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Effect of Acid Treatment on the Formation of SiC Whiskers from Raw Rice Husks

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Abstract

Raw rice husks have been treated by boiling for 1 h in 5 N hydrochloric acid. The washed and dried acid-treated raw rice husks (TRRH) and untreated raw rice husks (RRH) were directly pyrolysed (without precoking) in argon atmosphere at different temperatures between 1050 and 1600°C. Silica obtained from TRRH has a lower level of impurities than that obtained from RRH. Acid treatment has been found to decrease the degree of crystallization of silica and carbon in rice husks. The whisker formation has been decreased in TRRH. As the carbon loss due to the formation of CO was high, the SiC content in the pyrolysed TRRH was higher than that in pyrolysed RRH.

1 Introduction

Silicon carbide (SiC) whiskers, useful in reinforcing light metal alloys and ceramics, are produced by thermal decomposition of rice husks (RHs). Lee and Cutler[1] performed the pioneering work on the formation of SiC from RHs. Later several reports appeared in the literature.[2–16]

A rice husk can be regarded as consisting of SiO_2 embedded in a matrix whose approximate average composition is 51 wt% carbon, 7 wt% hydrogen and 42 wt% oxygen.[6] Rice husks produce a high ash content, varying from 13 to 29 wt% depending on the variety, climate and geographical location. The ash is largely composed of silica (87–97%) with small amounts of alkalis and trace elements.[17] When RHs are converted, these impurities will enter into SiC. In this investigation the raw RHs were treated with hydrochloric acid to decrease the level of impurities. The acid-treated RHs (TRRH) and untreated raw RHs (RRH) were directly pyrolysed without precoking and the formation of SiC was studied.

2 Experimental Procedure

Dry raw RHs, which had been sieved to eliminate residual rice and clay particles, were used in this work. They contain 81·52 wt% of organic material and 18·48 wt% of ash (silica). The RRH were fed into 5 N hydrochloric acid and boiled for 1 h. The treated RHs were thoroughly washed with water and dried in an oven at 90°C. The acid-treated RHs (TRRH) were found to contain 74·64 wt% organic material and 25·36 wt% silica. The silica obtained by burning of organic material from RRH and TRRH was analysed by a Varian model AA-5 atomic absorption spectroscope (AAS).

A 15g sample of RHs was taken in a 2·5 mm thick walled cylindrical graphite container closed with a graphite lid. An ASTRO high temperature furnace, model 1000-3060-FP20 equipped with a Honeywell small target radiation pyrometer, model 939A3 was used for pyrolysis experiments. The RRH and TRRH were subjected to pyrolysis at different temperatures from 1050 to 1600°C for 1 h in an inert atmosphere of Ar at atmospheric pressure. Heating rate employed was ≈ 40°C min^{-1}. Argon flow was maintained at 0·1 l min^{-1}.

The product of pyrolysis was analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and chemical analysis. A Philips X-ray diffractometer, model PW1840 with Cu *K* radiation through Ni filter, was used. A scanning electron microscope from International Scientific Instruments, model ISI-100A, was used to study the morphology of SiC. The excess carbon content in the pyrolysed RH was determined by burning at 700°C for 3 h. The unreacted SiO_2 content was estimated by treating the carbon-eliminated sample with HF.

3 Results

SEM micrographs of the outer epidermis of RRH and TRRH are shown in Fig. 1. The part of the

RHs leached out due to acid treatment can be seen in Fig. 1(b). The XRD pattern of TRRH was not much different from that of RRH (Fig. 2(a)).

