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Formation of SiC Whiskers from Raw Rice Husks in Argon Atmosphere

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Abstract: Raw rice husks without pre-coking were directly pyrolysed at different temperatures between 1050 and 1600°C in argon atmosphere. The furnace chamber pressure was varied from atmospheric pressure (14.7Psi or 101.35KPa) to 24Psi (165.47KPa). The increase in chamber pressure resulted in (i) an increase in the crystallization of silica and carbon in rice husks, (ii) an increase in the temperature of SiC formation from 1100 to 1150°C, and (iii) a decrease in the formation of SiC whiskers, and the total SiC content. Formation of considerable quantities of SiC whiskers was observed up to a temperature of 1300°C. At higher pyrolysis temperature formation of particulates through coagulative recrystallization of whiskers has been observed. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Silicon carbide (SiC) whiskers are used to produce strong and tougher composite ceramics and light metal alloys for structural uses. SiC whiskers can be produced through several routes: by reacting metallic silicon and coal tar pitch mixture,[1] through reaction of SiO_2 and CH_4,[2] by reduction of methyl trichlorosilane,[3,4] by vaporization of bulk SiC,[5,6] by reacting Si_3N_4 with carbon,[7–9] and by thermal decomposition of potentially inexpensive agricultural waste such as rice husk. Lee and Cutler have done a pioneering work on the formation of SiC from rice husks (RHs).[10] Later several reports appeared in the literature on the formation of SiC whiskers from RHs.[11–26] 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. Lee and Cutler[10] and Sharama *et al.*[15] have used the coked RHs for conversion into SiC in argon atmosphere. Raw RHs without any pre-coking can also be used.[18,19] Through extensive experiments Lee and Cutler studied the kinetics of SiC formation from RHs. Distribution of Si in RH, and the structure of SiC whiskers formed from RHs were studied by Sharama *et al.* In this work raw RHs were used to study the formation of SiC in argon atmosphere. The effect of pressure in the furnace reaction chamber on the formation of SiC whiskers, SiC particulates, crystallization of silica in RH, and on graphitization of amorphous carbon formed from RH has been studied.

2 EXPERIMENTAL PROCEDURE

Dry raw RHs were sieved to eliminate residual rice and clay particles. They contain 81.52 wt% of organic material and 18.48 wt% of ash (silica). A 15g sample of RHs was taken in a 2.5mm 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. RHs were subjected to pyrolysis at 1050, 1100, 1150, 1200, 1300, 1400, 1500, and 1600°C for 1 h in an inert atmosphere of argon. Argon flow was maintained at 0.1 litre/min. The temperature was maintained through a Honeywell small target radiation pyrometer (model 939A3). The heating rate employed was ≃40°C/min. Two sets of experiments were conducted. In the first set of experiments, the furnace chamber pressure was maintained at atmospheric pressure (14.7Psi or 101.35KPa). 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 (165.47KPa).

Through X-ray diffraction (XRD), scanning electron microscope (SEM), optical microscope, and chemical analysis, the products of pyrolysis were analysed. A Philips X-ray diffractometer (model PW1840) with CuKα 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 unreacted SiO_2 content was determined by treating the carbon eliminated sample with HF acid. The remainder was taken to represent the SiC content. The RHs after pyrolysis in argon at atmospheric pressure and at a pressure of 24Psi were designated as $RRH_{(Aro)}$ and $RRH_{(Arp)}$, respectively.

3 RESULTS

The XRD patterns of $RRH_{(Aro)}$ samples are shown in Fig. 1. Crystallization of amorphous silica to form cristobalite was the dominant process up to 1150°C. The peak of SiC appeared from 1100°C. All the peaks of β-SiC appeared at and above 1300°C. At 1500 and 1600°C, a graphitic carbon peak appeared from the excess carbon in converted RHs. From the XRD patterns in Fig. 2, it is clear that the degree of crystallization of silica and carbon in $RRH_{(Arp)}$ is higher than that of silica and carbon in $RRH_{(Aro)}$. The SiC peak started to appear from 1150°C. All the peaks of β-SiC appeared from 1300°C. One can notice from Figs 1 and 2 that the intensities of SiC peaks of $RRH_{(Arp)}$ samples are lower than that of SiC peaks of $RRH_{(Aro)}$.

