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Effect of cobalt catalyst on the formation of SiC from rice husk silica–carbon black mixture

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Cobalt has been found to act as a strong catalyst in increasing the formation of total SiC by decreasing the crystallization of carbon black. The formation of SiC whiskers in the presence of cobalt catalyst is found to be low. No α-SiC has formed in the presence of Co catalyst. With Co catalyst needle-like whiskers are formed. Without any catalyst (a) slow heating has decreased the reactivities of carbon black and rice husk silica by increasing their degree of crystallization and (b) rapid heating has increased the formation of SiC particulates. With Co catalyst rapid heating has been found to be beneficial in increasing the whisker content.

1. Introduction

Silicon carbide (SiC) whisker has been widely considered as one of the best reinforcements for various composite materials because of its high strength and high resistance to heat and chemicals. At present most commercial SiC whiskers are produced by carbothermal reduction of silica. Various sources of silica and carbon are used [1]. SiC whiskers can be produced by thermal decomposition of rice husks (RHs) as pioneered by Lee and Cutler [2]. There are several reports on the formation of SiC whiskers from RHs [3–15].

The catalytic effect of iron on the formation of SiC from RHs has been studied by Lee and Cutler [2]. They showed that iron enhances the reaction rate and that SiC whiskers form with and without iron. Mansour and Hanna [4] showed that the amount of SiC increases with increase in the Fe/SiO_2 ratio up to a limiting value of 0.075. Patel and Kareera [9] have claimed that iron and cobalt catalysts have little effect on the SiC yield, and that SiC whiskers form with and without a catalyst. The formation of SiC whiskers from pulverized RH ashes has been reported by Krishnarao and co-workers [16, 17]. In the present work a detailed investigation has been carried out to study the effect of Co on the formation of SiC whiskers and total SiC from RH silica–carbon black mixture.

2. Experimental procedure

The dry raw RHs were used in this investigation after sieving to eliminate residual rice and clay particles. They consist of 85% of carbon (organic material) and 15 wt % of silica and trace elements. The RHs were burnt in a tubular furnace at 700 °C for 3 h. The ash (rice husk silica) obtained was ground in a mortar for 10 min. The RH silica powder was ball-milled in a plastic container for 4 h using Al_2O_3 balls. A Malvern Instruments particle size analyser (Model 3601) was used for particle size analysis. The particle size $D_{0.5}$ of the pulverized powder was 14.44 μm. Equal quantities of pulverized RH silica and carbon black (grade N220) were dry mixed for 3 h by ball milling with Al_2O_3 grinding media.

Two grams of $CoCl_2$ crystals (analytical reagent grade) were dissolved in 100 ml of distilled water. 10 ml of the aqueous solution of $CoCl_2$ was added to a 10 g sample of pulverized RH silica–carbon black mixture in a mortar. After mixing for 10 min in the mortar the mix was allowed to dry in air for 24 h. Finally, drying was continued for 1 h with an infrared lamp. The pulverized RH silica–carbon black mixture was designated as SAC. The $CoCl_2$-treated pulverized RH silica–carbon black mixture was designated as SAC + Co.

Samples of SAC and SAC + Co were taken in separate cylindrical graphite containers of 10 mm diameter and 2.5 mm wall thickness. The containers were closed with graphite stoppers and inserted into an alumina tubular furnace (Model CTF 16/75). The ends of the furnace tube were closed with an alumina felt. Pyrolysis was carried out for 1h at different temperatures (1200, 1300, 1400, 1500, 1550 and 1600 °C). Heating rates employed were 15 °C min^{-1} from room temperature to 1000 °C and 5 °C min^{-1} from 1000 °C to pyrolysis temperature. The SAC samples were also pyrolysed at 1600 °C at two other heating rates: 15 °C min^{-1} from room temperature to 1600 °C (rapid heating), and 5 °C min^{-1} from room temperature to 1600 °C (slow heating). Finally a sample of SAC + Co was pyrolysed at 1600 °C by heating rapidly at a rate of 20 °C min from room temperature to 1600 °C.

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A Philips X-ray diffractometer (Model PW 1940) with CuK_α radiation was used for phase analysis of pyrolysed samples. Microstructural evaluation was carried out through a CamScan (DV-2) scanning electron microscope (SEM) equipped with energy dispersive spectroscope (EDS).

Residual carbon content in the reaction product was determined by burning in air for 3 h at 700 °C. The carbon-eliminated sample was treated with 40% hydrofluoric acid to determine the unreacted silica. The remainder was taken to represent the SiC content in the reaction product.

