Effect of Cobalt Chloride Treatment on the Formation of SiC from Burnt Rice Husks

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Abstract

The effect of cobalt chloride ($CoCl_2$) treatment on the formation of SiC from burnt rice husks has been studied over a temperature range of 1200 to 1600°C. It has been shown that $CoCl_2$ decreases the crystallization of carbon and silica in rice husk and accelerates the formation of SiC. Formation of SiC whiskers from $CoCl_2$ treated burnt rice husks has been found to be negligible. The untreated burnt rice husks have yielded a maximum quantity of SiC whiskers at 1600°C. Slow heating (at 5 C/min) to 1600°C has decreased the reactivity of silica and carbon in the rice husk by increasing their degree of crystallization. No α-SiC formed from the $CoCl_2$ treated burnt rice husks.

Der Effekt der Kobaltchloridbehandlung ($CoCl_2$) auf die Bildung von SiC aus gebrannten Reishülsen wurde für einen Temperaturbereich von 1200 bis 1600°C untersucht. Es konnte gezeigt weden, daß $CoCl_2$ die Kristallisation von Kohlenstoff und Silikat in den Reishülsen vermindert und die Bildung von SiC beschleunigt. Die Bildung von SiC-Whiskern in $CoCl_2$ behandelten, gebrannten Reishülsen kann vernachlässigt werden. Der Anteil an Whiskern in den unbehandelten, gebrannten Reishülsen ist bei 1600°C am höchsten. Ein langsames Erhitzen (5°C/min) verminderte die Reaktivität von Silikat und Kohlenstoff in den Reishülsen durch die Erhöhung ihres Kristallisationsgrades. In den $CoCl_2$ behandelten, gebrannten Reishülsen bildete sich kein α-SiC.

On a étudié l'effet du chlorure de cobalt ($CoCl_2$) sur la formation de SiC à partir d'écorce de riz calcinée, entre 1200 et 1600°C. On montre que $CoCl_2$ diminue le taux de cristalisation du carbone et la silice dans l'écorce de riz, et accélère la formation de SiC. La formation de whiskers de SiC dans cette écorce calcinée traitée au $CoCl_2$ est négligeable. Pour l'ecorce de riz calcinée non traitée, la maximum de formation de whiskers de SiC est atteint à 1600°C. Une montée en température lente (5°C/min) jusqu'à 1600°C diminue la réactivité de la silice et de carbone dans l'écorce de riz en augmentant leur taux de cristallisation. Il n'y a pas formation de SiC-α dans l'écorce de riz calcinée traitée avec $CoCl_2$.

1 Introduction

Silicon carbide whiskers useful in reinforcing metal matrix and ceramic matrix composites are produced from rice husks (RHs). Lee & Cutler[1] have done pioneering work on the formation of SiC whiskers from RHs. Later several reports[2–10] have appeared in the literature. Formation of SiC whiskers from raw RHs,[11] burnt RHs,[12] pulverized RH ashes,[13] and crystallized RH silica–carbon black[14] has been reported earlier.

Lee & Cutler[1] have studied the effect of iron as a catalyst on the formation of SiC from RHs. They concluded that iron enhances the reaction rate and SiC whiskers form with and without iron. Mansour & Hanna[3] have shown that the amount of SiC increases with increase in the Fe/SiO_2 ratio, up to a limiting value of 0·075. Cobalt has been found to accelerate the formation of total SiC and to decrease the formation of SiC whiskers from RH silica–carbon black mixture.[15] In previous work burnt RHs have been shown to form a smaller quantity of SiC whiskers than raw RHs.[11,12] In this work a systematic investigation has been carried out to study the effect of Co on the formation of SiC from burnt RHs.

2 Experimental Procedure

The dry raw RHs used in this investigation consists of 85 wt% of organic material and 15 wt% of silica

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and trace elements. The dry raw RHs were sieved to eliminate residual rice and clay particles. The raw RHs were put in a stainless steel container and inserted into a tubular furnace held at 700°C.

