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Conversion of Raw Rice Husks to SiC by Pyrolysis in Nitrogen Atmosphere

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Abstract

Raw rice husks without precoking were directly pyrolysed in a graphite resistance heating furnace at 1100–1400°C in nitrogen atmosphere. The furnace chamber pressure was varied from atmospheric pressure (14·7Psi or 101·3KPa) to 24Psi (165KPa). Considerable quantities of SiC whiskers were formed at 1200–1400°C. Small quantities of Si_2N_2O were also formed at 1100 and 1200°C. No Si_3N_4 was formed. The increase in chamber pressure has resulted in (i) an increase in the crystallization of silica and carbon in rice husks, (ii) decrease in the formation of SiC whiskers. Pyrolysis in nitrogen atmosphere resulted in the formation of good quality (needle type) SiC whiskers. © 1997 Elsevier Science Limited.

1 Introduction

Silicon carbide (SiC) whiskers are used to produce strong and hard-wearing composite ceramics and light metal alloys for structural uses. SiC whiskers can be produced by thermal decomposition of potentially inexpensive agricultural waste such as rice husk (RH). Lee and Cutler [1] have done a pioneering work on the formation of SiC from rice husks (RHs). Later, several reports appeared in the literature on the formation of SiC whiskers from RHs.[2–8] In the conventional process, the formation of SiC from RHs is accomplished in two steps. The RHs are coked in the absence of air at a temperature of 700–900°C and then fired at higher temperature (1500°C) in an inert or reducing atmosphere. Different RH precursors viz., raw RHs,[9,10] burnt RHs,[11–13] mixtures of RH silica and carbon black [14–17] can also be used. The yield of SiC whiskers from raw RHs was shown to be higher than that from burnt RHs.[10] As the raw RHs occupy a large volume they can be compacted and the resulting compacts can be converted to SiC.[18] Formation of SiC whiskers from raw RHs by pyrolysis in air or argon has been reported by Krishnarao *et al.*[18,19] In this work raw RHs without any precoking or catalyst were directly pyrolysed in nitrogen and the formation of SiC was studied.

2 Experimental procedure

Dry raw RHs were sieved to eliminate residual rice and clay particles. They contained 81·52 wt% of organic material and 18·48 wt% of ash (silica). A 15 g sample of raw RHs was taken in a 2·5 mm thick walled cylindrical graphite container closed with a graphite lid. An Astro furnace model 1000-3060-FP20 was used for conversion of RHs into SiC. During the pyrolysis of raw RHs in argon,[19] a negligible quantity of SiC forms first at 1050°C. Therefore, in this work the RHs were subjected to pyrolysis at 1100, 1200, 1300, and 1400°C for 0·75 h in nitrogen atmosphere. Nitrogen flow was maintained at 0·1 L min^{-1}, the temperature was maintained via a Honeywell small target radiation pyrometer, model 939A3; the heating rate employed was ≃35°C min^{-1}. Two sets of experiments were conducted. In the first set of experiments, the furnace chamber pressure was maintained at atmospheric pressure (14·7Psi or 101·3KPa). In the second set of experiments the gas outlet valve of the furnace was closed adequately to maintain the pressure inside the furnace at 24Psi (165KPa).

Through X-ray diffraction (XRD), scanning electron microscopy (SEM), optical microscopy, and chemical analysis, the products of pyrolysis were analyzed. A Philips X-ray diffractometer model PW1840 with Cu Kα radiation through Ni filter was used. An SEM (International Scientific Instruments) model ISI-100A was used to study the morphology of SiC. The excess carbon content in the pyrolysed RHs was estimated by burning in air at 700°C for 3 h. The wt% (a) of (unreacted $SiO_2 + Si_2N_2O$ formed) was determined by treating the carbon-eliminated sample with 40% HF acid. The remainder was taken to represent the SiC content. By determining the nitrogen content in the as pyrolysed RHs the wt % (b) of Si_2N_2O was calculated; nitrogen analyser Leco-TC-136 (Leco Corporation, Michigan, USA) was used. The silica content was calculated as (a)−(b). The raw RHs after pyrolysis in nitrogen at atmospheric pressure and at a pressure of 24Psi, were designated as $RRH_{(No)}$ and $RRH_{(Np)}$, respectively.