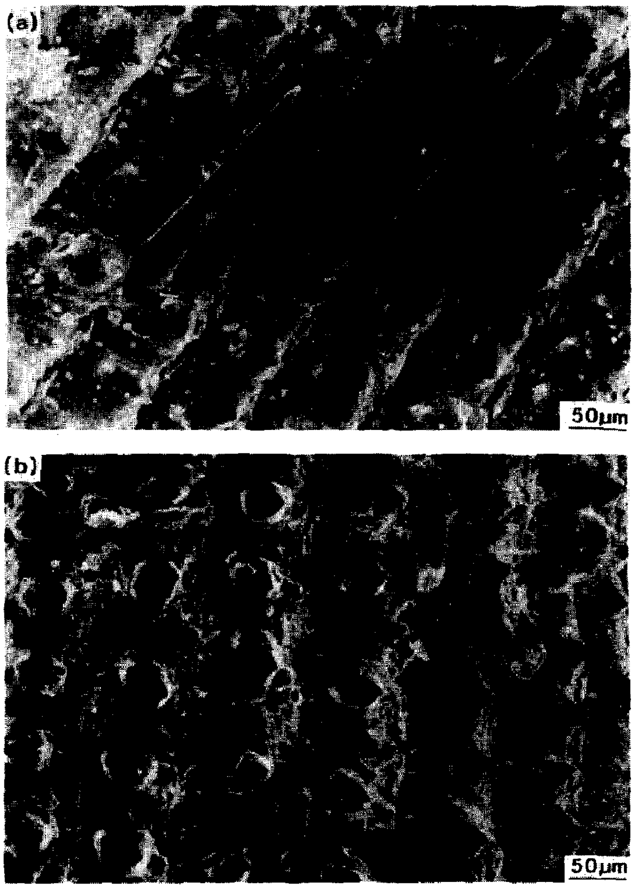

Fig. 1. SEM micrographs of outer epidermis of (a) RRH and (b) TRRH.

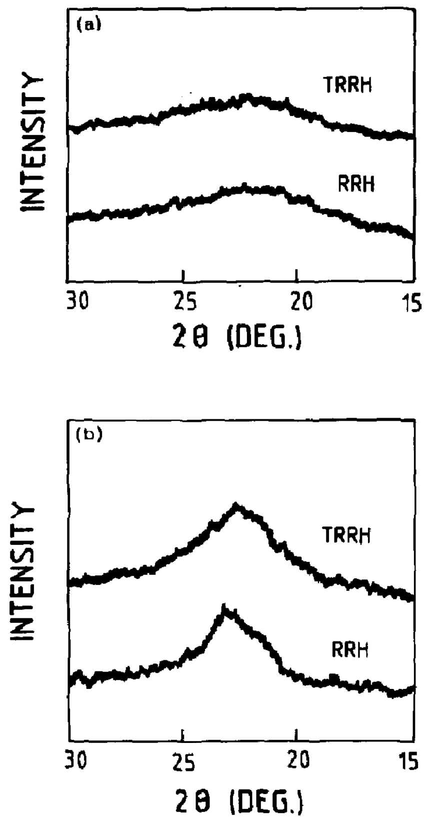

Fig. 2. XRD patterns of (a) RRH and TRRH, (b) silica from RHs.

Similarly, the XRD pattern of silica obtained from TRRH did not show any difference from

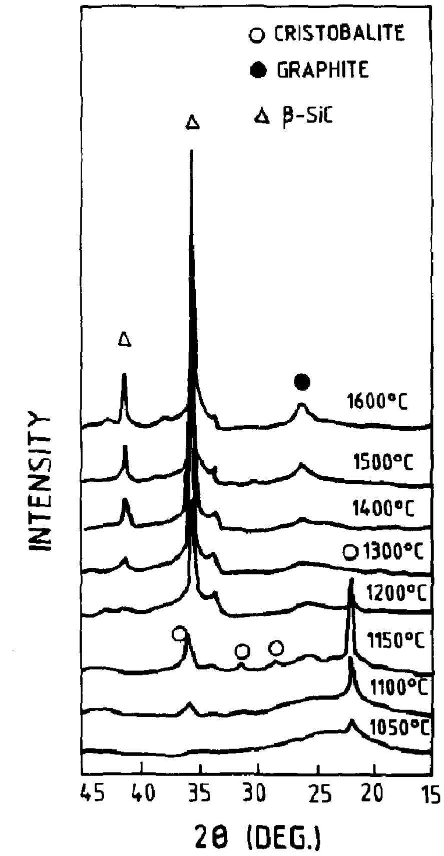

Fig. 3. XRD patterns of pyrolysed RRH samples.