As soon as the flame disappeared the container with partially burnt RHs was quenched in air. The burnt RHs obtained were put in a plastic container and ground for 4 h by ball milling using Al_2O_3 balls. The particle size analysis of the ground RHs was carried out with a Malvern particle size analyser (3601). The particle size $D_{0.5}$ of the powder was 21·8 μm.

An aqueous solution of $CoCl_2$ (analytical reagent grade, supplied by Sterling Brand Laboratory Chemicals, Stratford, UK) was prepared by dissolving 2 g of $CoCl_2$ in 100 cm³ of distilled water. A 10 g sample of pulverized burnt RHs was put in a mortar. $CoCl_2$ solution (10 cm³) was added to it. Mixing was carried out for 10 min in the mortar followed by drying in air for 24 h. Finally, drying was continued for 1 h with an infrared lamp. The pulverized burnt RHs were designated as PBRH. The $CoCl_2$ treated pulverized burnt RHs were designated as PBRH + Co.

Samples of PBRH and PBRH + Co were put in separate cylindrical graphite containers of 10 mm outer diameter and 2·5 mm wall thickness. The graphite containers were closed with graphite stoppers. The containers with samples were pyrolysed in an alumina tubular furnace (Model CTF 16/75, Carbolite Furnace Ltd, Sheffield, UK). The ends of the furnace tube were closed with an alumina felt. Pyrolysis was carried out for 1 h at 1200, 1300, 1400, 1500, 1550 and 1600°C. Heating rates were 15°C/min from room temperature to 1000°C and 5°C/min from 1000°C to pyrolysis temperature. The PBRH samples were also pyrolysed at 1600°C at two other heating rates: 15°C/min from room temperature to 1600°C, and 5°C/min from room temperature to 1600°C. Finally the PBRH + Co sample was pyrolysed at 1600°C by heating at a rate of 20°C/min from room temperature to 1600°C.

After pyrolysis the phase analysis was carried out with a Philips X-ray diffractometer (Model PW 1940) with CuK radiation. A scanning electron microscope (SEM) (DV-2, Cam Scan, Cambridge, UK) equipped with an energy dispersive spectrometer (AN 10000, Link Analytical Ltd, High Wycombe, UK) was used for microstructural evaluation.

3 Results

The X-ray diffraction (XRD) patterns of pyrolysed PBRH samples are shown in Fig. 1. Peaks of crystalline silica and carbon (cristobalite and graphite) can be seen at 1200°C. The degree of
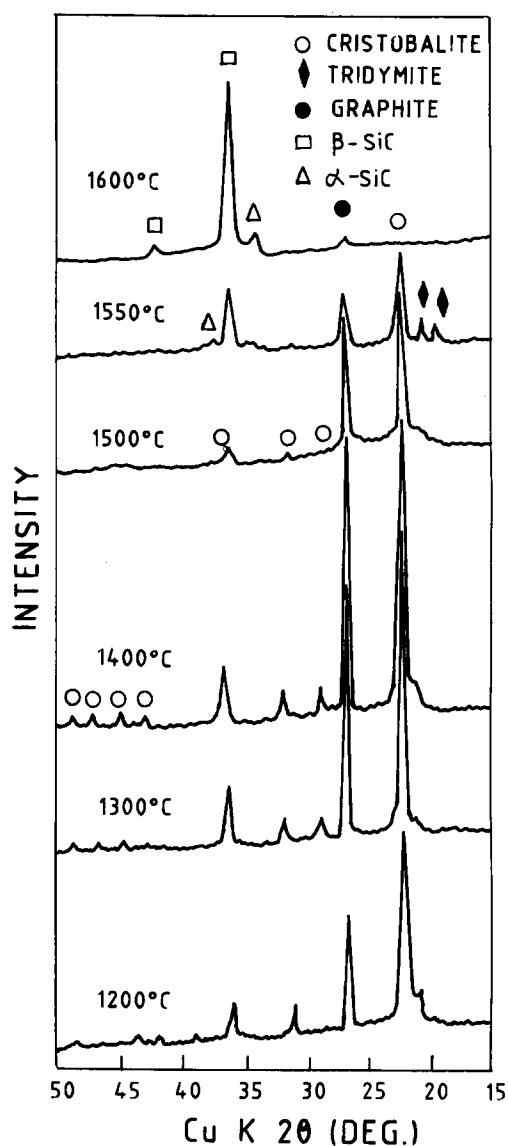
Fig. 1. XRD patterns of pyrolysed PBRH samples.

