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Formation of SiC whiskers from compacts of raw rice husks

R. V. KRISHNARAO
National Metallurgical Laboratory (CSIR), Jamshedpur-831007, India

M. M. GODKHINDI, M. CHAKRABORTY, P. G. MUKUNDA
Department of Metallurgical Engineering, Indian Institute of Technology, Kharagpur-721302, India

The formation of SiC whiskers from compacts of raw rice husks without coking and catalyst has been studied. A pyrolysis temperature of 1600°C has yielded a considerable quantity of SiC whiskers. The formation of spherical particles of silica is observed. Whisker formation occurs by reaction between $SiO_{(g)}$ and $CO_{(g)}$.

1. Introduction

A whisker is usually defined as a single crystal of very high aspect ratio, i.e. the ratio of length to diameter, with $l/d \geq 10$ and the diameter in the range 0.01–10 μm [1]. Inherent to their chemically pure nature and highly ordered structure are strengths that begin to approach interatomic bonding forces [2]. Among ceramic whiskers, SiC whisker is expected to be the reinforcing constituent in ceramic and metal matrix composites. At present the major bulk of SiC whiskers is produced by carbothermal reduction of silica [3]. Production of SiC whiskers by a process which involves the pyrolysis of silica and carbon produced from rice husks is considered to be the most economical. There are several reports on the formation of SiC whiskers from rice husks [4–12].

In the conventional process, rice husks are first coked at 700–900 °C for 1–3 h in the absence of air or in an inert atmosphere. The coked rice husks are converted to SiC by firing at high temperature (> 1500 °C) in an inert or reducing atmosphere. An investigation on the formation of SiC whiskers from rice husks has been carried out by Krishnarao [13].

Even with the selection of optimum values of processing parameters, both whiskers and particles will be formed. Separation of whiskers from the particulates can be achieved by liquid–liquid separation [14], froth flotation [15], selective flocculation liquid extraction [16] and surface chemical methods [17, 18]. In an earlier work [19] on vacuum pyrolysis, the yield of SiC whiskers from raw rice husks was shown to be higher than that from burnt husks. But raw rice husks occupy a large volume which limits their use for bulk production of SiC whiskers by vacuum pyrolysis. Raw rice husks can be compacted to decrease the volume, and the resulting compacts can be easily handled. In the present investigation, the formation of SiC whiskers from raw rice husks compacts without any precoking and catalyst was studied using a tabular furnace without any protective atmosphere.

2. Experimental procedure

The raw rice husks used in this investigation consisted of 85 wt % of organic material and 15 wt % silica and trace elements. The dry, raw rice husks were sieved to eliminate residual rice particles and mud particles. The loose, raw husks were poured into a measuring jar to determine the apparent density. The measuring jar with raw rice husks was gently tapped about 50 times to measure the tap density. The compacts of raw rice husks ($\simeq$ 40 mm diameter and $\simeq$ 20 mm length) were made by pressing the husks in a steel die at a pressure of 60 MPa. The average values of apparent density and tap density of raw rice husks were 0.092 and 0.116 g cm^{-3}, respectively. The average density of rice husk compacts was 0.5 g cm^{-3}.

The raw rice husk compacts were placed in a cylindrical graphite container of 2.5 mm wall thickness and closed with a graphite lid. The graphite container containing compacts was inserted into an alumina tube furnace (model CTF 16/75, Carbolite Furnace Ltd, Sheffield, UK), and the ends of the furnace tube were closed with an alumina felt. Pyrolysis was carried out at different temperatures (1200, 1300, 1400, 1500 and 1600 °C for 1 h). Heating rates were 15° C min^{-1} from room temperature to 1000° C and 5° C min^{-1} from 1000 °C to pyrolysis temperature.

The residual carbon in the pyrolysed samples was eliminated by burning at 700 °C for 3 h. The unreacted silica was leached out by treating the carbon eliminated sample with 40% HF acid. A Philips X-ray diffractometer (XRD) (model PW1840) with Cu*K* radiation was used for phase analysis. A Cam Scan DV-2 scanning electron microscope (SEM) was used for microstructural evaluation.

3. Results

The layers of rice husks in the pyrolysed compacts were broken and analysed by XRD and SEM. The appearance of rice husks after pyrolysis is shown in

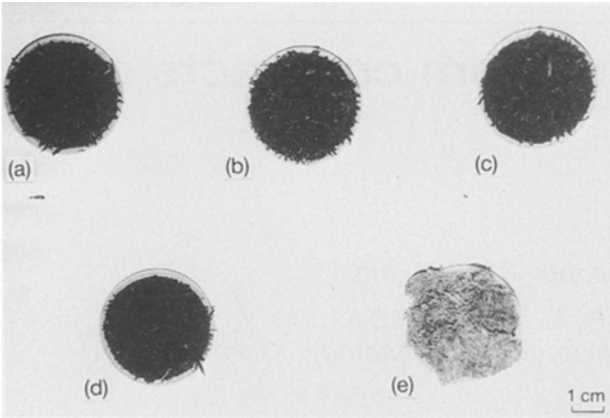

Figure 1 Appearance of rice husks after pyrolysis at different temperatures: (a) 1200, (b) 1300, (c) 1400, (d) 1500, (e) 1600 °C.