3 Results

The XRD patterns of $RRH_{(No)}$ samples are shown in Fig. 1. Crystallization of amorphous silica to form cristobalite was the dominant process at 1100°C. All the peaks of β-SiC and α-SiC appeared at and above 1200°C. At 1300 and 1400°C, graphitic carbon peaks appeared from the excess carbon in the converted RHs. At 1200°C peaks of Si_2N_2O were also observed for $RRH_{(No)}$. From the XRD patterns in Fig. 2, it is clear that the degree of crystallization of silica and carbon in $RRH_{(Np)}$ is higher than that of silica and carbon in $RRH_{(No)}$. Peaks of α-SiC and β-SiC appeared from 1200°C. It can be noticed from Figs 1 and 2 that the intensities of SiC peaks of $RRH_{(Np)}$ samples are lower than that of SiC peaks of $RRH_{(No)}$ at 1200°C. Si_2N_2O peaks were not observed in the XRD patterns of $RRH_{(Np)}$.

Through SEM few SiC whiskers were observed in $RRH_{(No)}$ pyrolysed at 1100°C (Fig. 3(a)). The surface of the RH appeared smooth. Spheroidization of small particles on the outer epidermis occurred. With an increase in pyrolysis temperature the quantity of SiC whiskers increased, their morphology also changed drastically. At 1200°C, thin and long whiskers formed (Fig. 3(b)); at a temperature of 1300°C, thick and short whiskers formed. Further increases in pyrolysis temperature has resulted in the formation of a few platelets and needle type whiskers (Fig. 3(d)). The $RRH_{(Np)}$ samples even after pyrolysis at 1100°C only appeared charred (Fig. 4(a)). The smoothing of the surface of RH and spheroidization of small particles on the outer epidermis was observed. This could be due to the high degree of crystallization of silica in RHs. At a temperature of 1200°C, considerable quantities of whiskers were observed. At

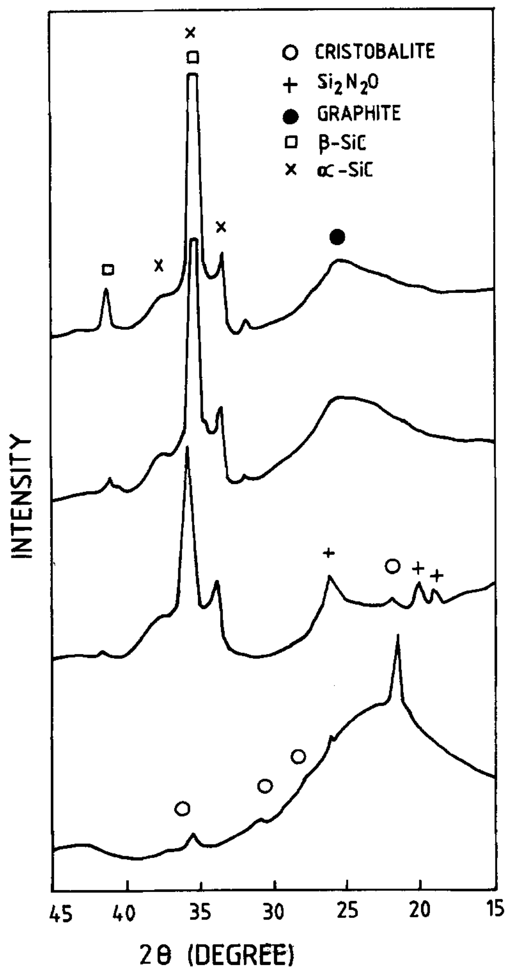

Fig. 1. XRD patterns of pyrolysed $RRH_{(No)}$ samples.

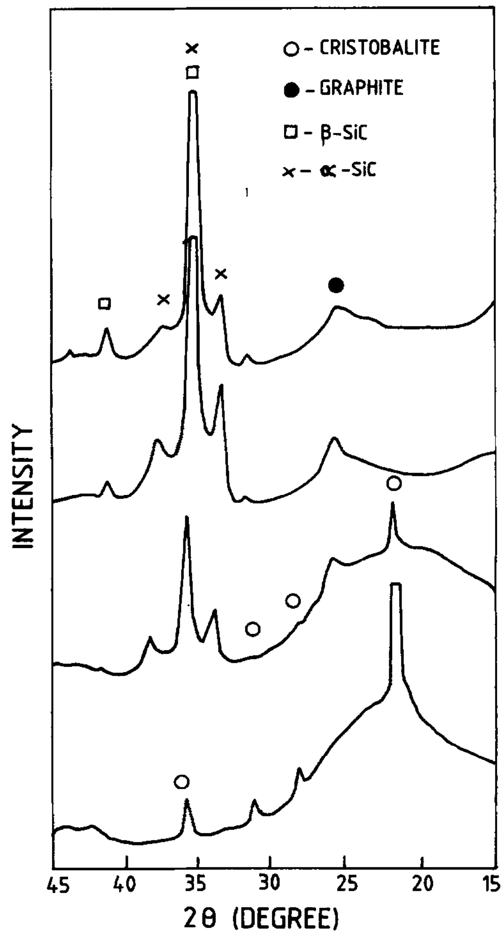

Fig. 2. XRD patterns of pyrolysed $RRH_{(Np)}$ samples.