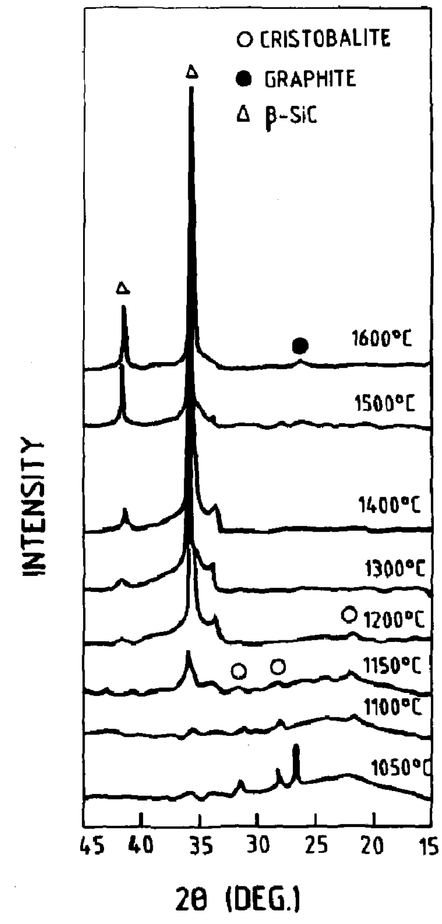

Fig. 4. XRD patterns of pyrolysed TRRH samples.