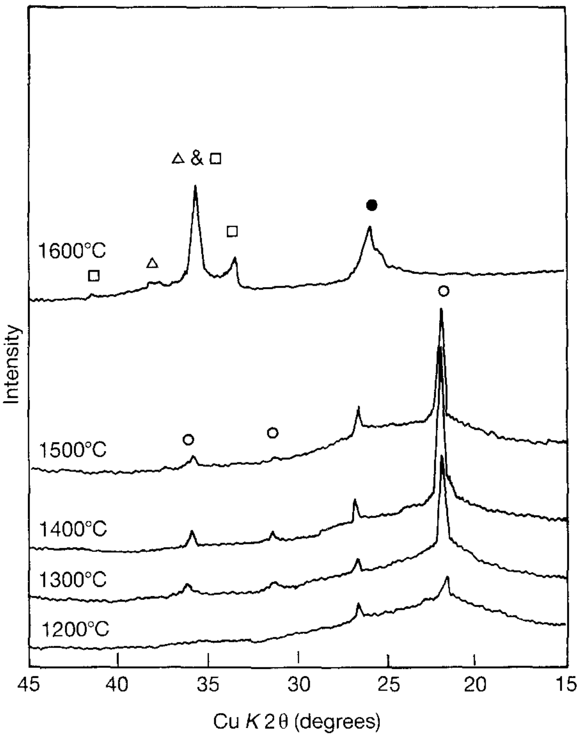

Figure 2 XRD patterns of pyrolysed rice husks. ○, cristobalite; ●, graphite; □, β-SiC; △, α-SiC.

Fig. 1. After pyrolysis up to 1400 °C, the husks appeared charred. At 1500 °C few husks were seen coated with some white deposition. At 1600 °C the rice husks were entangled in the container and could not be tipped out easily. The husks appeared bluish black with some white deposition (Fig. 1).

The XRD patterns of the pyrolysed rice husk compacts are shown in Fig. 2. At 1200 °C the peaks of partially crystalline silica and carbon (cristobalite and graphite) were observed at $2\theta = 22°$ and 26.7°, respectively. The crystallization of silica increased with pyrolysis temperature. At 1500 °C the peak height of cristobalite slightly decreased. At 1600 °C no peak of silica could be observed, whereas the peak height of graphitic carbon continuously increased up to 1600 °C. At 1600 °C, peaks corresponding only to SiC and graphitic carbon were seen. The SiC was primarily β- and some α-SiC peaks [20] were also seen.

Scanning electron micrographs of pyrolysed rice husks are shown in Figs 3–5. Spherical particles were observed on husks after pyrolysis at 1500 °C (Fig. 3). Whiskers were seen on a few isolated husks at 1500 °C. Typical SiC whiskers formed at 1600 °C are shown in Fig. 4a. Spherical balls which have been reported as appearing on the tips of whiskers grown by the vapour-liquid-solid (VLS) process [21] were not seen here (Fig. 4b). Some particles (probably the spherical particles at 1500 °C) appear to be corroded (Fig. 5a). Whiskers of some unusual shapes were seen at a few isolated sites (Fig. 5b and c). The maximum yield of SiC whiskers was observed after pyrolysis at 1600 °C (Fig. 1e).

4. Discussion

It can be seen from the XRD pattern (Fig. 2) that pyrolysis at 1600 °C results in α- and β-SiC. The reason for obtaining α-SiC at low temperature might be associated with planar defects in SiC whiskers. McMahon *et al.* [22] have shown that the regions of low defect density were 3C β-SiC and the regions of high defect density were consistent with a mixture of SiC polytypes, with the 3C and 6H polytypes being the most predominant as a result of microtwins.