Through SEM the formation of considerable quantities of SiC whiskers has been observed in the

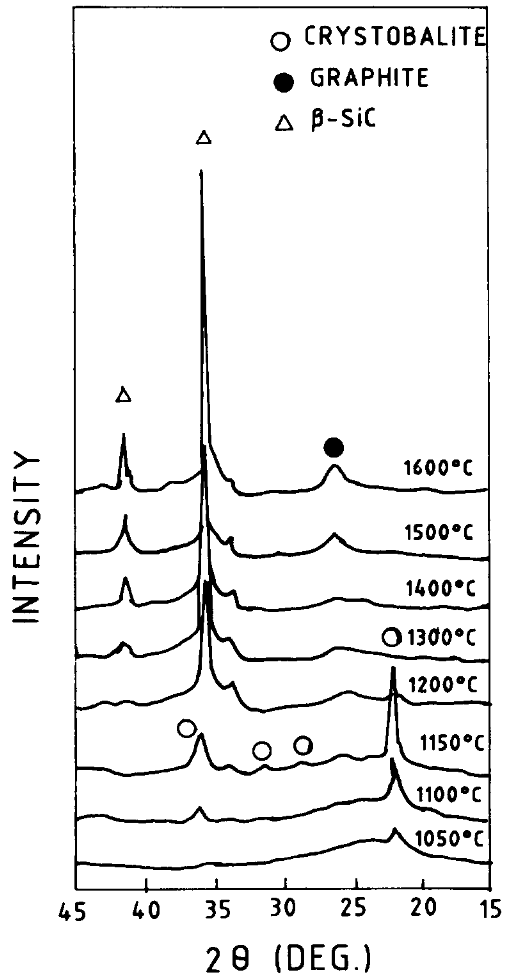

Fig. 1. XRD patterns of pyrolysed $RRH_{(Aro)}$ samples.

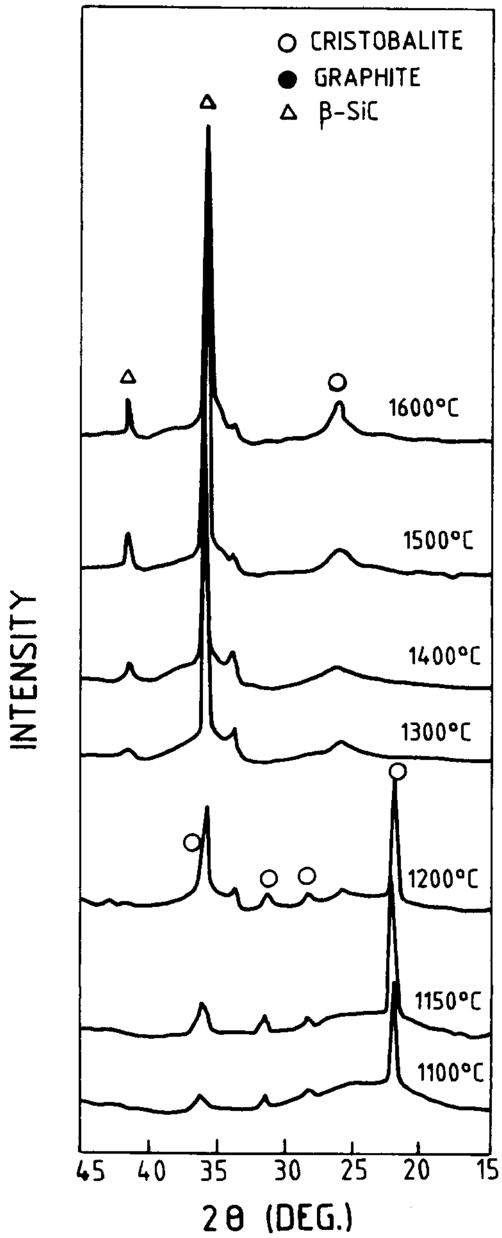

Fig. 2. XRD patterns of pyrolysed $RRH_{(Arp)}$ samples.

