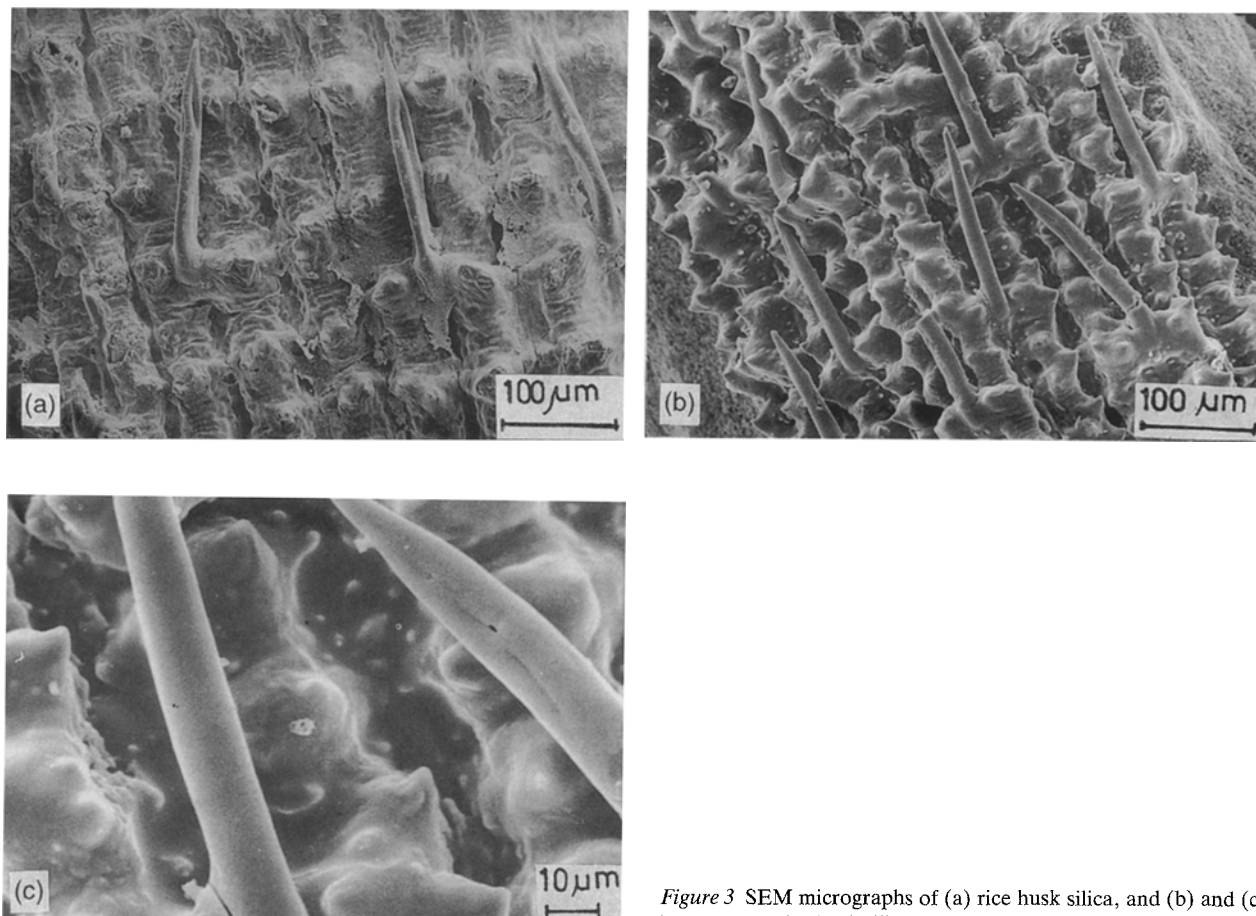


Figure 3 SEM micrographs of (a) rice husk silica, and (b) and (c) heat-treated rice husk silica.