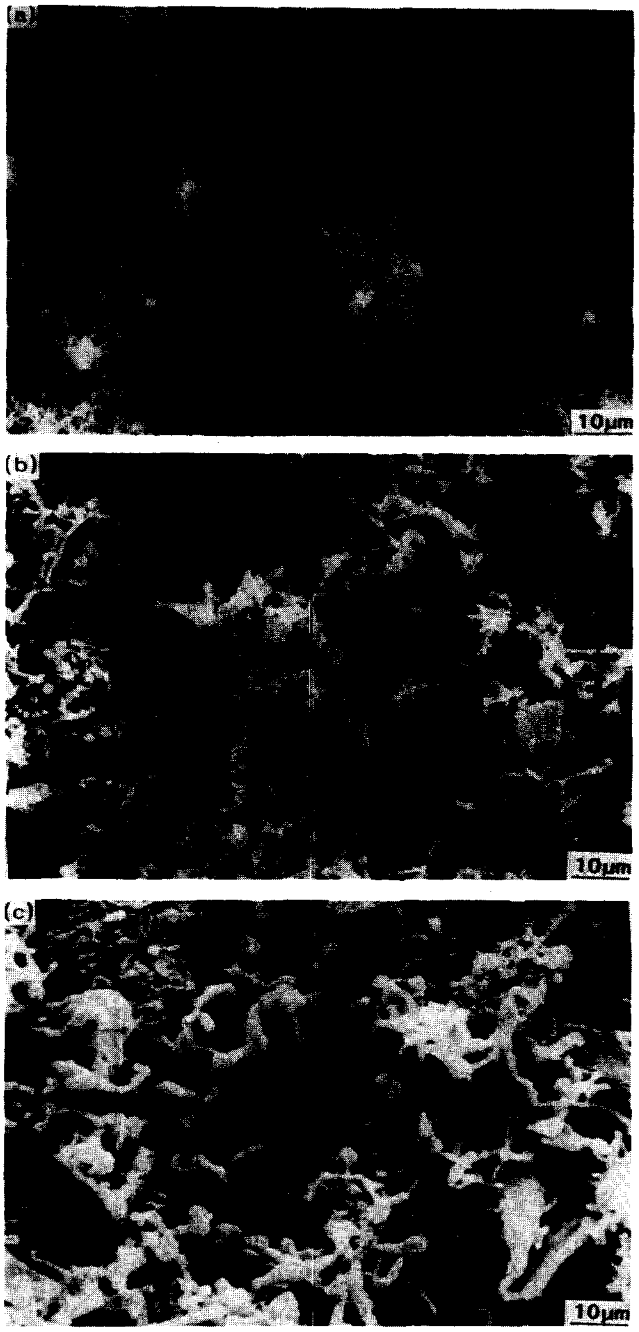

Fig. 5. SEM micrographs of RRH after pyrolysis at (a) 1200°C, (b) 1300°C and (c) 1600°C.

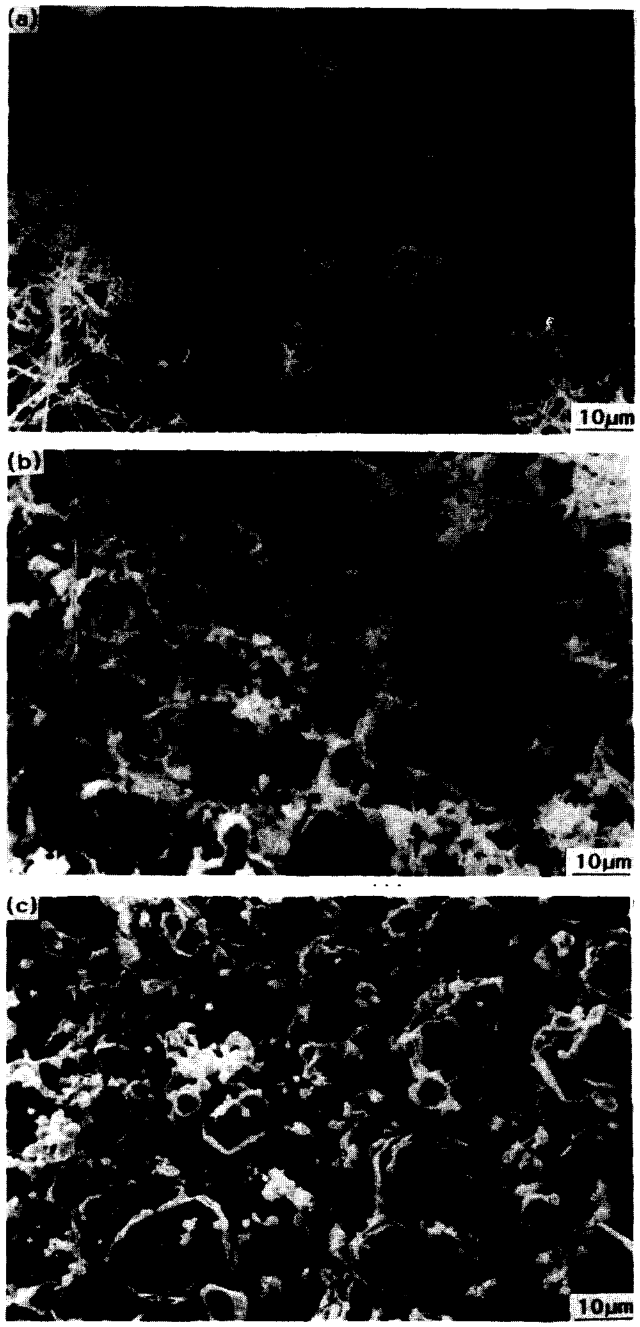

Fig. 6. SEM micrographs of TRRH after pyrolysis at (a) 1200°C, (b) 1500°C and (c) 1600°C.

that of silica obtained from RRH (Fig. 2(b)). The silica from TRRH appeared bright white. An AAS analysis revealed that the level of impurities in RH silica decreased considerably after acid treatment (Table 1).