crystallization of silica and carbon increased up to 1400°C. At 1500°C the intensities of peaks of cristobalite and graphite decreased and a peak of SiC appeared. At 1550°C peaks corresponding to tridymite were also observed. At 1600°C no silica peak could be observed. At 1600°C peaks of SiC and residual carbon only were seen. The SiC was primarily β-SiC and some α-SiC peaks[16,17] were also seen.

In Fig. 2 the XRD patterns of pyrolysed PBRH + Co samples are shown. The degree of crystallization of silica and carbon increased up to 1400°C. At 1500°C the intensities of silica and carbon peaks decreased with the appearance of the SiC peak. No silica peak was observed at 1550°C. At 1600°C peaks corresponding to β-SiC and graphitic carbon only were seen. On comparing Fig. 1 with Fig. 2 one can observe that the degree of crystallization of silica and carbon in PBRH + Co samples is lower than that in PBRH samples. At 1550°C itself no silica peak could be observed in PBRH + Co samples. The intensities of SiC peaks
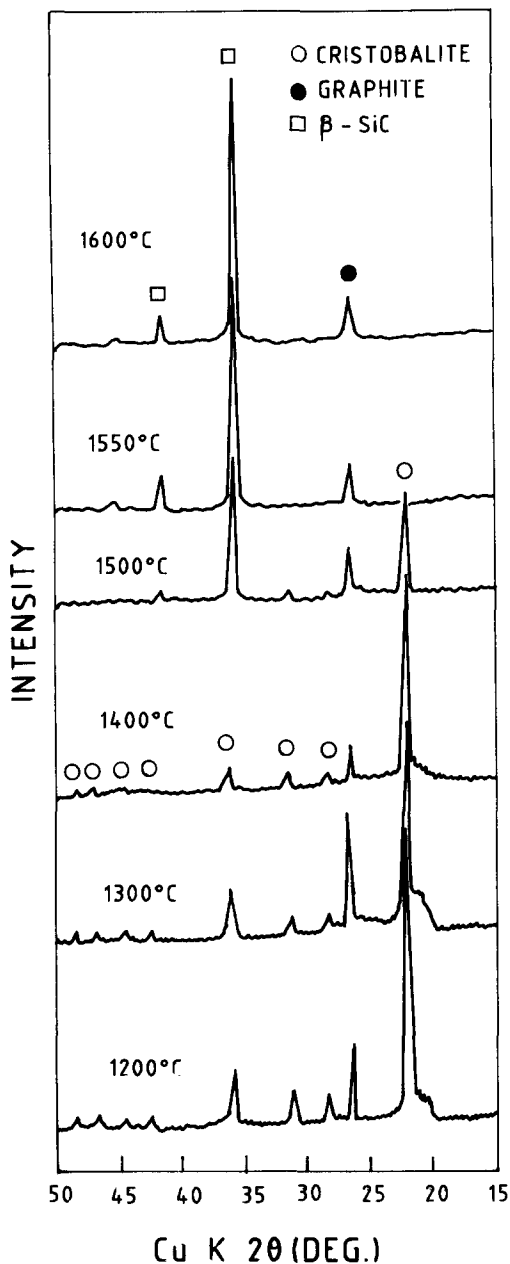
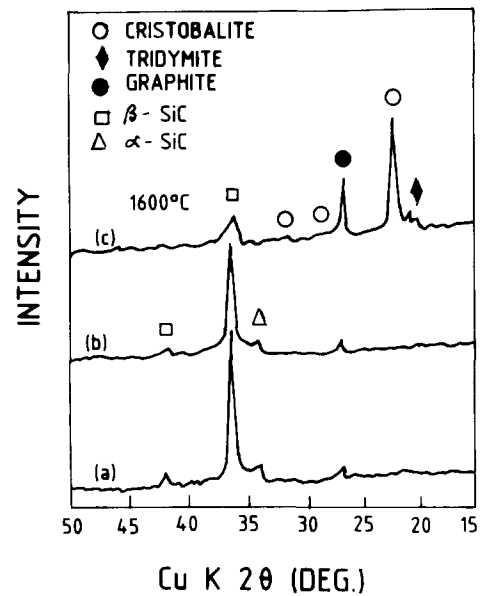Fig. 2. XRD patterns of pyrolysed PBRH + Co samples.