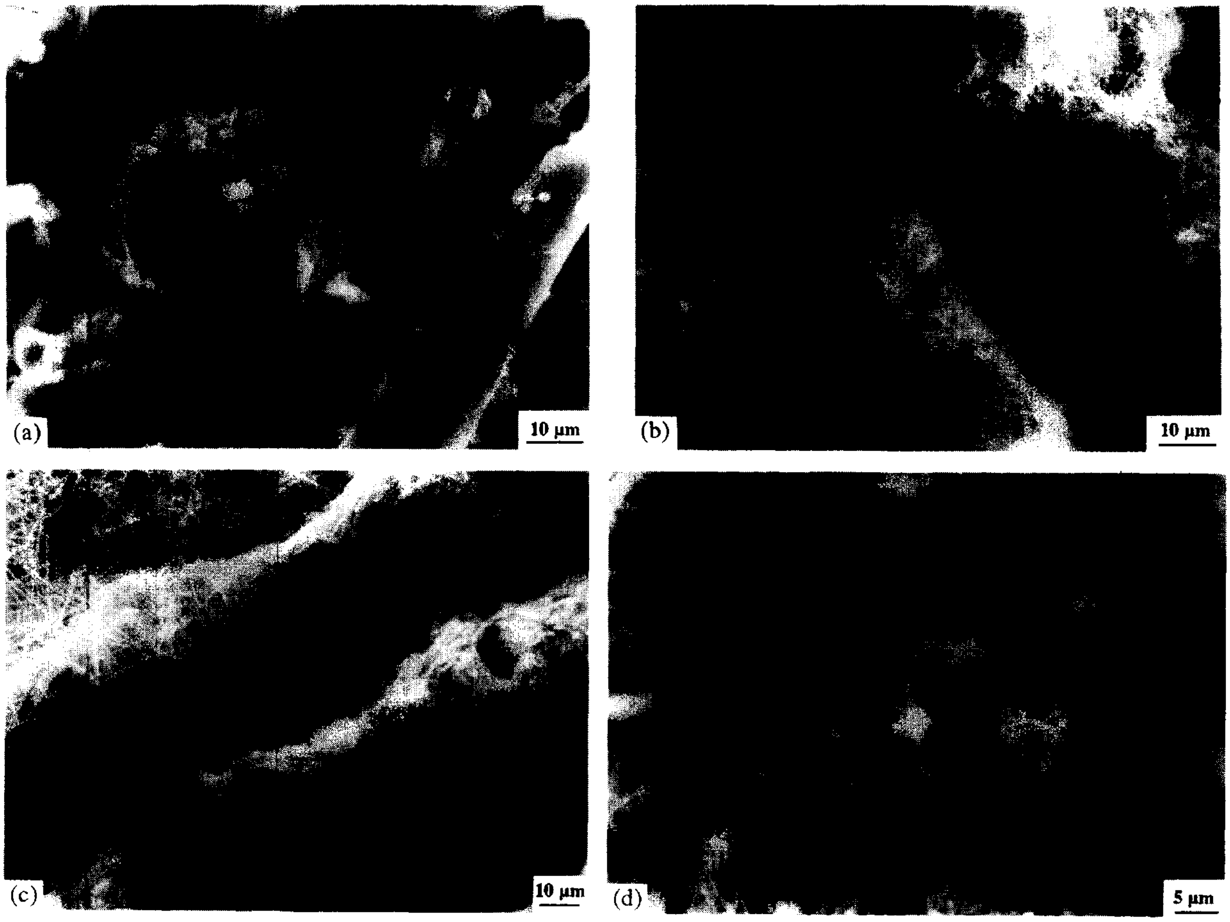

Fig. 3. Morphology of whiskers formed on $RRH_{(No)}$ at (a) 1100°C, (b) 1200°C, (c) 1300°C and (d) 1400°C.