The silica and carbon in rice husks start to crystallize at a temperature of 900 °C [23]. Some degree of crystallization of silica is helpful to release $SiO_{(g)}$ at a controlled rate to form SiC whiskers [11, 13, 19]. In the present work, rapid heating (at 15 °C min^{-1}) up to 1000 °C and slow heating (at 5 °C min^{-1}) above

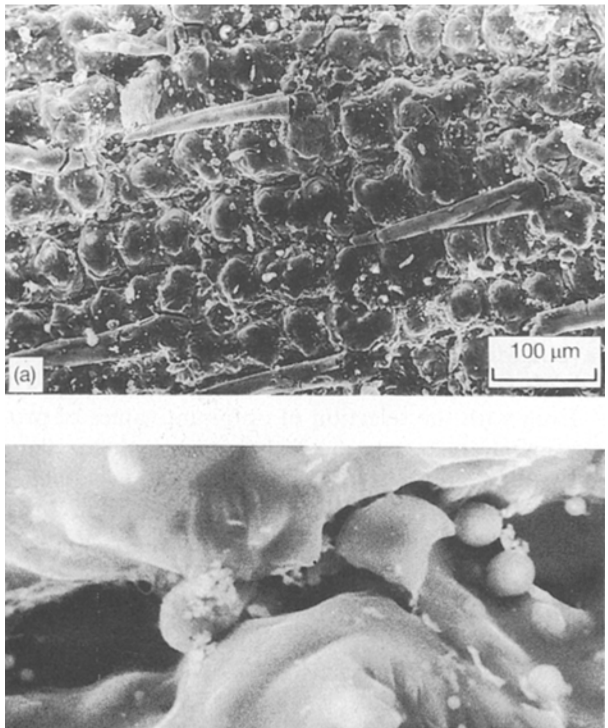

Figure 3 (a) Scanning electron micrograph of rice husks after pyrolysis at 1500 °C; (b) as in (a) at high magnification, showing spherical particles.

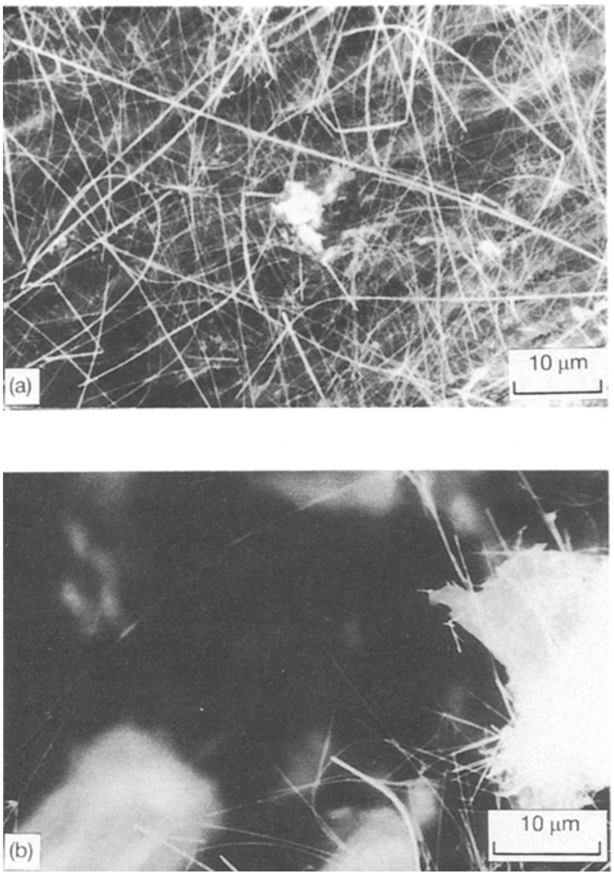

Figure 4 (a) Typical SiC whiskers formed on rice husks after pyrolysis at 1600 °C; (b) as in (a) showing the tips of whiskers.

1000 °C favoured the crystallization of silica and carbon (Fig. 2). This causes a marked decrease in the surface area, pore volume and adsorption capacity of silica [24] and carbon [25]. Due to the decrease in adsorption capacity, considerable quantities of SiO could be evolved at a favourable rate from crystalline silica and carbon in rice husks according to reaction 1 or 2, and form SiC whiskers according to reaction 3 or 4.

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (1)$$

$$SiO_{2(s)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)} \quad (2)$$

$$SiO_{(g)} + 3CO_{(g)} \rightarrow SiC_{(s)} + 2CO_{2(g)} \quad (3)$$

$$3SiO_{(g)} + CO_{(g)} \rightarrow SiC_{(s)} + 2SiO_{2(s)} \quad (4)$$

The spherical particles seen on rice husks after pyrolysis at 1500 °C (Fig. 3b) appear to be due to the crystallization of silica. Through energy-dispersive X-ray analysis (EDAX), Sharma *et al.* [8] have shown that small particles surrounding the protuberances on the outer epidermis of raw rice husks are rich in silica. Potassium in the husks causes surface melting and accelerates the crystallization of amorphous silica to cristobalite [26]. During heating above 1000 °C, the silica particles crystallize and transform to spherical particles. Further heating to higher temperatures (1600 °C) causes these spherical particles to react with $CO_{(g)}$ and form $SiO_{(g)}$ according to reaction 2. Therefore these particles appear to be corroded at 1600 °C (Fig. 5a).