Fig. 3. XRD patterns of PBRH samples pyrolysed at 1600°C. Heating rates: (a) 15°C/min from room temperature to 1000°C and 5°C/min from 1000°C to 1600°C; (b) 15°C/min from room temperature to 1600 C; (c) 5 C/min from room temperature to 1600 C.

were higher in PBRH + Co samples than that in PBRH samples. Peaks corresponding to α-SiC were not seen in PBRH + Co.

In Fig. 3 the XRD patterns of PBRH samples pyrolysed at 1600°C are shown. Very slow heating at 5°C/min from room temperature to 1600°C resulted in an increase in the intensities of silica and carbon peaks, and decrease in the intensity of SiC peak (Fig. 3(c)). The XRD patterns of PBRH + Co samples pyrolysed at 1600°C are shown in Fig. 4. No difference in the shape of XRD patterns with heating rate was observed in PBRH + Co.

Formation of spherical particles was observed through SEM in PBRH samples after pyrolysis. Typical spherical particles formed at 1200, 1400 and 1500°C are shown in Fig. 5(a), (b) and (c) respectively. Energy dispersive spectroscopic (EDS) analysis of spherical particles revealed the presence of Si, Al, K

and Au (Fig. 6). The Au peak occurred from the gold coating used for SEM examination. At 1550°C whisker formation was widespread (Fig. 5(d)). Typical SiC whiskers formed at 1600°C are shown in Fig. 7.

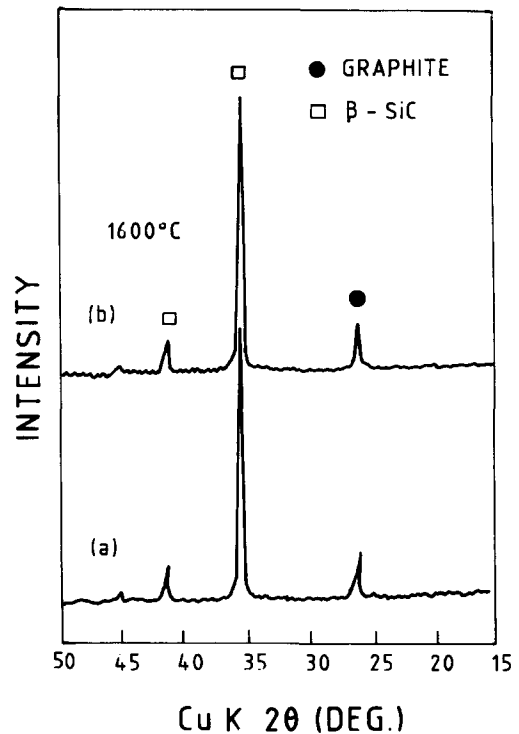Similarly, sphericle particles were also seen in PBRH + Co samples (Fig. 8(a) and (b)). Whisker