$RRH_{(Aro)}$ sample pyrolysed at 1100°C (Fig. 3). With increase in pyrolysis temperature the morphology of whiskers has changed drastically. At a temperature of 1300°C, short, thick whiskers have formed. Further increase in pyrolysis temperature resulted in the formation of particles of SiC through a process of coagulative recrystallization of SiC whiskers. The $RRH_{(Arp)}$ samples, even after pyrolysis at 1100°C, appeared only charred (Fig. 4(a)). The surface of RH appeared smooth and spheroidization of small particles on the outer epidermis has been observed. This could be due to the high degree of crystallization of silica in RHs. At a temperature of 1150°C, considerable quantities of whiskers were observed. Even at 1300°C the whiskers formed are long and thin (Fig. 4(b)), whereas the whiskers formed at 1300°C on $RRH_{(Aro)}$ were short and thick (Fig. 3(b)). Short, thick whiskers formed on $RRH_{(Arp)}$ at 1400°C. At higher temperatures the formation of SiC particles through coagulative recrystallization of whiskers has also been observed for $RRH_{(Arp)}$ (Fig. 4(c). But at any pyrolysis temperature the quantity of whiskers formed on $RRH_{(Arp)}$ samples was lower than that formed on $RRH_{(Aro)}$. The relative abundance of whiskers on pyrolysed RHs can be correlated with the relative whitish appearance of pyrolysed RHs.[19] After identifying whiskers through SEM, the appearance of pyrolysed RHs is shown in Fig. 5. In this optical micrograph, the appearance of

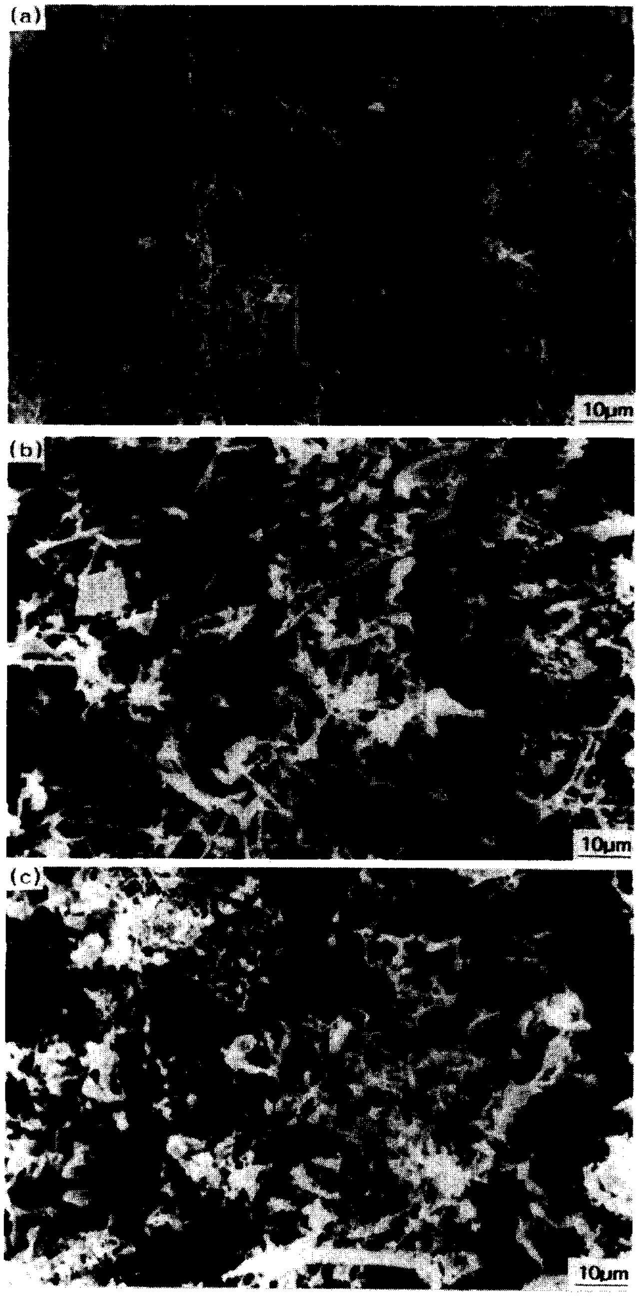

Fig. 3. Morphology of whiskers formed on $RRH_{(Aro)}$ at (a) 1100°C, (b) 1300°C and (c) 1600°C.

