Synthesis of Silicon Carbide Nanowhiskers from Coconut Fibres and Sol-Gel Derived Silica

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Abstract

Silicon carbide whiskers (SiC_w) having the diameter in the range of 20-80 nm were synthesised from coconut fibres through sol-gel process. The coconut fibres were impregnated with tetraethoxysilane and methyltriethoxysilane derived sol and pyrolyzed at 1400°C in argon. X-ray of the pyrolyzed samples showed the formation of β-SiC.

1. Introduction

Silicon carbide whiskers are an important class of reinforcing materials for the development ceramic and metal matrix composites (CMC, MMC) like SiC-Si_3N_4, SiC-SiC and SiC-Al, because of their high strength, stiffness and thermal stability [1, 2]. SiC is preferred in place of carbon fibres as reinforcing materials for the development of MMC since it does not react with metals to form metal carbides during the processing of the composites [3]. The composites made with SiC_w are expected to enhance their mechanical properties since the applied load is transferred to SiC_w, resulting in shear type failure instead of catastrophic failure. These unique properties of SiC_w initiated extensive research on their synthesis.

SiC_w are generally synthesized by chemical vapor deposition and carbothermal reduction of silicon containing compounds [4-10]. Synthesis of SiC_w using rayon fibres and activated fibres as carbon source and sol-gel derived silica and silicon monoxide-silica mixtures as silicon sources have been reported [11-13]. SiC_w are also synthesized from agro-wastes like rice husks and coconut shell which contain silica and carbon in their structure [14-18]. Since coconut is grown in many coastal areas of India, efforts were made in the present investigation to synthesize silicon carbide whiskers from coconut fibres by impregnating them with sol-gel derived silica.

2. Experimental

2.1. Preparation of sol-gel silica impregnated coconut fibres

The coconut fibres were used as a source of carbon and tetraethylorthosilicate (TEOS) and methyl tri-ethoxysilane (MTEOS) were used as source of silica. The silicon alkoxide were mixed with water and alcohol in 1 : 4 : 4 ratio and stirred for about 5 h using a magnetic stirrer to get silica sol. The coconut fibres were cut into pieces and soaked in the silica sol keeping the weight ratio of silicon alkoxides-to-coconut fibres as 1 : 1 and dried at 60°C to obtain coconut fibres impregnated with silica.

2.2. Estimation of carbon and silica in the precursors

The coconut fibres were carbonised (heat-treatment temperature, HTT = 1000°C) to estimate its carbon residue and silica content. The carbonised product which contained carbon residue and silica was oxidised in air at 700°C and the residue obtained after oxidation was treated with hydrofluoric acid to determine the silica content of the coconut fibres. The weight loss accompanying the oxidation of carbonised product gives the amount of carbon residue in the sample. The same procedure was repeated with coconut fibres impregnated with silica derived by the hydrolysis/poly-condensation of MTEOS and TEOS.

2.3. Carbonisation and carbothemal reduction of impregnated fibres

The silica impregnated coconut fibres with the TEOS and MTEOS were subjected to heat treatment (HTT) in argon atmosphere at 1000°C and the pyrolyzed product was oxidised at 700°C to determine the silica- to -carbon ratio which is crucial for the synthesis of silicon carbide from

carbon and silica. The carbonised product was further heated to 1400°C in argon gas using a heating rate of 100°C/h upto 1000°C and 30°C/h from 1000°C to 1400°C and soaking at 1400°C for two hours. The temperature for the synthesis was kept as 1400°C only because it was found by many researchers that at 1400°C, good quantity of whiskers could be formed and at temperatures higher than 1400°C, the formation of SiC particulate takes place [19]. The cooling of the pyrolyzed product was carried out in argon atmosphere.

2.4. Purification of pyrolysed product (HTT = 1400°C)

The pyrolysed product was oxidised in air at 800°C to remove excess carbon followed by hydrofluoric acid (48%) treatment to eliminate the traces of silica.

2.5. Characterization studies

The pyrolysed products were characterized by Scanning Electron Microscope (SEM, LEO-440). Transmission Electron Microscopy (TEM, Jeol JEM 2000 CX) with electron accelerating voltage 200 kV and by X-ray diffraction studies using D-8 Advanced Bruker powder X-ray diffractometer, using Cu K_α radiation ($\lambda = 1.5418$ A), to see the silicon carbide formation.

3. Results and Discussion

3.1. Chemical analysis of the precursor and the pyrolysed precursor

The carbon and the silica contents of coconut fibers were found to be around 30% and 3%, by weight respectively. The silica content in the coconut fibres is much less as compared to the carbon content and hence sol-gel silica was used to impregnate the fibres. Silica and carbon contents in the carbonised products were estimated and ratio of silica-to-carbon in these products was found to be as 1 : 6.