Fig. 4. XRD patterns of PBRH + Co samples pyrolysed at 1600 C. Heating rates: (a) 15 C/min from room temperature to 1000 C and 5 C/min from 1000°C to 1600°C; (b) 20°C/min from room temperature to 1600°C.
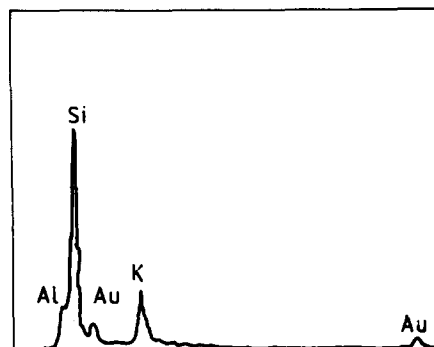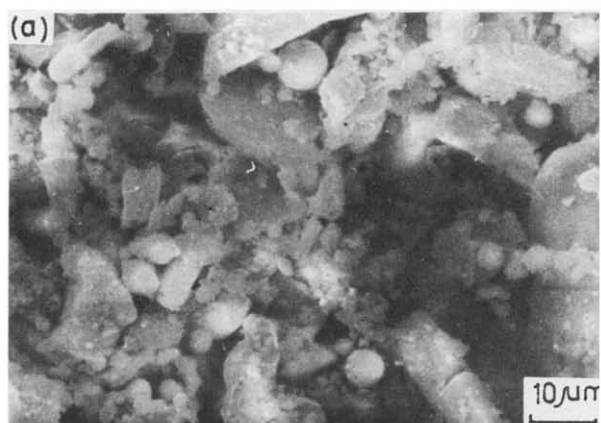
Fig. 6. EDS analysis of a spherical particle observed in PBRH after pyrolysis at 1200°C.
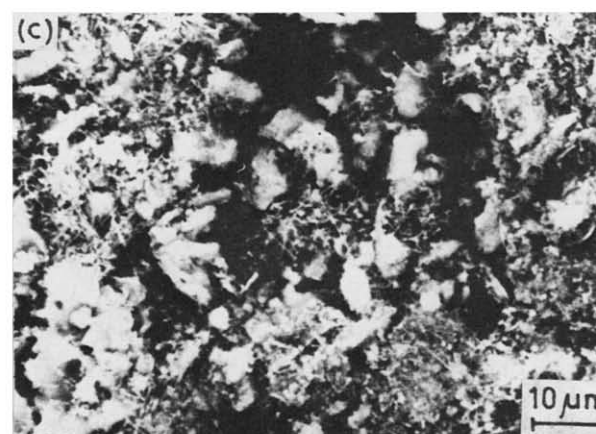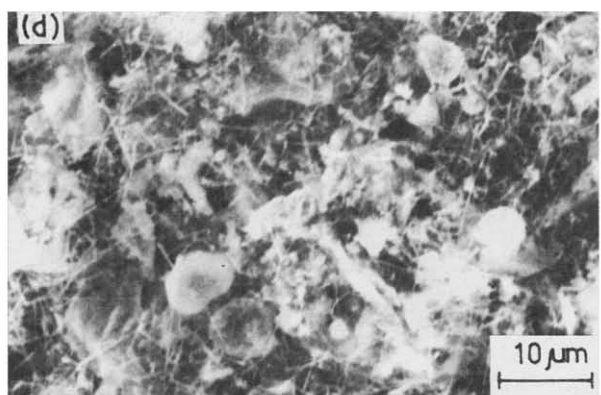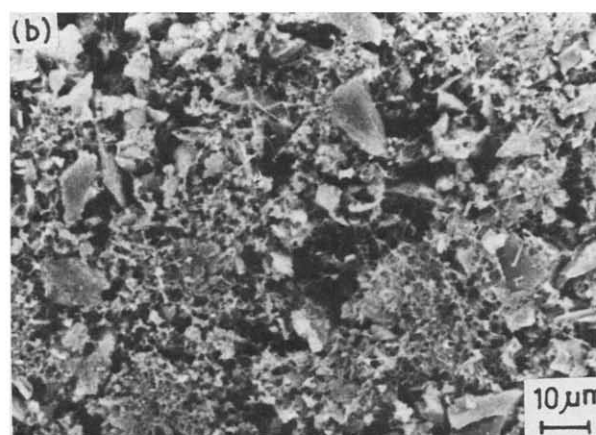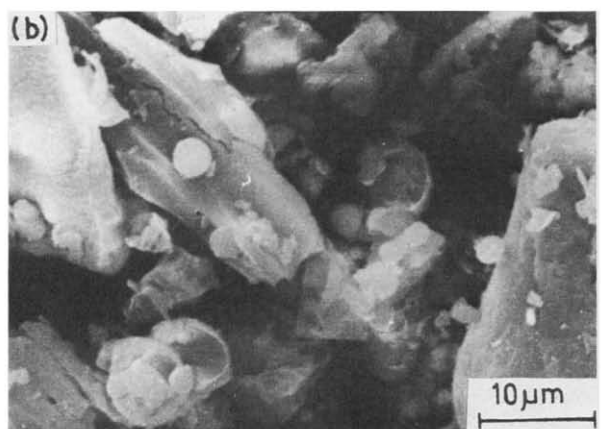

