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Formation of SiC from Rice Husk Silica–Carbon Black Mixture: Effect of Rapid Heating

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Abstract: Formation of SiC from rice husk silica and carbon black mixture with Co catalyst, and without any catalyst, has been studied by rapid heating to 1300–1600°C. Formation of SiC in $CoCl_2$ treated mixture was rapid at and above 1400°C. However, in the untreated mixture considerable quantities of SiC has formed only above 1500°C. Total SiC content and SiC whisker yield in the treated mixture were higher than that in the untreated mixture. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Silicon carbide (SiC) whiskers are potential reinforcement for producing strong and tough ceramic and metal matrix composites. SiC whiskers can be produced through several routes.[1–22] At present most SiC whiskers are produced by carbothermal reduction of silica. Various sources of silica and carbon are used. Rice husks (RHs) produce a high ash content, varying from 13 to 29 wt% depending on the variety, climate, and geographic location. The ash is largely composed of silica (87–97%) with small amounts of alkalis and other trace elements.[23] The effect of carbon content and preheat treatment on the formation of SiC from RH silica and carbon black mixture has been reported.[24,25]

The effect of cobalt catalyst on the formation of SiC whiskers from burnt RHs and RH silica-carbon black mixture has been reported by Krishnarao.[26,27] Under similar experimental conditions, slow heating (5°C/min) has been found to form smaller quantity of SiC whiskers in $CoCl_2$ treated mixture than that formed in untreated mixture.[27] In this work the $CoCl_2$ treated and untreated RH silica–carbon black mixtures were heated rapidly to pyrolysis temperature and the formation of SiC whiskers was studied.

2 EXPERIMENTAL PROCEDURE

The dry raw RHs, after sieving 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 RHs were burnt at 700°C for 3 h in a tubular furnace. The ash (RH silica) obtained was ground in a mortar for 10 min. The RH silica powder was taken in a plastic container and ball milled for 4 h using Al_2O_3 balls. Equal quantities of pulverized RH silica and carbon black (grade N220, ISAF, supplied by Philips Carbon Black Ltd, Durgapur, India) were dry mixed for 3 h by ball milling.

Two grams of $CoCl_2$ crystals (analytical reagent grade, supplied by Loba Chemie, Bombay, India) 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 dried in an oven at 110°C. The dried cake was further subjected to ball milling for 2 h. The pulverized RH silica–carbon black mixture was designated as (SOC). The $CoCl_2$ treated (SOC) was designated as (SOC + Co).

Powder sample was taken in a cylindrical graphite container of 10 mm inner diameter and 2.5 mm wall thickness. The container was closed

with a graphite stopper and inserted into a 12KW r.f. induction heater (Telycom, Bombay, India). To avoid oxidation of graphite container and carbon felt around the graphite container, argon at a flow rate of 0.2 litre/min was fed around the container. Conversion was carried out at different temperatures (1300, 1400, 1450, 1500, 1550 and 1600°C) for 20 min. Heating rate employed was 200°C/min. One sample each of (SOC) and (SOC + Co) were also pyrolysed at 1450°C by heating at a rate of 100°C/min.

A Philips X-ray diffractometer (model PW1373) with Cu K radiation through Ni filter was used for phase analysis of the reaction product. Scanning electron microscope (International Scientific Instruments) model ISI-100A was used to study the morphology of SiC. The excess 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.

3 RESULTS

XRD patterns of pyrolysed (SOC) samples are shown in Fig. 1. Crystallization of amorphous silica to form cristobalite was dominant process up to 1450°C. At 1550°C a noticeable peak of SiC appeared. The intensity of SiC peak increased at 1600°C with disappearance of silica peak. XRD patterns of pyrolysed (SOC + Co) samples are shown in Fig. 2. At 1300°C no SiC peak was observed. The cristobalite peak was very prominent. At 1400°C SiC peak appeared with decrease in the intensity of silica peak. The intensity of peak of SiC increased with increase in temperature.