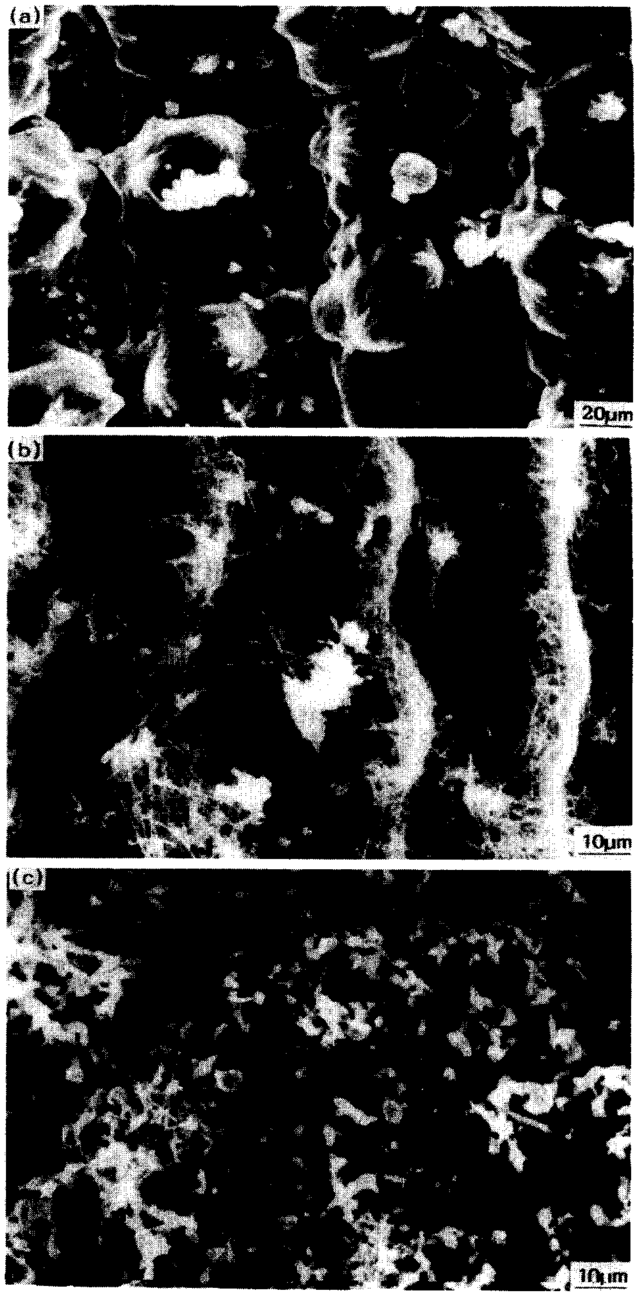

Fig. 4. Morphology of whiskers formed on $RRH_{(Arp)}$ at (a) 1100°C, (b) 1300°C and (c) 1600°C.

$RRH_{(Arp)}$ pyrolysed at 1100°C can be compared with $RRH_{(Aro)}$ pyrolysed at 1050°C. Similarly, the samples of $RRH_{(Aro)}$ pyrolysed at a particular temperature can be compared with the $RRH_{(Arp)}$ pyrolysed at the next higher temperature.

The weight percent of excess carbon, unreacted SiO_2, and the total SiC in the pyrolysed RHs is plotted in Fig. 6. Though there is not much difference in the quantity of excess carbon content, the unreacted silica content is slightly higher in $RRH_{(Arp)}$ up to 1200°C. Above this temperature the difference in the unreacted SiO_2 content between $RRH_{(Aro)}$ and $RRH_{(Arp)}$ is negligible (Fig. 6(b)). It is evident from XRD patterns in Figs 1 and 2 that silica (either amorphous or crystalline) is very much unstable at and above 1300°C. Similarly, the quantity of SiC formed in $RRH_{(Arp)}$ was lower than that in $RRH_{(Aro)}$. This difference was high up to 1200°C and negligible at higher temperatures (Fig. 6(c)).

4 DISCUSSION

During pyrolysis at higher temperature, the four following processes advance simultaneously: (i) crystallization of silica to form cristobalite, (ii) graphitization of amorphous carbon, (iii) formation of SiC whiskers, and (iv) formation of SiC particulates. 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

$$SiO_2 + C \rightarrow SiO + CO \quad (1)$$
$$SiO + 2C \rightarrow SiC + CO \quad (2)$$

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

When SiO_2 and carbon are gradually consumed by reaction (1), they no longer remain in contact.