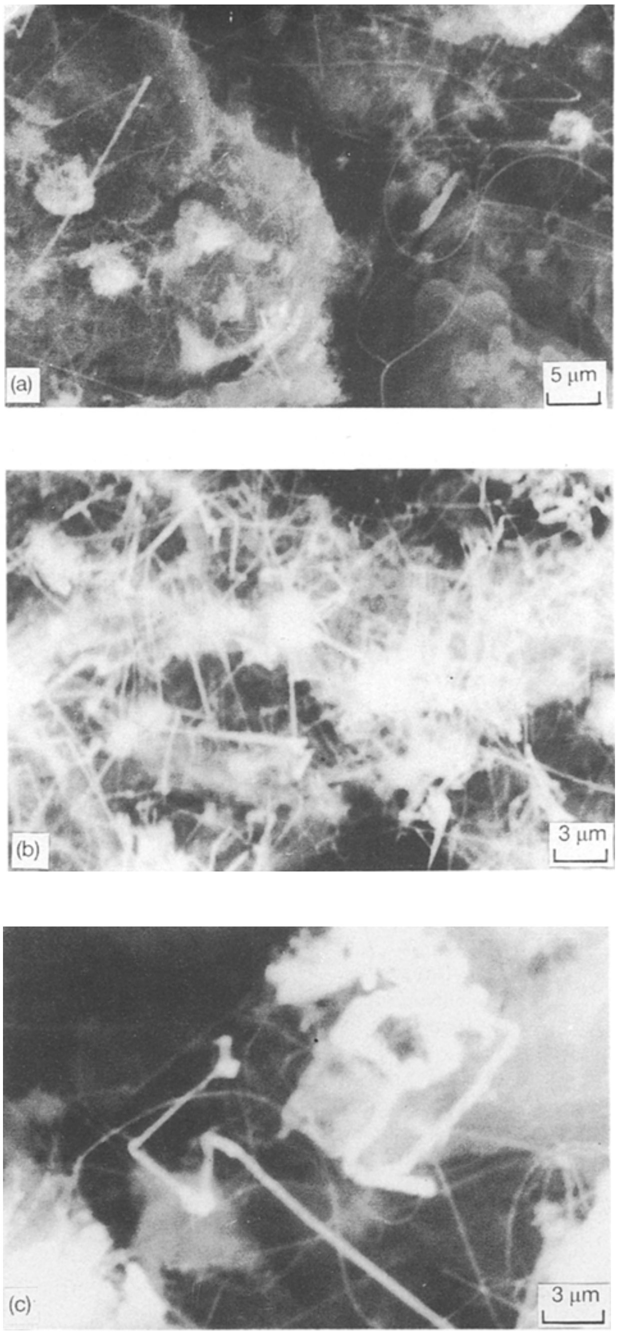

Figure 5 Rice husks after pyrolysis at 1600 °C. (a) Spherical particles appear to be corroded; (b) whiskers associated with bulbous material; (c) bead-like whisker with thick white depositions.

The absence of spherical balls on the tips of whiskers (Fig. 4b) confirms that the rice husks SiC whiskers are formed by the vapour-solid mechanism through a reaction between $SiO_{(g)}$ and $CO_{(g)}$. The morphology of SiC whiskers depends on the partial pressure of $SiO_{(g)}$ and $CO_{(g)}$. Saito *et al.* [3] showed that the SiC whiskers with thick surface deposition of SiO_2 form by reaction 4. The type of whiskers seen at 1600 °C (Fig. 5b and c) could be due to rapid deposition of $SiO_{(g)}$ at isolated sites where the SiC whiskers would have formed by reaction 4. Pickard *et al.* [1] showed that the bulbous structures and surface coatings sometimes seen on SiC whiskers contain predominantly amorphous SiO_2. In this work, although the XRD pattern did not yield any silica peak, treatment with HF acid revealed that rice husks after pyrolysis at

1600 °C contain about 15 wt % of silica. A part of this silica could be in the amorphous state.

The apparent density of loose, raw rice husks depends on the size and shape of the husks. The size and shape of raw rice husks depends on the variety of paddy (rice). The decrease in the volume occupied by raw rice husks can be noticed from the five-fold increase in density from loose to compacted rice husks. Thus the present investigation shows that compacted raw rice husks can be used for the bulk production of SiC whiskers.

5. Conclusions

1. The formation of SiC whiskers from compacts of raw rice husks without coking and catalyst has been studied.
2. A pyrolysis temperature of 1600 °C was shown to yield a considerable quantity of SiC whiskers.
3. The formation of spherical particles of silica has been observed.

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