Table 1. Impurity analysis (in wt%) of RH silica

Element	*Silica from*	
	RRH	*TRRH*
Al	0·50	0·25
Fe	0·60	0·30
Ca	0·44	0·33
Mg	0·41	0·13
Mn	0·069	0·0054
K	1·51	0·054
Na	0·064	0·063

The XRD patterns of pyrolysed RRH samples are shown in Fig. 3. The crystallization of amorphous silica to form cristobalite was the dominant process up to 1150°C. All the peaks of SiC appeared at and above 1300°C. At higher temperatures (1500 and 1600°C), the degree of graphitization of amorphous carbon was rapid. From Fig. 4 it is clear that the degree of crystallization of silica and carbon is negligible in TRRH samples.

Through SEM, the formation of considerable quantities of SiC whiskers has been observed in RRH samples pyrolysed up to 1400°C (Fig. 5). As the temperature of pyrolysis increased, thick and short whiskers formed (Fig. 5(b)). At higher temperatures, the whiskers formed at lower temperatures were converted into particulates

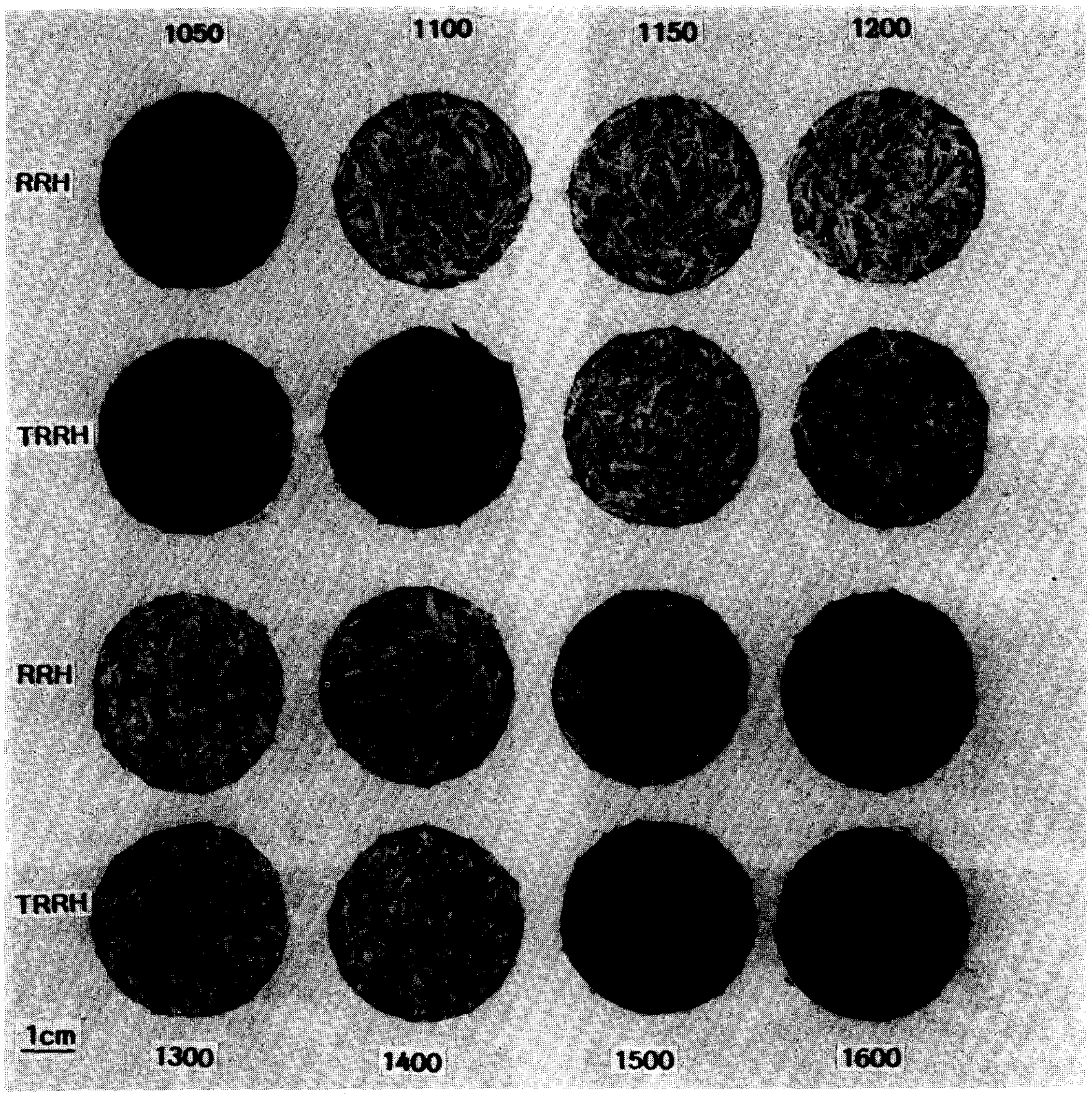

Fig. 7. Optical photograph of rice husks pyrolysed at different temperatures.

(Fig. 5(c)). Similarly in TRRH samples with increase in pyrolysis temperatures, formation of particulates has been observed (Fig. 6). However, the formation of SiC whiskers in TRRH samples was found to be lower than that in RRH samples. After identifying whiskers through SEM, the relative whitish appearance of pyrolysed RHs can be compared for a rough estimation of the percentage of SiC whiskers formed.[11] The appearance of RHs after pyrolysis is shown in Fig. 7. From this optical micrograph one can observe that the whitish deposition on TRRH at any pyrolysis temperature is lower than that on RRH.