The weight percentage yield of SiC after the removal of excess carbon and silica from the pyrolysed product (HTT = 1400°C) was found to be around 30-40%.

3.2. X-ray analysis

The X-ray diffractogram of SiC_W derived from silica impregnated coconut fibres with MTEOS is shown in Fig. 1. The diffractogram clearly shows characteristic peaks at $2\theta = 35.7, 60.0$ and $72.0°$. The peaks at $2\theta = 22°$ (assignable to silica) indicates that the carbothermal reduction of silica is not complete in the present investigation, even though the silica-to-carbon molar ratio was adjusted to be more than 3. This incomplete carbothermal reduction explains the low yield of SiC (30-40%) in the pyrolysed product obtained in
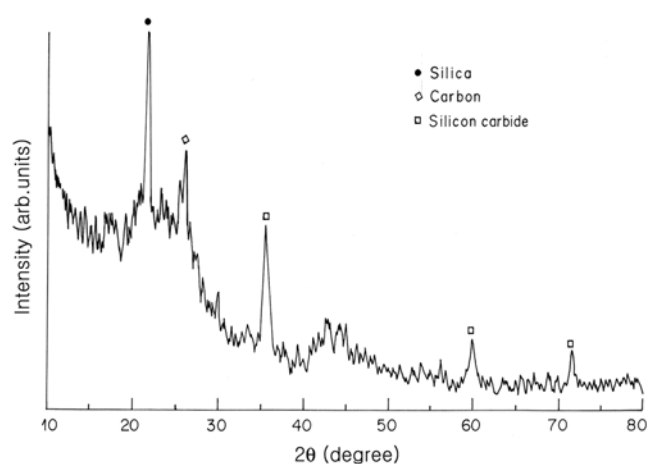

Fig. 1. X-ray diffraction pattern of the pyrolyzed product derived from silica impregnated coconut fibre with MTEOS.

the present investigation. The peak at $2\theta = 25°$ is due to the unreacted carbon obtained by heating coconut fibres in argon at 1400°C.

3.3. The SEM and TEM studies

The SEM micrographs of the pyrolyzed products are shown in Fig. 2. The micrographs reveal the formation of SiC_W. The whiskers appear to be fine, needle like and curved and hence may be less stable compared to straight whiskers when incorporated in composites, because curved whiskers cannot be processed at temperatures higher than 1800°C [20]. It is also seen from the micrographs that there are nodules in the whiskers, which are assigned to unreacted silica. This observation agrees with the results of X-ray studies where peak due to silica was observed. This observation also supports the low yield of SiC in present investigation.. The earlier work on the synthesis of SiC_W from rayon fibres, impregnated with sol-gel derived silica showed that the whiskers grew from the surface of the carbonised fibres but in the present study, the same is not observed [11]. Instead, it appears that the fibres are not able to keep their identity on heat-treatment as seen in the SEM micrographs of the carbonised product (HTT = 1000°C) of silica impregnated coconut fibres (Fig. 3) and in the pyrolysed products (HTT = 1400°C) (Fig. 2), and hence the growth of the whiskers from the surface of the carbonised coconut fibres are not observed.