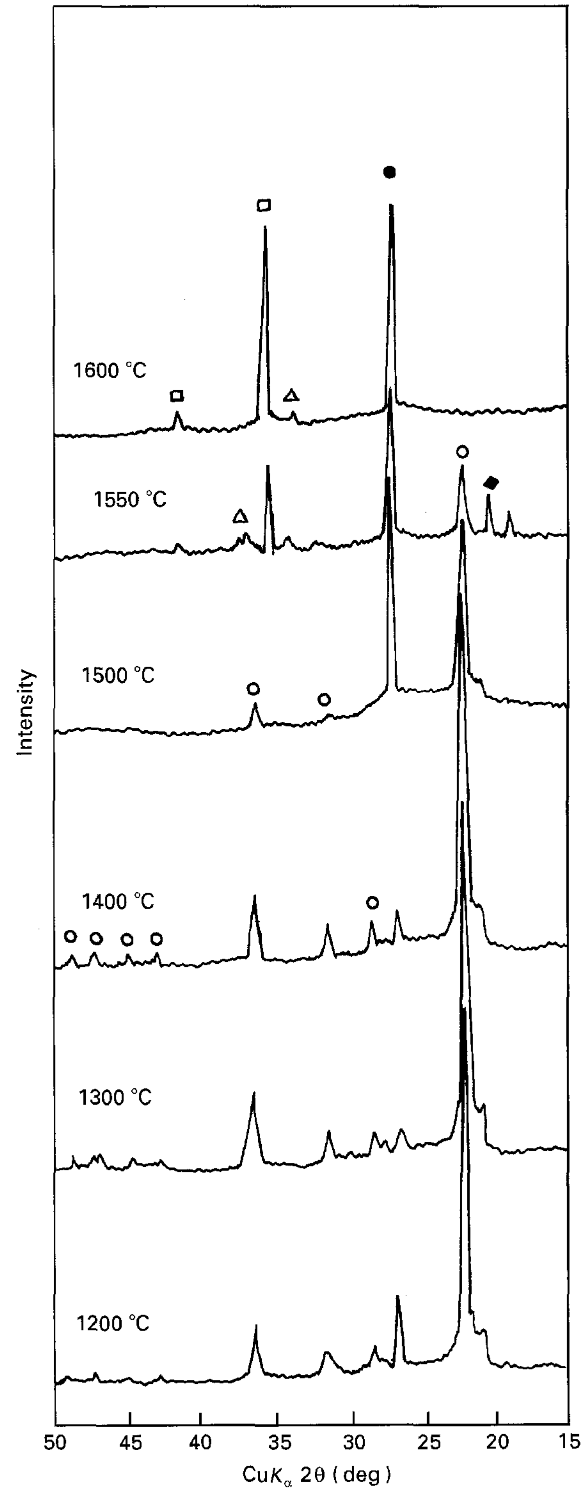


Figure 1 XRD patterns of pyrolysed SAC samples. ○ cristobalite; ◆ tridymite; ● graphite; □ β-SiC; △ α-SiC.