The weight % of excess carbon, unreacted SiO_2, and the total SiC in the pyrolysed RHs is shown plotted in Fig. 8. The excess carbon content is very low in TRRH. The unreacted silica was slightly higher in TRRH up to 1150°C. The SiC content in TRRH is slightly low up to 1150°C and much higher above 1200°C. After acid treatment of RHs, as the part of organic matter was leached out, the silica content in TRRH has increased from 18·48 to 25·36%. Assuming that all the SiO_2 in the RHs becomes converted to SiC according to reaction $SiO_2 + 3C + C_{(excess)} \rightarrow SiC + 2CO + C_{(excess)}$, the theoretical values of SiC content and excess carbon in the product of pyrolysis can be calculated.[13] The theoretical values of SiC content in the converted RRH and TRRH are 14·88 and 22·14 wt%, respectively.

Similarly, the theoretical values of excess carbon are 81·52 wt% for RRH, and 77·86 wt% for TRRH. During the carbothermal reduction of silica to form SiC, the carbon loss as CO is generally higher than the theoretical value.[13] From Fig. 8 it is clear that the carbon loss as CO in TRRH is much higher than that in RRH.

4 Discussion

During pyrolysis of RHs at higher temperatures, four processes, i.e. graphitization of carbon, crystallization of amorphous silica, formation of SiC