Fig. 5. SEM micrographs of PBRH after pyrolysis at: (a) 1200°C, (b) 1400°C, (c) 1500°C, and (d) 1550°C.

Fig. 7. SEM micrographs of PBRH after pyrolysis at 1600°C. Heating rates for (a), (b) and (c): refer to Fig. 3.
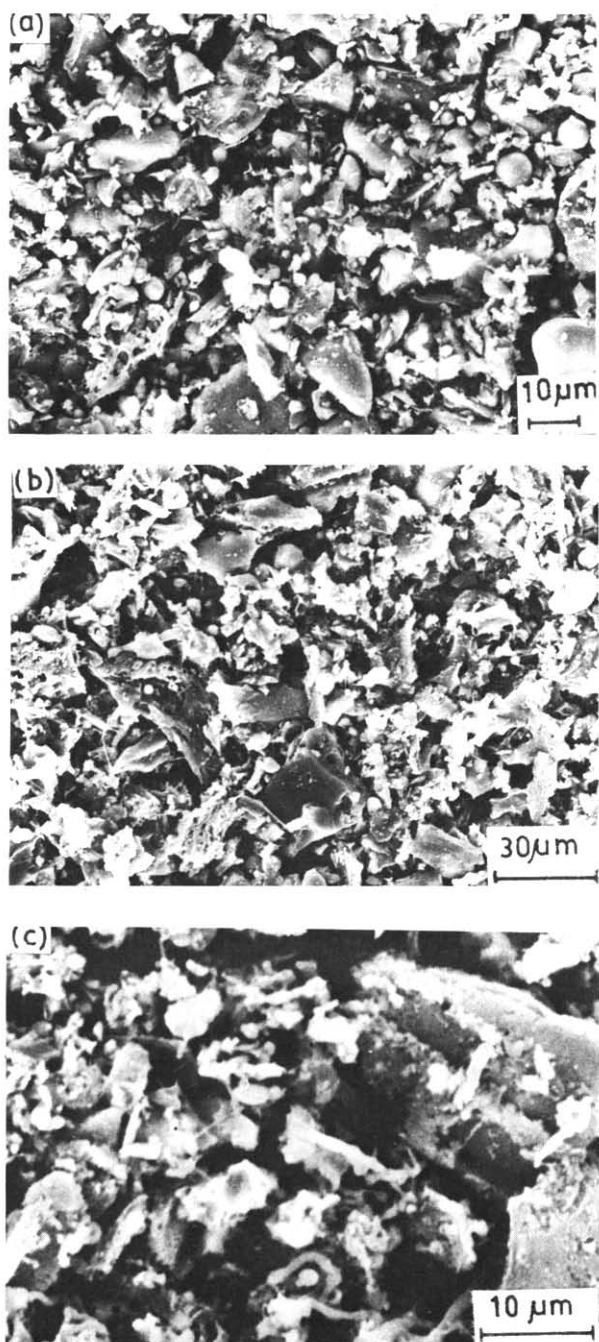
Fig. 8. SEM micrographs of PBRH + Co after pyrolysis at: (a) 1400°C, (b) 1500°C and (c) 1550°C.
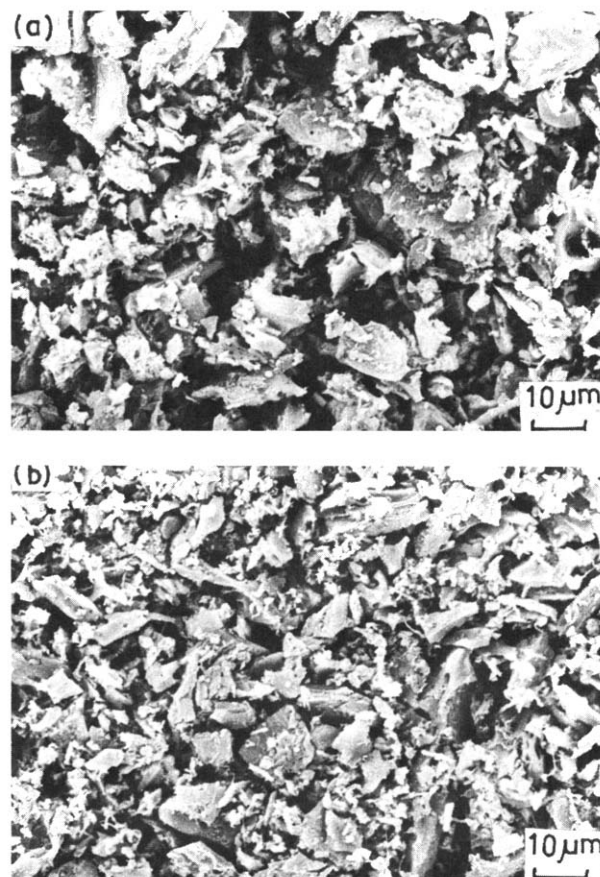