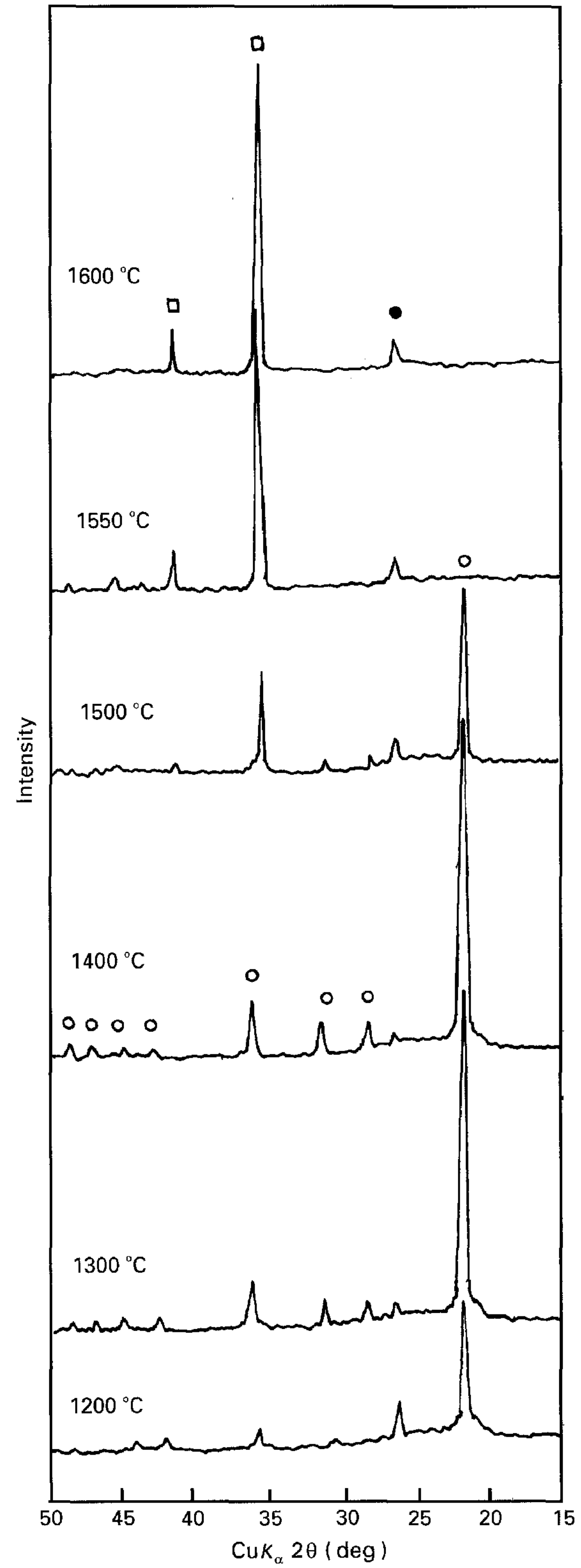


Figure 2 XRD patterns of pyrolysed SAC + Co samples. ○ cristobalite; ● graphite; □ β-SiC.

3. Results

One can see peaks of crystalline silica and carbon (cristobalite and graphite) in XRD patterns of the SAC sample at 1200 °C (Fig. 1). The intensity of the cristobalite peak increased up to 1400 °C and decreased at 1500 °C with the appearance of the SiC peak, but the degree of crystallization of carbon black was rapid at and above 1500 °C. At 1550 °C peaks of tridymite were also seen. At 1600 °C peaks of SiC and graphitic carbon only were seen. Though the SiC formed was primarily β-SiC some α-SiC peaks [18, 19] were also observed.

XRD patterns of pyrolysed SAC + Co samples are shown in Fig. 2. The intensity of the silica peak increased up to 1400 °C and decreased at 1500 °C. On comparing Fig. 2 with Fig. 1 one can observe that at any temperature the intensity of carbon peak in SAC + Co is lower than that in SAC. No silica peak could be observed in SAC + Co at 1550 °C. The intensities of SiC peaks in SAC + Co samples were higher than that in SAC samples. Peaks of α-SiC were not observed in SAC + Co.

In Fig. 3 the XRD patterns of SAC samples pyrolysed at 1600 °C are shown. Upon rapid heating the intensity of the graphitic carbon peak decreased whereas the intensity of the SiC peak increased (Fig. 3(b)). Slow heating has resulted in an increase in the stability of silica and carbon black and decrease in the intensity of SiC peak. Similarly the XRD patterns of SAC + Co samples pyrolysed at 1600 °C are shown in Fig. 4. Rapid heating (at 20 °C min^{-1}) has little effect on the shape of the XRD pattern.

The results of the chemical analysis of the reaction product are shown in Table I. It is evident from the table that the residual carbon content in SAC has increased up to 1500 °C and decreased above 1500 °C. The variation in residual carbon content with pyrolysis temperature was very small in SAC + Co. The SiC content in the SAC + Co system was considerably higher than that in the SAC system. Rapid heating to 1600 °C has resulted in an increase in the SiC content in SAC. Though the residual carbon content has decreased from 37.66 to 34.01%, the quantity is good enough to yield a strong peak in XRD pattern. But the intensity of the carbon peak was very small (Fig. 3(b)). The lowest quantity of residual carbon content (17.01%) was noticed in the slow-heated SAC sample. But XRD has yielded a strong peak for carbon (Fig. 3(c)). Upon rapid heating at 20 °C min^{-1} to 1600 °C the residual carbon content has decreased from 30.54 to 22.36% in SAC + Co. The highest quantity of SiC content was observed in the rapidly heated SAC + Co sample.

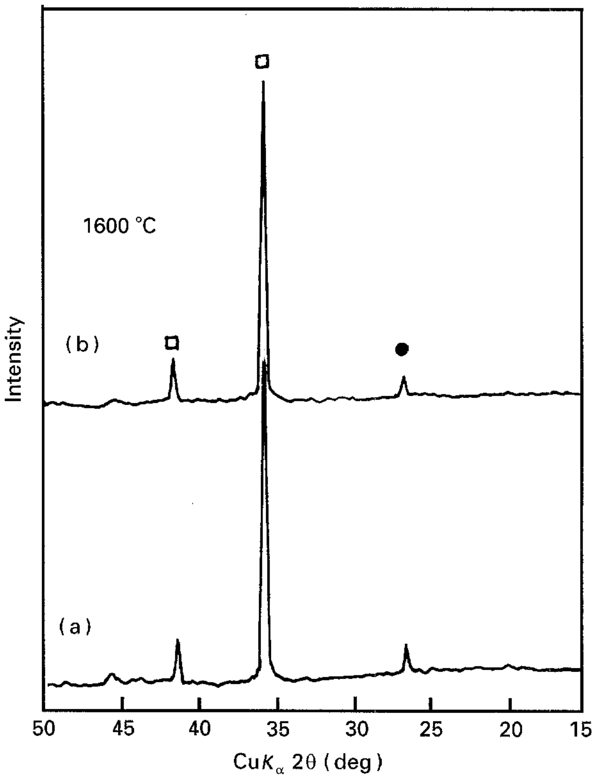


Figure 4 XRD patterns of SAC + Co samples pyrolysed at 1600 °C. Heating rates: (a) 15 °C min^{-1} from room temperature to 1000 °C and 5 °C min^{-1} from 1000 to 1600 °C; (b) 20 °C min^{-1} from room temperature to 1600 °C. ● graphite; □ β-SiC.