The results of chemical analysis of pyrolysed (SOC) samples are plotted in Fig. 3(a). Though the XRD patterns did not show peak for SiC, a small quantity of SiC has formed in (SOC) at 1500°C. At 1550 and 1600°C considerable quantities of SiC has formed. From the plot in Fig. 3(b) it is clear that considerable quantity of SiC has formed in (SOC + Co) at a temperature as low as 1400°C.

Through SEM, the (SOC + Co) sample pyrolysed at 1300°C appeared unreacted. Whiskers were observed in the (SOC + Co) sample pyrolysed at 1400°C. At higher temperature (1550 and 1600°C) thick whiskers were formed. The maximum quantity of whiskers were observed in the (SOC + Co) sample pyrolysed at 1450°C with a heating rate of 200°C/min. No whiskers could be observed in the (SOC) samples up to a temperature of 1500°C. At 1550 and 1600°C whiskers were observed in the (SOC) samples, but the quantity of whiskers formed was quiet low.

4 DISCUSSION

During pyrolysis of RHs at higher temperatures four competitive processes, viz. crystallization of

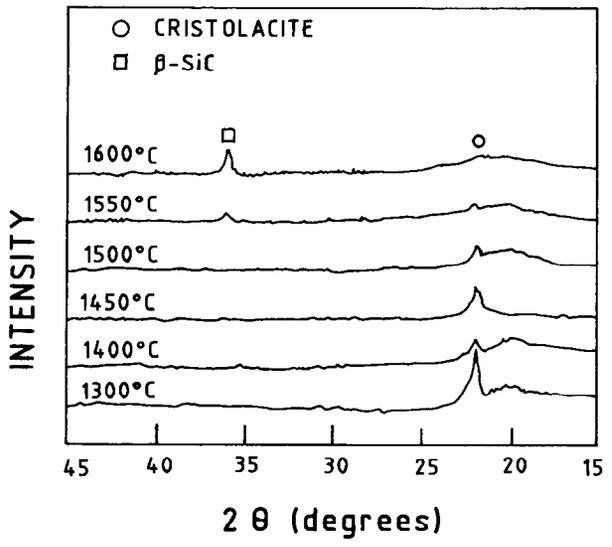

Fig. 1. XRD patterns of (SOC) pyrolysed at different temperatures.

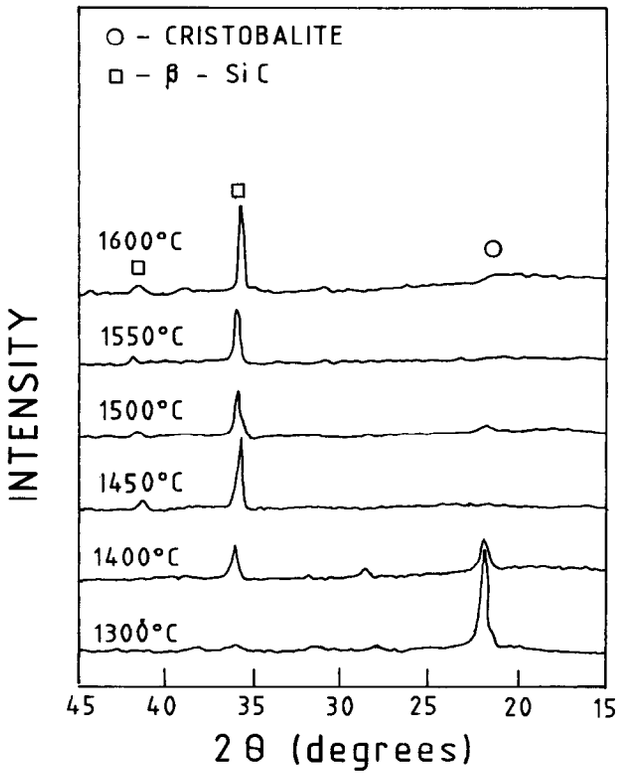

Fig. 2. XRD patterns of (SOC + Co) pyrolysed at different temperatures.

amorphous silica, crystallization of amorphous carbon, formation of SiC whiskers and formation of SiC particles, are simultaneously advancing.[19] At temperatures lower than that of SiC formation, the crystallization of silica was observed to be the dominant process. But no peak of crystalline carbon was observed in this work. This could be the result of rapid heating (200°C/min) and short dwell time of 20 min at pyrolysis temperature.