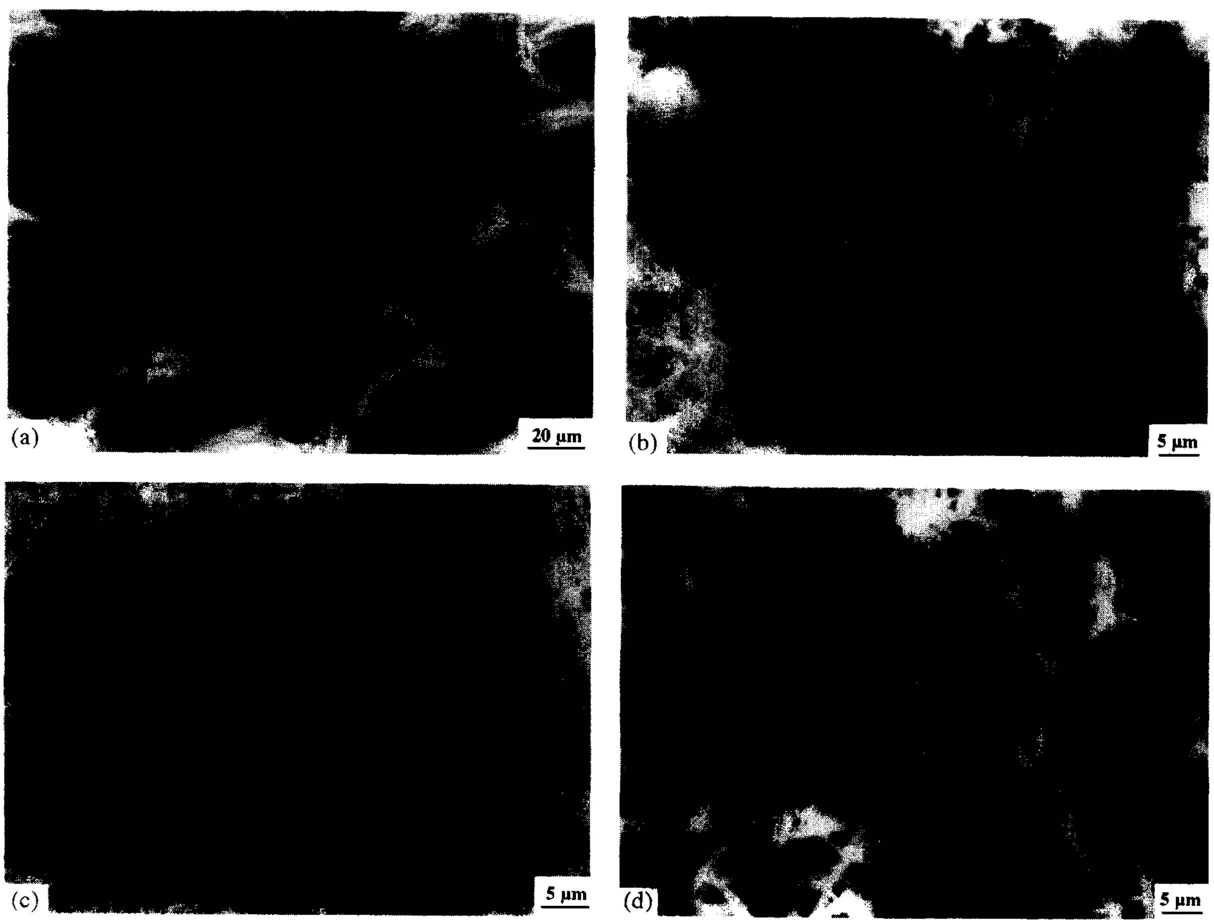

Fig. 4. Morphology of $RRH_{(Np)}$ after pyrolysis at (a) 1100°C, (b) 1200°C (c) 1300°C and (d) 1400°C.