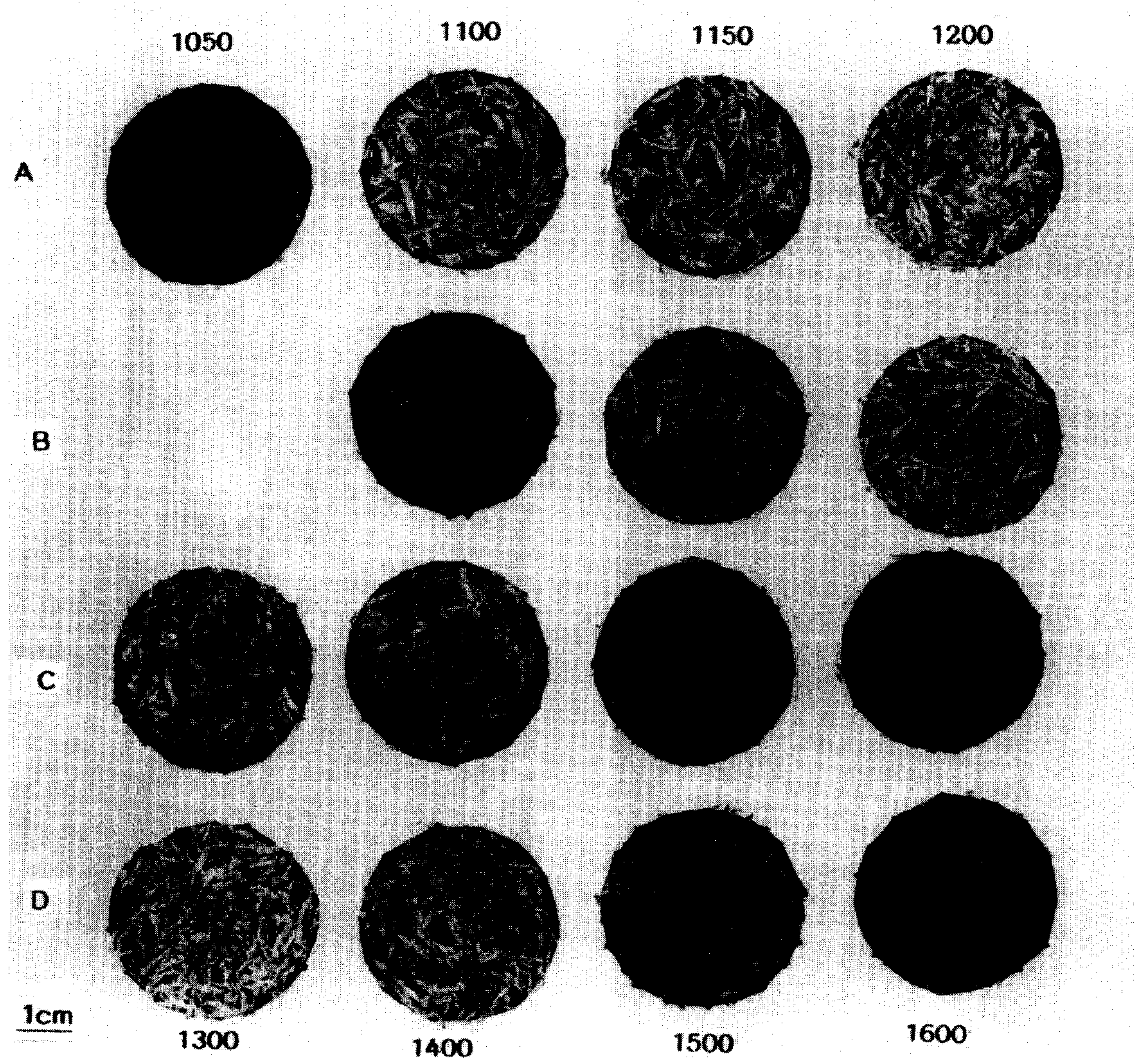

Fig. 5. Appearance of rice husks after pyrolysis at different temperatures. (A) and (C) $RRH_{(Aro)}$, (B) and (D) $RRH_{(Arp)}$.