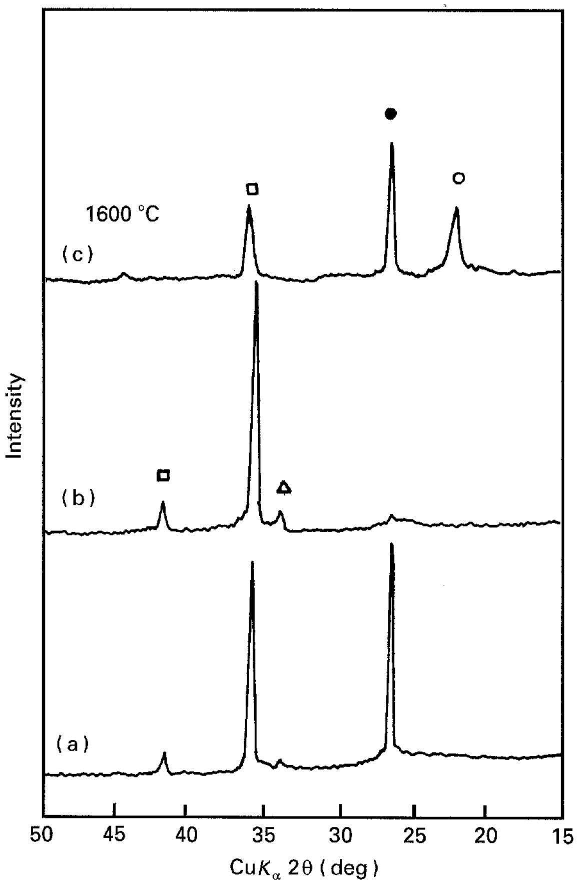


Figure 3 XRD patterns of SAC samples pyrolysed at 1600 °C. Heating rates: (a) 15 °C min^{-1} from room temperature to 1000 °C and 5 °C min^{-1} from 1000 to 1600 °C; (b) 15 °C min^{-1} from room temperature to 1600 °C; (c) 5 °C min^{-1} from room temperature to 1600 °C. ● cristobalite; ○ graphite; □ β-SiC; △ α-SiC.

The morphology of the SAC samples after pyrolysis is shown in Figs 5 and 6. The agglomerate formed at 1400 °C can be seen in Fig. 5. At 1500 °C formation of spherical particles has been observed. The presence of Si, Al, and K was identified through energy dispersive X-ray microanalysis of the spherical particles. Formation of SiC whiskers at a few places was observed (Fig. 5(c)). At 1550 °C SiC whisker formation was widespread (Fig. 5(d)). Typical SiC whiskers formed in SAC after pyrolysis at 1600 °C can be seen in Fig. 6. Rapid heating resulted in an increase in the formation of particulates. In the slow-heated sample a large number of spherical particles were observed.

SEM micrographs of pyrolysed SAC + Co samples are shown in Figs 7 and 8. Spherical particles and a few whiskers were seen at 1500 °C (Fig. 7(c)). Formation of SiC whiskers at 1550 and 1600 °C in the SAC + Co sample was less than that in SAC sample

TABLE I Composition of the reaction product

System	Reaction temperature (°C)							
	1200	1300	1400	1500	1550	1600	1600^a	1600^b
	Residual carbon							
SAC	27.37	34.21	38.32	44.12	43.65	37.66	34.01	17.01
SAC + Co	32.44	37.55	35.43	37.15	31.32	30.54	22.36	–
	Unreacted silica							
SAC	72.62	65.78	61.67	41.79	10.31	8.75	2.34	48.63
SAC + Co	67.55	62.44	64.56	29.79	4.96	2.02	1.13	–
	SiC content							
SAC	nil	nil	nil	14.08	46.03	53.58	63.63	34.35
SAC + Co	nil	nil	nil	29.79	63.71	67.43	76.49	–

Rate of heating: 15 °C min^{-1} from room temperature to 1000 °C and 5 °C min^{-1} from 1000 °C to pyrolysis temperature.

^{a} for SAC 15 °C min^{-1} from room temperature to 1600 °C, for SAC + Co 20 °C min^{-1} from room temperature to 1600 °C.