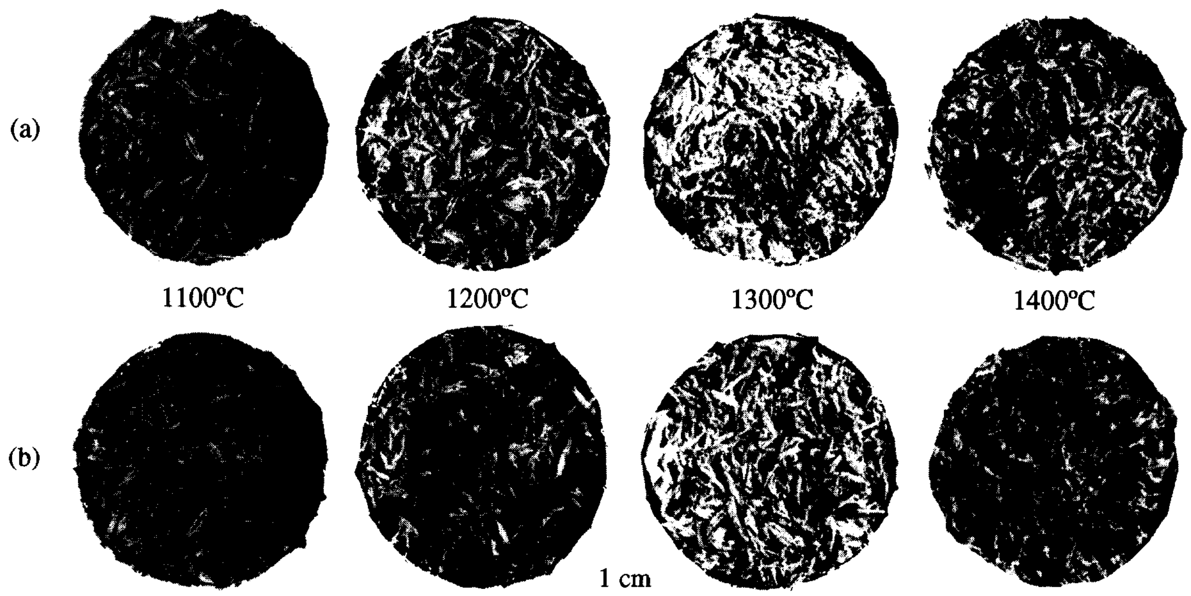

Fig. 5. Appearance of rice husks after pyrolysis at different temperatures. (a) $RRH_{(No)}$ (b) $RRH_{(Np)}$.

1300 and 1400°C, needle-type whiskers formed (Figs 3(c) and 4(d)).

At any pyrolysis temperature the quantity of whiskers formed on $RRH_{(Np)}$ samples was slightly lower than that formed on $RRH_{(No)}$. The relative abundance of whiskers on pyrolysed RHs can be correlated with the relative whitish appearance of pyrolysed RHs.[10] The appearance of pyrolysed RHs is shown in Fig. 5 . It can be observed that at any pyrolysis temperature the white deposit on $RRH_{(Np)}$ is lower than that on $RRH_{(No)}$.

The chemical analysis of as pyrolysed RHs is given in Table 1. Though there is not much difference in the quantity of excess carbon content, the unreacted silica content is high in $RRH_{(Np)}$ up to 1200°C. Above this temperature the difference in the unreacted SiO_2 content between $RRH_{(No)}$ and $RRH_{(Np)}$ is small. It is evident from XRD patterns in Figs 1 and 2, that silica (either amorphous or crystalline) is very unstable above 1200°C. Similarly the quantity of SiC formed in $RRH_{(Np)}$ is lower than that in $RRH_{(No)}$ up to 1200°C; the difference is negligible at higher temperatures. The formation of Si_2N_2O was negligible in $RRH_{(Np)}$; the highest quantity of Si_2N_2O was formed at 1200°C.

4 Discussion

During pyrolysis of RHs at higher temperatures, four processes: (i) crystallization of silica to form cristobalite, (ii) graphitization of amorphous carbon, (iii) formation of SiC whiskers, and (iv) formation of SiC particulates are proceeding simultaneously.[10] Because of the intimate contact available for carbon and silica in RH, SiC forms at a relatively low temperature. The reaction between silica and carbon to form SiC can be represented as[1]

$$SiO_2 + C \rightarrow SiO + CO \quad (1)$$

$$SiO + 2C \rightarrow SiC + CO \quad (2)$$

$$SiO_2 + 3C \rightarrow SiC + 2CO \quad (3)$$

When SiO_2 and carbon are gradually consumed by reaction (1), they no longer remain in contact. Then CO produced by reaction (1) reacts with SiO_2 to form SiO and CO_2 (reaction (4)). The CO_2 then reacts with carbon to form CO (reaction (5)).[20]