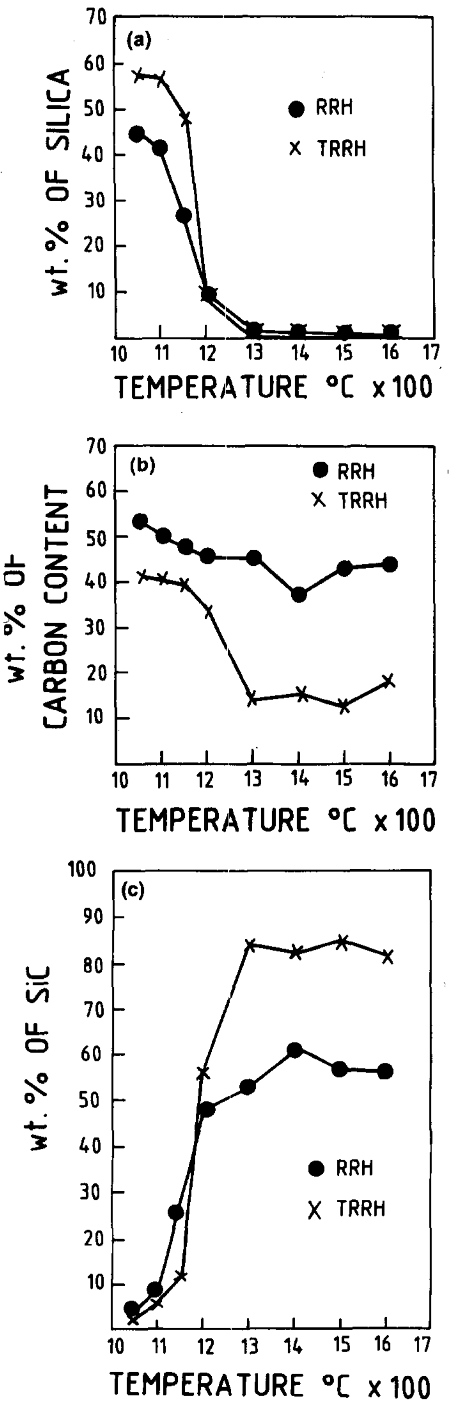

Fig. 8. Plots of (a) residual carbon, (b) unreacted silica and (c) SiC content, all versus pyrolysis temperature.

particles and formation of whiskers, are simultaneously advancing.[11] When RRHs are treated with acid, the cellulose which forms the main body of raw RHs is reduced and the carbohydrate is blackened due to the removal of oxygen. The proteins in the RHs are decomposed into amino acids, and the cellulose of large molecular weight is leached out as smaller molecular weight compounds.[18] The impurities in the RH are substantially removed (Table 1). This results in higher purity of RHs with a porous structure. Potassium (K) in the RH causes surface melting and accelerates the crystallization of amorphous silica to form cristobalite.[19] Due to the porous structure and low level of impurities like K, the crystallization of silica and carbon in TRRH was negligible (Fig. 4).

It is well known that SiC forms at relatively low temperature because of the intimate contact available for carbon and silica in RHs. The reaction between silica and carbon to form SiC can be represented as

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

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

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

Since the TRRH is porous, the intimacy between silica and carbon is disturbed. The quantity of SiC formed in TRRH up to 1150°C was slightly low (Fig. 8). 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)).

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

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

Because of porous structure and low degree of crystallization, carbon in TRRH can form a larger quantity of CO. This is evident from the very low quantity of residual carbon in TRRH (Fig. 8). The SiO formed by reaction (1) or (4) can be adsorbed by carbon and form isometric SiC particles. The carbon in TRRH could adsorb a larger quantity of SiO than the carbon in RRH. As the quantity of SiO that could be evolved from TRRH is low, the possibility of whisker formation is low (Fig. 7).

At higher temperatures, due to the rapid deposition of SiO and the high rate of formation of SiC, the whiskers formed at lower temperatures are converted into particulates through a process of coagulative recrystallization. Formation of particulates through coagulative recrystallization of SiC whiskers is observed in both RRH and TRRH (Figs 5 and 6).

The results from this investigation clearly show that under similar conditions of pyrolysis the formation of SiC whiskers is low in TRRH.

5 Conclusions

(i) Relatively pure and bright white silica is formed from acid-treated raw rice husks.
(ii) The degree of crystallization of silica and carbon in pyrolysed TRRH is decreased.
(iii) The formation of SiC whiskers in TRRH is lower than in RRH.

(iv) At pyrolysis temperatures higher than 1300°C the formation of SiC particulates is the dominant process.
(v) Residual carbon content in TRRH is lower than that in RRH.

Acknowledgements

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