^{b} 5 °C min^{-1} from room temperature to 1600 °C.

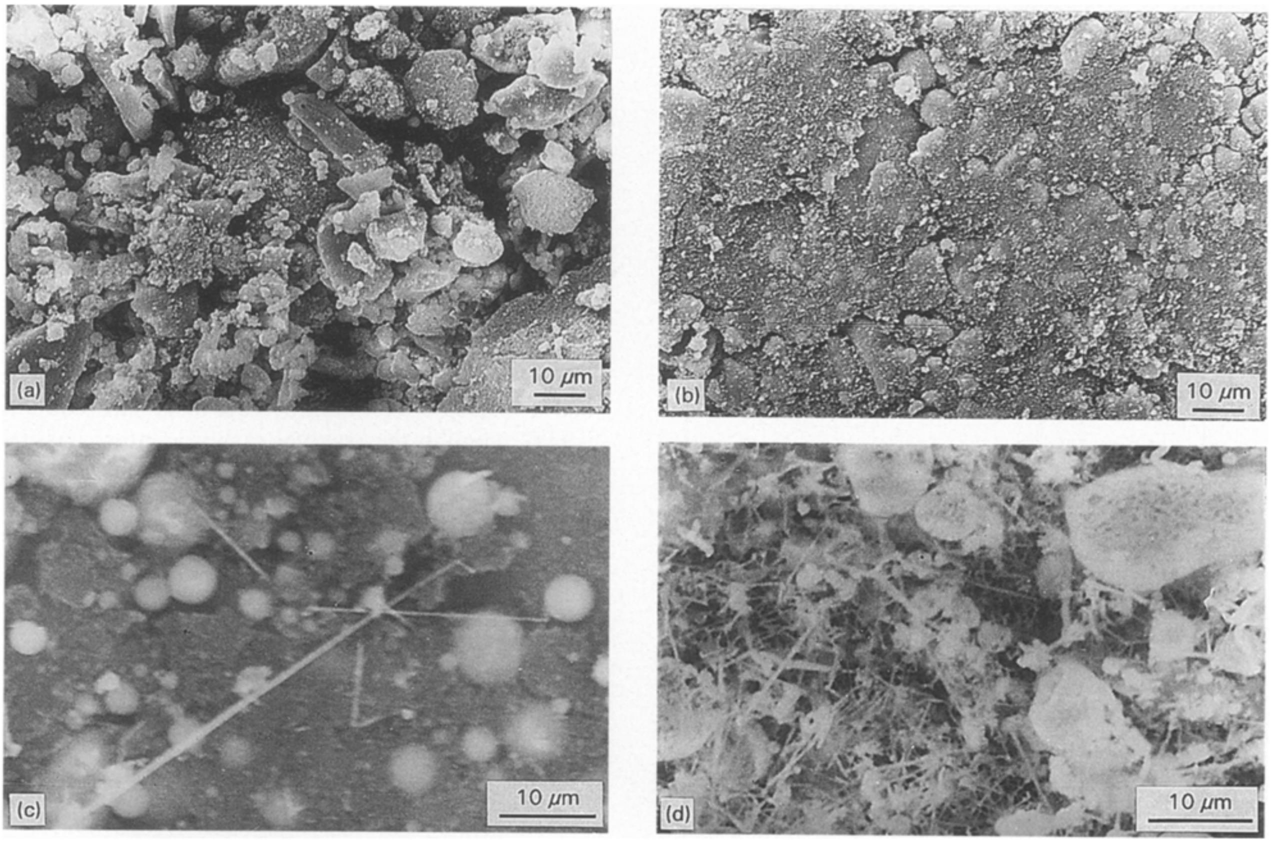
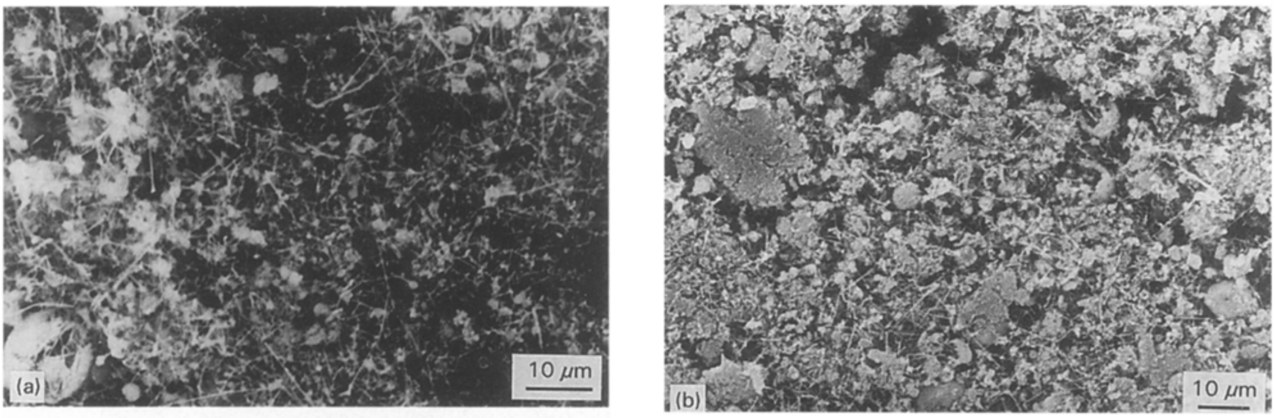