Table 1. Analysis (in wt%) of the pyrolysed RHs

Temperature° C	*RRHs*	*C*	*SiC*	*SiO_2*	*Si_2N_2O*
1100°C	(No)	49	3	41	7
	(Np)	50	2	46	2
1200°C	(No)	44	36	10	10
	(Np)	50	21	25	4
1300°C	(No)	42	50	7	1
	(Np)	44	51	4	1
1400°C	(No)	41	52	6·4	0·6
	(Np)	43	54	2·8	0·2

$$CO + SiO_2 \rightarrow SiO + CO_2 \quad (4)$$

$$CO_2 + C \rightarrow 2CO \quad (5)$$

During the reaction between silica and carbon to form SiC, SiO formation is the rate-controlling step.[1] When the furnace chamber pressure was increased to 24Psi (165KPa), all the above reactions would have been suppressed due to an increase in the (N_2+CO) pressure in the furnace. This could result in an increase in the stability of silica and carbon in RH through an increase in their crystallinity. Higher temperature is required to bring about the reaction between crystalline silica and carbon.[10] As the silica and carbon in $RRH_{(Np)}$ are more stable due to a high degree of crystallinity, at 1100 and 1200°C the quantity of SiC formed is lower in $RRH_{(Np)}$ than that formed in $RRH_{(No)}$. This is evident from the intensities of peaks of SiC (Figs 1 and 2), and from chemical analysis (Table 1). From the optical micrographs (Fig. 5), it is clear that the whisker formation on $RRH_{(Np)}$ was slightly lower than that on $RRH_{(Np)}$.

In the present work, formation of Si_3N_4 was not observed. Patel and Prasanna[21] reported that during pyrolysis of acid-treated RHs in nitrogen atmosphere, no Si_3N_4 was formed at temperatures below 1500°C. Hanna *et al.*[22] showed that conversion of coked RHs to Si_3N_4 at temperatures below 1550°C is not practical without a catalyst. The addition of iron is essential to the formation of Si_3N_4. Two reaction schemes were proposed for the formation of Si_3N_4. Komeya and Inoue.[23] suggested that gaseous SiO reacts with N_2 on the surface of the carbon particle.

$$3SiO + 2N_2 + 3C \rightarrow Si_3N_4 + 3CO \quad (6)$$

According to Zhang and Cannon,[24] seeding of the initial silica–carbon mixture with fine Si_3N_4 powder is important for increasing the rate of formation of Si_3N_4 by gas phase reaction.

$$3SiO + 3CO + 2N_2 \rightarrow Si_3N_4 + 3CO_2 \quad (7)$$

The concentration of CO is to be kept low to avoid the partial pressure of N_2 to drop and to avoid the formation of SiC.[25] In the present work since raw RHs were used, the simultaneous decomposition of the organic matter in raw RHs can cause the evolution of large quantities of CO. Thereby no Si_3N_4 was formed.

The CO reacts with SiO_2 and forms SiO (eqn (4)). Increased partial pressure of CO and SiO favours the formation of Si_2N_2O phase.[26,27] Therefore a small quantity of Si_2N_2O was formed at 1100–1300°C. Patel and Prasanna.[21] reported the formation of Si_2N_2O from acid-treated RHs at 1300–1500°C. Si_3N_4 formed slowly in the absence of a catalyst from coked RHs.[22] Furthermore Si_2N_2O was formed at the expense of Si_3N_4 and SiO_2.

Ekelund *et al.*[28] found that the carbothermic nitridation rate is not enhanced by an increase in N_2 pressure. In this work the Si_2N_2O content was decreased with an increase in reaction chamber pressure; this could be due to an increase in the crystallization of SiO_2, which inhibits the formation of SiO.

Thin, long and branched SiC whiskers are generally formed from raw RHs by pyrolysis in air[18] or argon.[19] In this work good quality (needle-type) SiC whiskers were formed; this could be due to the pyrolysis in N_2 atmosphere. Nitrogen forms HCN and acts as a carbon transfer source.[29] During VLS SiC whisker growth, with nitrogen gas flow, formed needle-type whiskers; without nitrogen gas flow, thin and branched whiskers were formed.[30] The nitrogen content in the gas has a significant influence on size and morphology: an inclusion of 10% N_2 in argon gas would produce very straight, smooth and relatively thicker whiskers than without nitrogen.[31]

The results from this investigation clearly show that needle-type SiC whiskers can be formed from raw RHs without any precoking by pyrolysis in a nitrogen atmosphere at relatively low temperatures.

5 Conclusions

1. Raw RHs without any catalyst or precoking can be directly pyrolysed in nitrogen atmosphere to form SiC whiskers.
2. The increase in reaction chamber pressure has been shown to increase the crystallinity of silica and carbon in RHs, and to decrease the formation of SiC whiskers.
3. Small quantities of Si_2N_2O were also formed at 1100 and 1200°C.
4. Pyrolysis in nitrogen atmosphere resulted in the formation of good quality (needle-type) SiC whiskers.

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