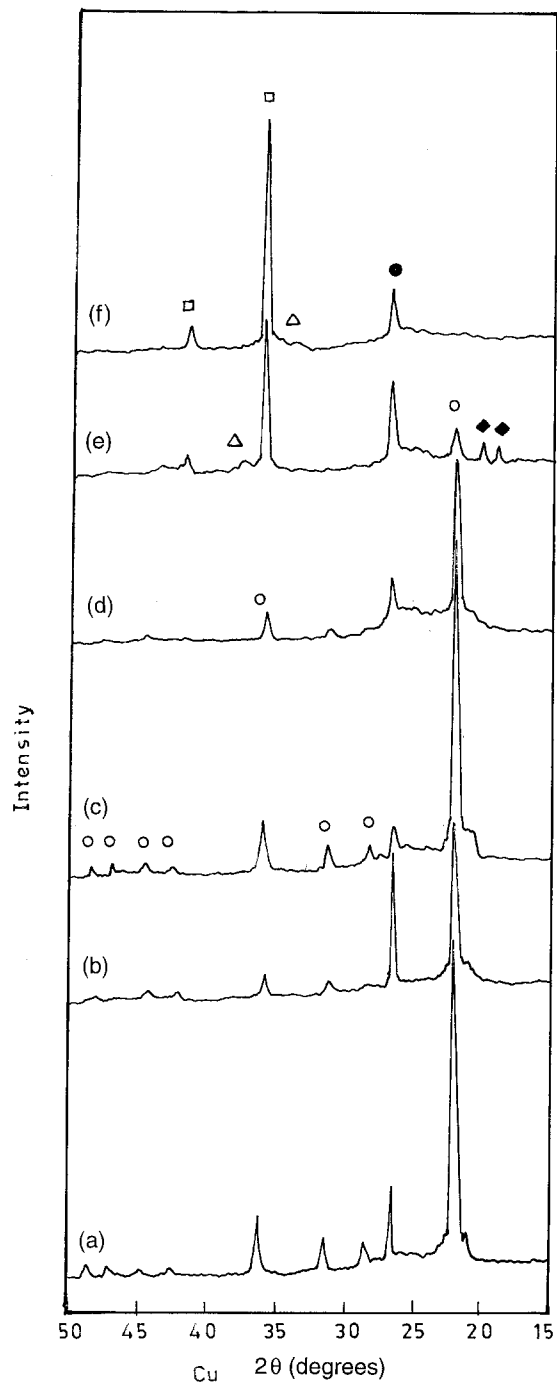
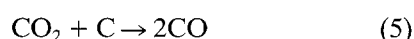
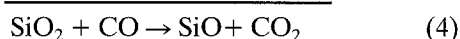
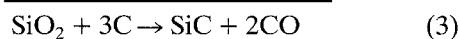
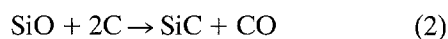
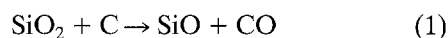


Figure 4 XRD patterns of pyrolysed (WA + GC) samples. (○) Cristobalite, (◆) tridymite, (●) graphite, (□)  $\beta$ -SiC and (△)  $\alpha$ -SiC. (a) 1200 °C, (b) 1300 °C, (c) 1400 °C, (d) 1500 °C, (e) 1550 °C and (f) 1600 °C.



The reactivities of silica and carbon depend on their degree of crystallization [13]. During rapid heating of (WA + GC) the reactivity of silica could be high because of the low degree of crystallization. Okada *et al.* [17] studied the effect of rapid heat treatment

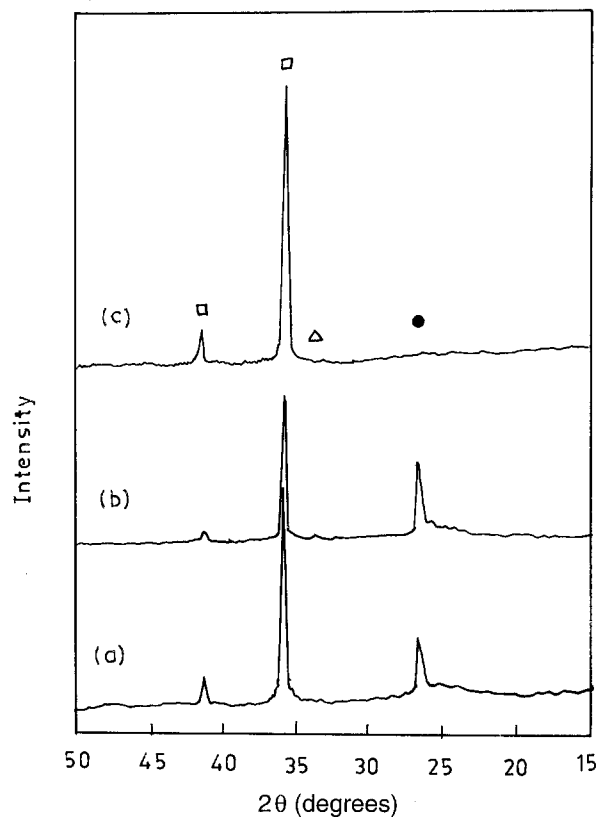


Figure 5 XRD patterns of samples after pyrolysis at 1600 °C. Heating rates: (a) (WA + GC) 15 °C min<sup>-1</sup> from room temperature to 1000 °C, and 5 °C min<sup>-1</sup> from 1000 °C to pyrolysis temperature; (b) (WA + GC) 20 °C min<sup>-1</sup> from room-temperature to 1600 °C; and (c) (CWA + C) 20 °C min<sup>-1</sup> from room temperature to 1600 °C. (●) Graphite, (□)  $\beta$ -SiC and (△)  $\alpha$ -SiC.