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)).

$$CO + SiO_2 \rightarrow SiO + CO_2 \quad (4)$$
$$CO_2 + C \rightarrow 2CO \quad (5)$$

During the reaction between silica and carbon to form SiC, SiO formation is the rate controlling step.[10] When the furnace chamber pressure was increased to 24Psi (165.47KPa), all the above reactions would have been suppressed due to an increase in the (Ar + 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. A higher temperature is required to bring about the reaction between crystalline silica and carbon.[19] SiC started to form at 1150°C in $RRH_{(Arp)}$ instead of 1100°C in $RRH_{(Aro)}$. As the silica and carbon in $RRH_{(Arp)}$ samples are more stable due to high crystallinity, at any pyrolysis temperature the quantity of SiC formed is lower in $RRH_{(Arp)}$ than that formed in $RRH_{(Aro)}$. This is evident from the intensities of peaks of SiC (Figs 1 and 2), and from chemical analysis (Fig. 6(c)). In the optical micrographs (Fig. 5), the $RRH_{(Arp)}$ sample pyrolysed at a particular temperature can be compared with the $RRH_{(Arp)}$ sample pyrolysed at the next higher temperature. It is clear from Fig. 5 that the temperature of formation of SiC whiskers and particulates has been raised by 50°C due to the increase in the pressure in the reaction chamber to 24Psi (165.47KPa). At higher temperatures, due to rapid deposition of SiO and high rate of formation of SiC, the SiC whiskers formed at lower temperatures get converted into particulates through a process of coagulative recrystallization. Formation of particulates through coagulative recrystallization of SiC whiskers was observed in both $RRH_{(Aro)}$ and $RRH_{(Arp)}$ samples (Figs 3 and 4).

The results from this investigation clearly show that SiC whiskers can be formed from raw RHs, without any pre-coking, by pyrolysis in argon atmosphere at the relatively low temperature of 1050°C.

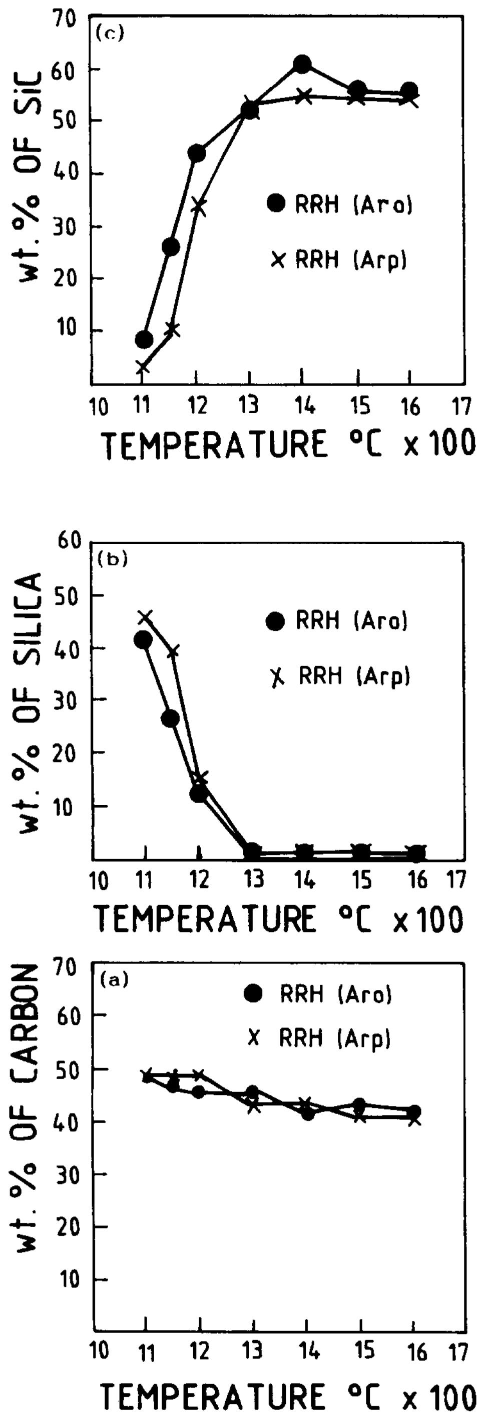

Fig. 6. Analysis of reaction product: (a) excess carbon, (b) unreacted SiO_2, and (c) total SiC.

5 CONCLUSIONS

The following conclusions can be drawn from the experiments carried out in this paper.

1. Raw RHs without any pre-coking can be directly pyrolysed in argon atmosphere to form SiC whiskers.
2. The increase in reaction chamber pressure has been shown to cause an increase in the temperature of formation of SiC through an increase in the crystallinity of silica and carbon in RHs, and to decrease the formation of SiC whiskers and the total SiC content.
3. At higher pyrolysis temperatures (1500 and 1600°C), formation of particulates through coagulative recrystallization of whiskers has been observed.

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