Figure 5 SEM micrographs of SAC after pyrolysis at: (a) 1200 °C; (b) 1400 °C; (c) 1500 °C; and (d) 1550 °C.

(Fig. 7(d) and Fig. 8(a)). Rapid heating (at 20 °C min^{-1}) to 1600 °C helped in increasing the formation of SiC whiskers (Fig. 8(b)). The SiC whiskers formed in SAC + Co were slightly thicker and longer than those formed in SAC.

4. Discussion

During pyrolysis of RHs four competitive processes namely, crystallization of amorphous silica, crystallization of amorphous carbon, formation of SiC whiskers and formation of SiC particles are simultaneously occurring [11]. In both SAC and SAC + Co samples the formation of spherical particles has been observed (Figs 5 and 7). Similarly, spherical particles of silica have been observed by Dijen and colleagues [20] and Ekelund and Forslund [21] during the carbothermal synthesis of β-SiC and Si_3N_4. Potassium in RH is known to cause surface melting and to accelerate the crystallization of amorphous silica to cristobalite [22]. Due to surface melting, silica could form dense agglomerates as can be seen in Fig. 5(b). At higher temperatures these silica particles could get converted into spherical particles (Fig. 5(c) and (d)). EDS analysis also revealed the presence of Si, K and Al on the spherical particles.



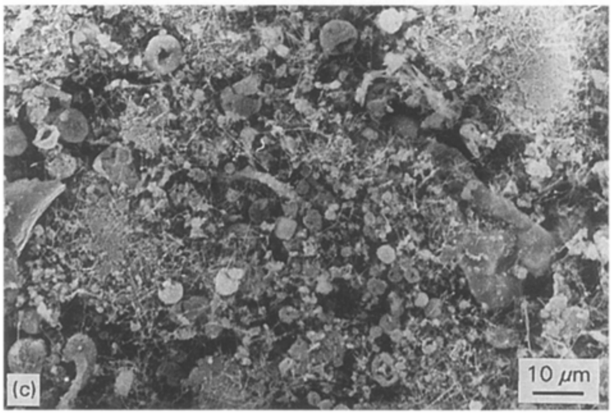


Figure 6 SEM micrographs of SAC after pyrolysis at 1600 °C. For heating rates, refer to Fig. 3.

From Table I it is evident that the SAC + Co system contains considerable quantities of residual carbon. XRD patterns have not yielded strong peaks for carbon, however. From Figs 1 and 2 it is clear that the degree of crystallization of carbon is lower in SAC + Co than that in SAC. Cobalt diffuses into graphite and opens up the layers of graphite [23] by channelling [24]. In SAC + Co the Co could diffuse into carbon black and decrease its degree of crystallization.

The degree of crystallization of carbon in SAC increased with temperature and was rapid at and above 1500 °C. When SAC samples were held at temperatures