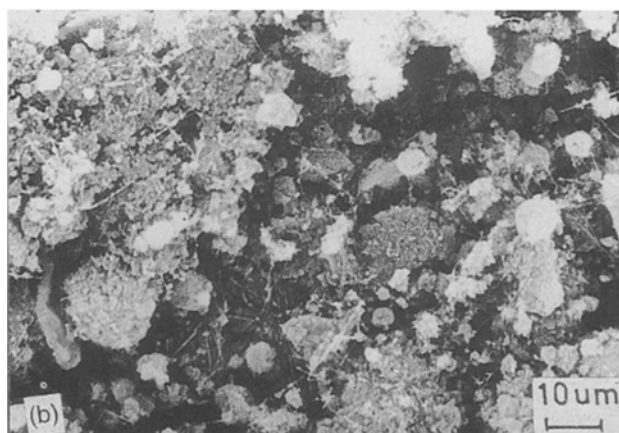
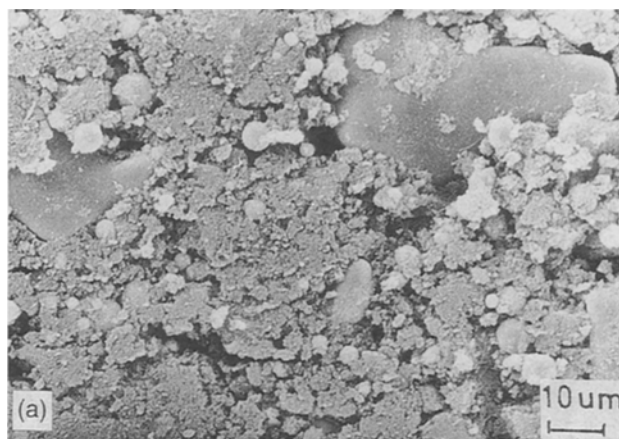


Figure 6 SEM micrographs of (WA + GC) pyrolysed at (a) 1500 °C and (b) 1550 °C.

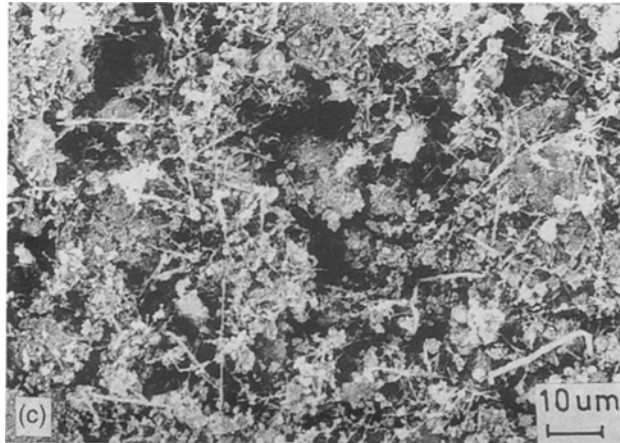
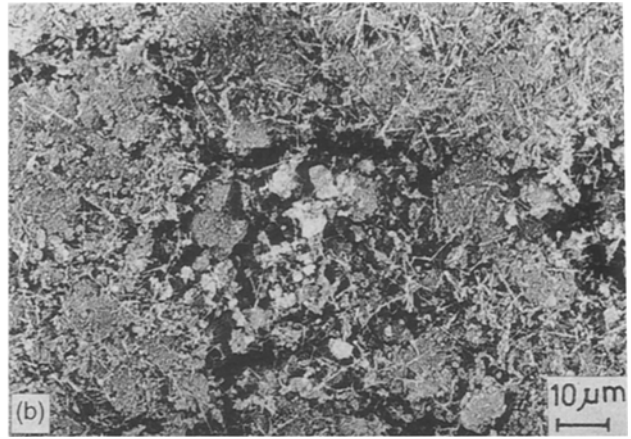
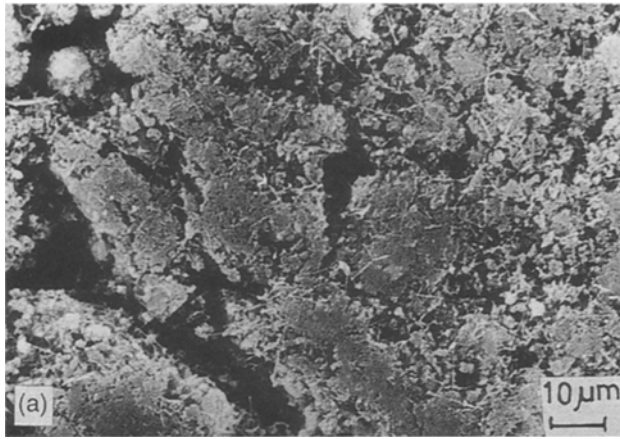


Figure 7 SEM micrographs of samples pyrolysed at 1600 °C. For heating rates, refer to Fig. 5.

on the properties of carbon. Slow heating of preheated carbon decreases the closed porosity. Rapid heating of preheated carbon increases the closed porosity. The carbon in (WA + GC) could absorb a greater quantity of SiO during slow heating than that adsorbed during rapid heating. Therefore, the intensity of the SiC peak in slowly heated (WA + GC) was higher than that in the rapidly heated sample.

As the carbon black was preheated the graphitized carbon black in (WA + GC) could form a smaller quantity of CO. In the (CWA + C) sample the amorphous carbon can form a large quantity of CO because of the low degree of crystallization due to rapid heating (Fig. 5c). Equations 4 and 5 are more favourable. The intensity of the SiC peak in (CWA + C) is therefore higher than that in (WA + GC) (Fig. 5).

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