Fig. 9. SEM micrographs of PBRH + Co after pyrolysis at 1600°C. Heating rates for (a) and (b): refer to Fig. 4.

formation was almost negligible at 1500 and 1550°C (Fig. 8(b) and (c)). It can be seen from Fig. 9 that irrespective of heating rate the whisker formation at 1600°C in (PBRH + Co) is very low.

4 Discussion

Although the atmosphere in the tubular furnace was not controlled, no peaks of Si_3N_4 or Si_2ON_2 were observed in the XRD patterns. The carbon in RH could burn and produce CO gas at low temperature before SiO_2 begins to react with carbon. The resulting CO gas makes a reduction atmosphere.[18]

No Si_2ON_2 is formed during the reaction of quartz with carbon even in nitrogen atmosphere.[19]

Formation of spherical particles has been observed up to 1500°C in both PBRH and PBRH + Co samples (Figs 5 and 8). Nakata *et al.*[20] showed that potassium (K) in the RH causes surface melting and accelerates the crystallization of amorphous silica to cristobalite. Protuberances and hairs (trichomes) on the outer epidermis of RH are rich in silica.[9] During grinding of burnt RHs these silica-rich parts of RH could get fragmented. Upon heating to higher temperatures these silica-rich particles tend to convert into spherical particles due to surface melting and crystallization (Fig. 5(c)). EDS analysis of spherical particles revealed the presence of K and Al (Fig. 6). On comparing Fig. 1 with Fig. 2 one can see that the crystallization of carbon and silica in PBRH is more rapid than that in PBRH + Co. Hanna *et al.*[21] have shown that in the presence of iron, the crystallization of silica and carbon in RH decreases and promotes the formation of SiC. A number of workers have investigated the catalytic effect of Co on the gasification of carbon. $CoCl_2$ diffuses into the graphite and opens up the layers of graphite[22] by channeling.[23] Similarly, $CoCl_2$ could diffuse into the burnt RH and decrease the degree of crystallization of carbon and silica.
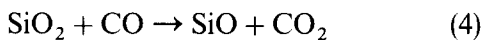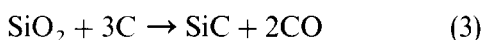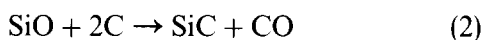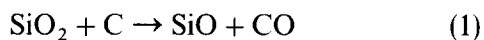
In PBRH tridymite formation was observed at 1550°C (Fig. 1) and at 1600°C (Fig. 3(c)) on slow heating at 5°C/min from room temperature to 1600°C. There exists a controversy over the relative stability of cristobalite and tridymite. The cristobalite is more stable as long as the crystallite nucleus is small. As it grows to larger dimensions the tridymite structure becomes the more stable but is produced slowly and with difficulty.[24] At 1550°C and at 1600°C on slow heating, the crystallite size of cristobalite could be large enough to form tridymite. Similarly, during slow heating (5°C/min) to 1600°C the degree of crystallization of silica and carbon could be very high because the sample was held for longer periods at lower temperatures before it reached the temperature of SiC formation (1500°C). This reduces the activities of silica and carbon to react with each other to form SiC.[21] Therefore the intensity of the SiC peak at 1600°C on slow heating (5°C/min) was very small (Fig. 3(c)).