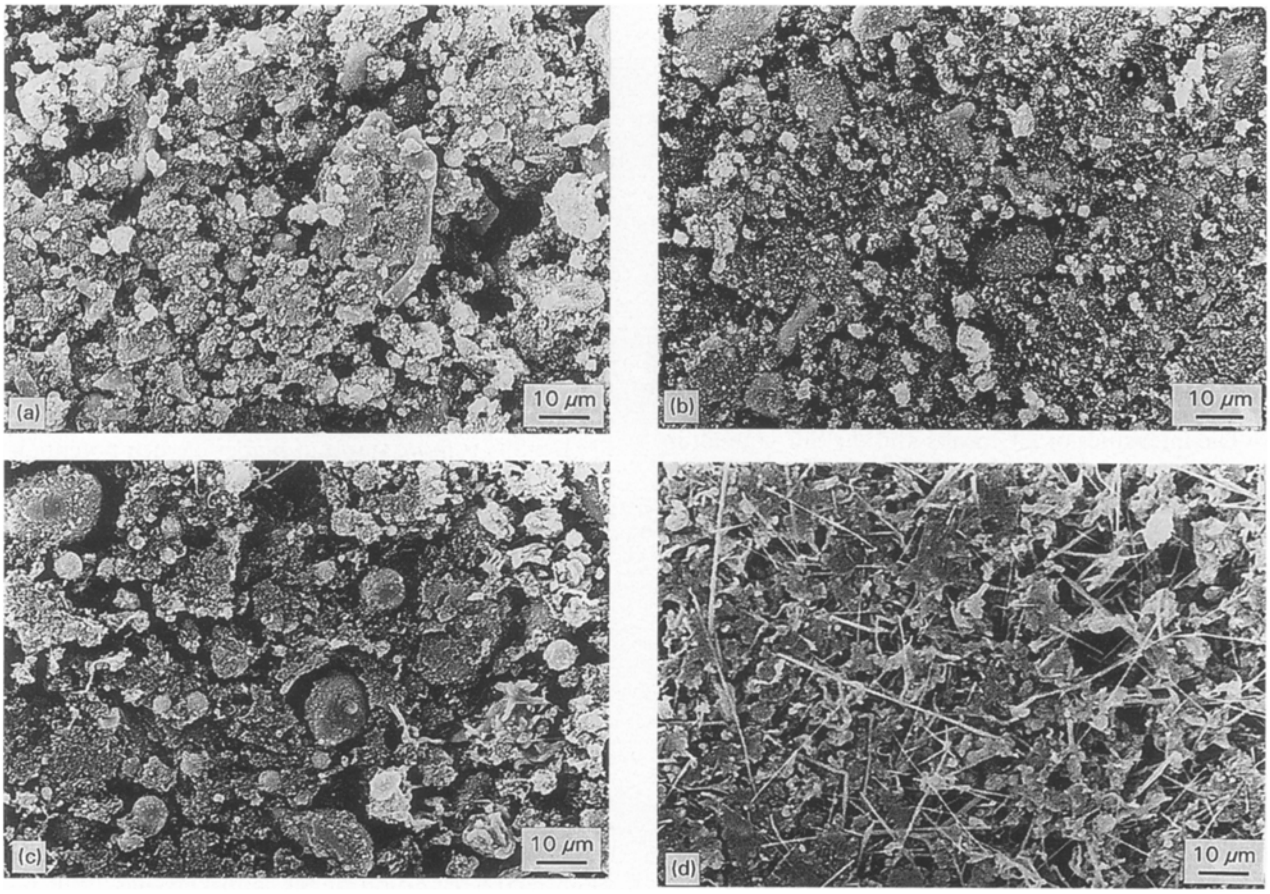


Figure 7 SEM micrographs of SAC + Co after pyrolysis at: (a) 1200 °C; (b) 1400 °C; (c) 1500 °C; and (d) 1550 °C.

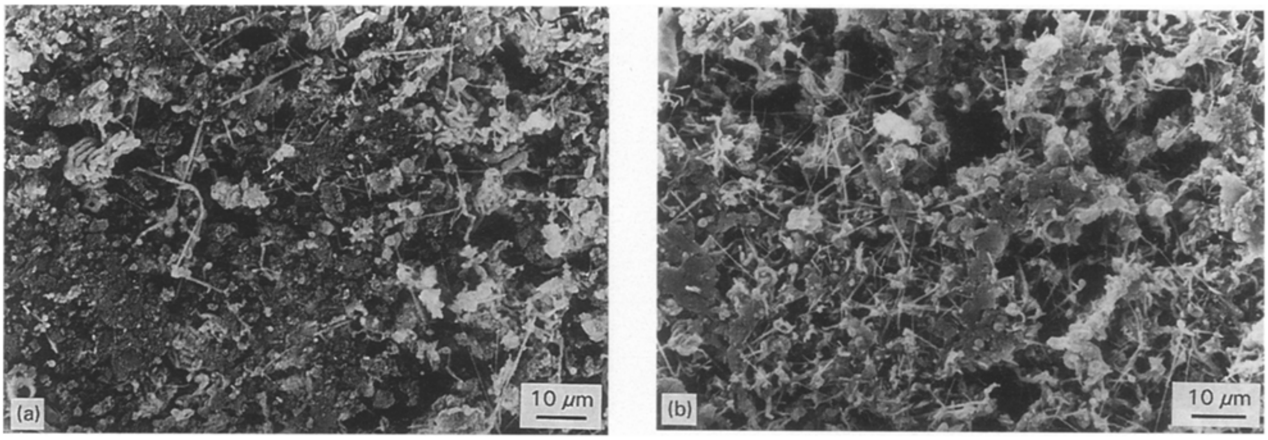


Figure 8 SEM micrographs of SAC + Co after pyrolysis at 1600 °C. For heating rates, refer to Fig. 4.

below 1500 °C, a considerable quantity of carbon could get oxidized due to the low degree of crystallization. As reaction of silica with carbon started from 1500 °C the residual carbon content in SAC decreased above 1500 °C. In SAC + Co there is no effect of crystallization on carbon. Therefore the variation in carbon content with pyrolysis temperature was small.