The intensity of SiC peak and the total SiC content in (SOC + Co) were higher than that in (SOC). Cobalt is known to diffuse into graphite and opens up the layers of graphite by channelling.[28,29] Cobalt acts as a strong catalyst to the gasification of carbon.[29,30] The increase in gasification rate is attributed to increase in surface area of carbon.[31] The total porosity and adsorption capacity of carbon in (SOC + Co) could be high because of channelling effect and high rate of gasification. The reaction scheme of formation of SiC from silica and carbon can be written as

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

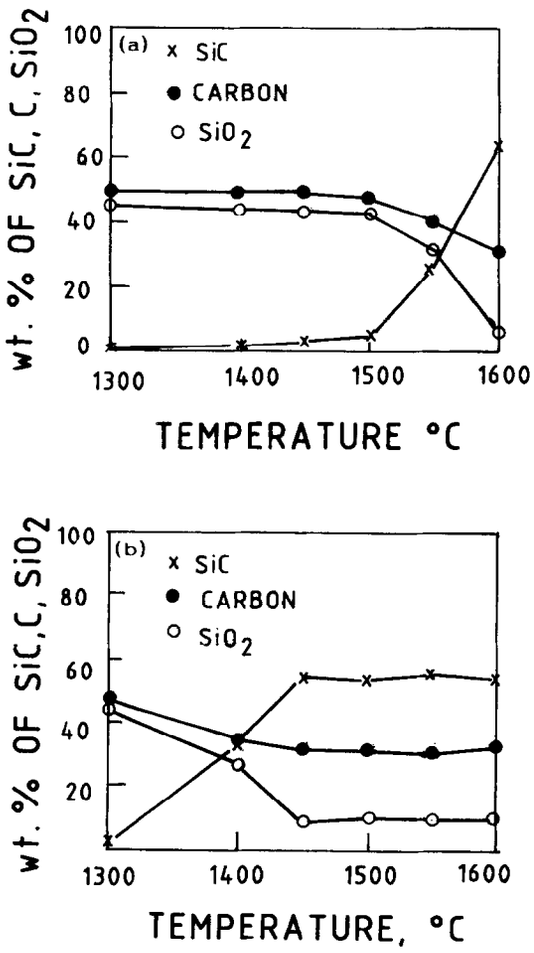

Fig. 3. Analysis of reaction product from (a) (SOC) and (b) (SOC + Co).

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

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

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

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

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). Due to the high rate of gasification, reactions (4) and (5) are more favourable in (SOC + Co). The SiO formed by reaction (1) or (4) could be adsorbed by carbon and form isometric SiC particles.[18] The carbon in (SOC + Co) could adsorb larger quantity of SiO than that in (SOC). Therefore, the formation of SiC was very rapid in (SOC + Co).

SiC whiskers are likely to form when SiO released by reaction (1) or (4) is redeposited on carbon substrate. This depends on the rate of SiO deposition and the temperature of carbon substrate for reaction (2).[19] The formation of SiC whiskers has been considered to occur by vapour phase reaction mechanism.[32]

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

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

In (SOC + Co), reaction (6) is favourable because of the high rate of gasification of carbon. Even small quantity of SiO released can form whiskers according to reaction (6). Though large quantity of SiO could be released in (SOC), its high rate of deposition at high temperature (1550–1600°C) and low availability of CO can lead to its conversion to particulate type of SiC through reaction (2). So the whisker type of SiC formed in (SOC) was low. Thus this work clearly shows that the formation of SiC whiskers upon rapid heating was higher in (SOC + Co) than in (SOC).

5 CONCLUSIONS

Cobalt has been shown to accelerate the formation of total SiC in rice husk silica–carbon black mixture. Without any catalyst, rapid heating has resulted in the formation of SiC particulates. In the presence of cobalt catalyst, rapid heating has been shown to form larger quantities of SiC whiskers.

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