The intensities of SiC peaks in PBRH + Co samples were higher than that in PBRH samples (Figs 1 and 2). The carbothermal reduction of silica to form SiC can be written as

$$SiO_2 + C \rightarrow SiO + CO \tag{1}$$

$$SiO + 2C \rightarrow SiC + CO \tag{2}$$

$$SiO_2 + 3C \rightarrow SiC + 2CO \tag{3}$$

$$SiO_2 + CO \rightarrow SiO + CO_2 \tag{4}$$

$$CO_2 + C \rightarrow 2CO \tag{5}$$

The SiO formation reaction (1) occurs as long as the silica and carbon are in contact. Further SiO formation occurs by reaction of silica with CO (reaction (4)). The CO_2 formed by reaction (4) will react with carbon and form CO according to reaction (5). Cobalt acts as a strong catalyst on the gasification of carbon.[23,25] The increase in gasification is attributed to an increase in the surface area of carbon.[26] This could lead to an increase in total porosity and adsorption capacity of carbon in PBRH + Co. The SiO formed by reaction (1) or (4) can be adsorbed by carbon and form isometric type SiC particles.[9] The carbon in PBRH + Co could adsorb larger quantity of SiO than that in PBRH. Therefore the intensities of peaks of SiC in PBRH + Co samples were higher than that in PBRH samples. As the quantity of SiO that could be released from PBRH + Co is low the possibility of SiC whisker formation is low. So, at any heating rate, the formation of SiC whiskers in PBRH + Co samples was negligible (Fig. 9).

In the XRD patterns of PBRH samples α-SiC peaks were also observed (Figs 1 and 3). It is well known that SiC whiskers contain discrete regions of crystallographic defects. McMahon et al.[27] showed

that the regions of high defect density are consistent with a mixture of SiC polytypes. Chrysanthou & Grieveson[28] concluded that the α-SiC is more stable at higher oxygen potential. During pyrolysis the oxygen potential in the PBRH system could be higher than that in the PBRH + Co system because of the catalytic effect of Co on the gasification of carbon. On the other hand, the quantity of SiC whiskers present in pyrolysed PBRH + Co samples was almost negligible. Therefore the peaks of α-SiC were not seen in the XRD patterns of PBRH + Co samples.

5 Conclusions

(i) The addition of $CoCl_2$ to burnt rice husks decreases the crystallization of silica and carbon and accelerates the formation of SiC.

(ii) The SiC whisker formation in $CoCl_2$ treated burnt rice husks has been found to be negligible.

(iii) Slow heating stabilizes the silica and carbon in burnt rice husks by increasing their degree of crystallization.

(iv) The untreated burnt rice husks yielded a maximum quantity of SiC whiskers at 1600°C.

(v) No α-SiC was formed in the $CoCl_2$ treated burnt rice husks.

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