A tridymite peak was observed in SAC at 1550 °C and at 1600 °C on slow heating. The relative stability of cristobalite and tridymite can change with the size of the crystalline unit. As the crystallite grows to larger dimensions the tridymite structure becomes the more stable, but is produced slowly and only with difficulty [25]. At 1550 and at 1600 °C on slow heating the crystallite size of silica could be large enough to form tridymite. During slow heating to 1600 °C a considerable quantity of carbon could have been lost as CO because the sample was held for a longer period at low temperatures before it reached the temperature of SiC formation (1500 °C). But the smaller quantity (17.01%) of residual carbon has yielded a strong peak on XRD (Fig. 3(c)). This clearly shows that the degree of crystallization has increased upon slow heating. The increase in the degree of crystallization decreases the reactivities of silica and carbon [11]. For the same reason the total quantity of SiC formed at 1600 °C on slow heating was very small (Table I and Fig. 3(c)). Consequently low formation of whiskers and large numbers of spherical particles were observed (Fig. 6(c)).

The intensities of SiC peaks and the SiC content in SAC + Co were higher than that in SAC. A number of investigators have studied the catalytic effect of Co on the gasification of carbon. Cobalt acts as a strong catalyst on the gasification of carbon [24, 26]. The increase in gasification rate is attributed to an increase in surface area of carbon [27]. The total porosity and adsorption capacity of carbon in SAC + Co could be high because the degree of crystallization was low and the gasification rate was high. On the other hand crystallization of carbon in SAC was more rapid at and above 1500 °C. This reduces the surface area of carbon black sharply [28]. The reaction scheme of SiC formation from silica and carbon can be written as

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

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

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

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

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

The SiO formation according to Reaction 1 occurs as long as silica and carbon are in contact. Further SiO formation occurs by reaction of silica with CO (Reaction 4). The CO_2 formed in Reaction 4 will react with carbon and form CO according to Reaction 5. The SiO formed by Reactions 1 or 4 could be adsorbed by carbon and form isometric SiC particles [10]. The carbon in SAC + Co could adsorb a larger quantity of SiO than that in SAC. Therefore the SiC content in SAC + Co was higher than that in SAC. As the quantity of SiO that could be released from SAC + Co is low, the possibility of whisker formation is low. Though the residual carbon content in rapidly heated SAC samples was 34.01%, its low intensity in XRD patterns (Fig. 3(b)) indicates its low degree of crystallization. As the carbon was not crystallized, its reactivity and adsortion capacity could be high. Therefore the total SiC content has increased from 53.58 to 63.63%, and whisker formation has decreased (Fig. 6(b)).

Peaks of α-SiC were also observed in SAC (Fig. 1). SiC whiskers are known to contain discrete regions of crystallographic defects. The regions of high defect density are consistent with a mixture of SiC polytypes [29]. α-SiC is more stable at higher oxygen potentials [30]. The formation of SiC whiskers has been considered to occur by a vapour phase reaction mechanism [31]

$$SiO + 3CO \rightarrow SiC + 2CO_2 \qquad (6)$$

$$3SiO + CO \rightarrow SiC + 2SiO_2 \qquad (7)$$

During pyrolysis the oxygen potential in the SAC system could be higher than that in the SAC + Co system because of the catalytic effect of Co on the gasification of carbon. In SAC whisker growth could occur by Reaction 7 and lead to the formation of α-SiC. No α-SiC was detected in SAC + Co. A thorough characterization of SiC whiskers has been reported by Karasek and co-workers [32–34]. The whiskers formed in the presence of Co catalyst are almost entirely β-SiC [32]. On the other hand the whiskers formed in SAC + Co are relatively thicker and longer (like needles). This could be due to whisker formation by Reaction 6 because in SAC + Co the gasification rate of carbon was high and SiO released was low. Saito and colleagues [31] have suggested that the needle-like whiskers grow by Reaction 6. The residual carbon content in the rapidly-heated SAC + Co sample has decreased from 30.54 to 22.36%. This must have been accompanied by an increase in the formation of CO. Since the amount of carbon which could adsorb SiO was low, a higher quantity of SiO would be released. Reactions 4 and 6 are more favourable and lead to the increase in SiC whisker formation (Fig. 8(b)).

5. Conclusions

Cobalt catalyst has been found to accelerate the formation of total SiC by decreasing the degree of crystallization of carbon black. The formation of SiC whiskers in the presence of Co catalyst is decreased. No α-SiC has formed in the presence of Co catalyst. With Co catalyst needle-like whiskers are formed. Without any catalyst (a) slow heating has increased the stability of carbon black and rice husk silica by increasing their degree of crystallization, and (b) rapid heating has resulted in an increase in the formation of SiC particulates. With Co catalyst rapid heating has increased the formation of SiC whiskers.

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