It is seen from the SEM micrographs that less whiskers are formed from coconut fibres impregnated with MTEOS as compared to the whiskers which were derived from coconut fibres impregnated with TEOS (Fig. 2b). This may be probably due to the alkyl group attached to the Si atom in MTEOS. The CH_3 group in MTEOS (I) remains as such during the hydrolysis/condensation and results in the formation of sol-gel silica network (II). The carbon of CH_3 which is
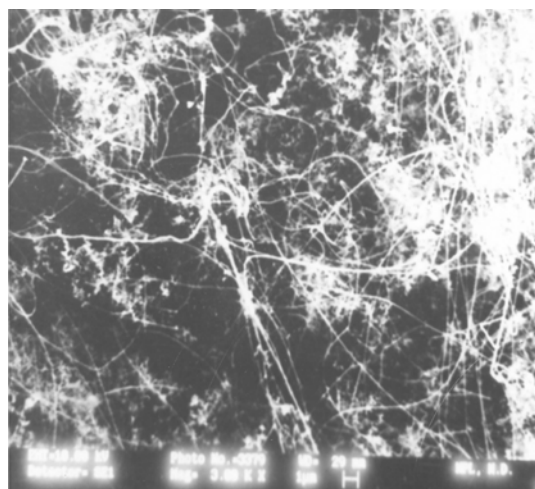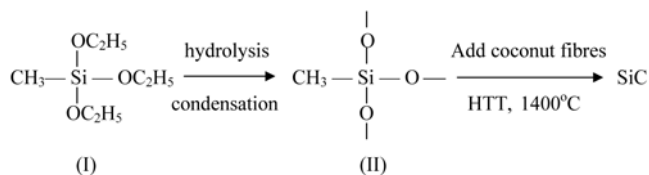
(a)
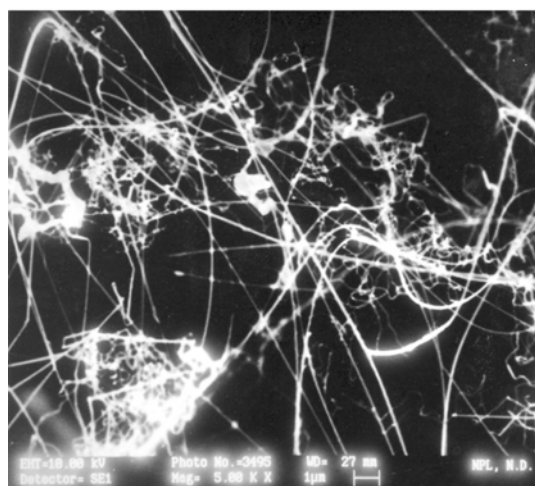
(b)

Fig. 2. Scanning electron micrographs of the pyrolyzed (HTT = 1400°C products derived from (a) silica impregnated coconut fibres with MTEOS (b) silica impregnated coconut fibres with TEOS.

linked to Si in the sol-gel derived silica remains intact [11, 21-23] when heated to 1400°C in argon gas to give Si—C linkage and the O in Si—O is replaced by carbon present in coconut fibres during the carbothermal reduction of silica to give SiC.

(I)   (II)

The SiC formed by the retention of carbon of CH_3 linked to silicon in the silica gel obtained by the hydrolysis/poly-
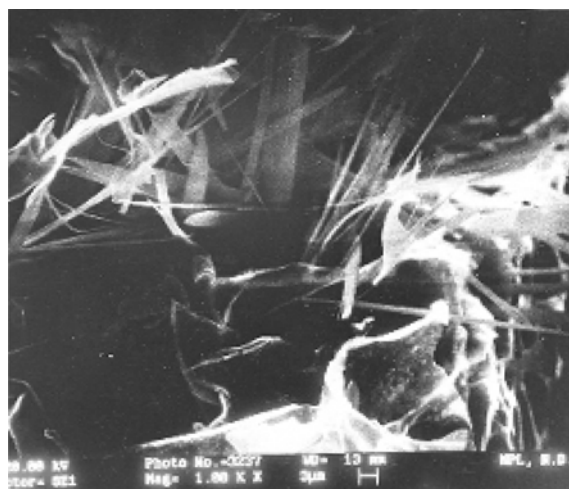

Fig. 3. Carbonised product (HTT = 1000°C) of silica impregnated coconut fibres.

condensation of MTEOS is probably in the particulate form in the present investigation.

The TEM photographs of the pyrolyzed products obtained from the silica impregnated coconut fibres with TEOS and MTEOS are shown in Fig. 4(a-c). The micrograph of whiskers prepared by taking coconut fibres and TEOS (Fig. 4a) show whiskers with varying diameter between 20-80 nm and the average diameter was found to be around 50 nm. The whiskers show a compartmental structure, repeated in length, which is similar to bamboo like structure normally present in whiskers.

The high magnification TEM of the sample derived from silica impregnated coconut fibres with MTEOS show individual whiskers having the diameter in the range of about 35 and 70 nm (Fig. 4b). These whiskers also show compartmental structure with regular periodicity, which may be attributed to the stacking fault in the structure. Silicon carbide whiskers are known to have stacking faults, which increase with decreasing diameter of the whiskers [24]. Since the nano-whiskers have the diameter in the range of 20-80 nm, they are expected to exhibit stacking faults.

A selected area diffraction pattern (Fig. 4c) recorded from the cluster of whiskers present in the microstructure of SiC derived from silica impregnated coconut fibres with MTEOS showed a ring pattern. The indexing of the electron diffraction rings of different diameter revealed that the whiskers have β-SiC face centered cubic cell of lattice parameter, a = 4.35 Å.

3.4. Carbothermal reactions

The formation of whiskers in the present investigation is made possible because of the closeness between silica and carbon, which are produced in-situ during the pyrolysis of coconut fibres impregnated with sol-gel derived silica. Further,
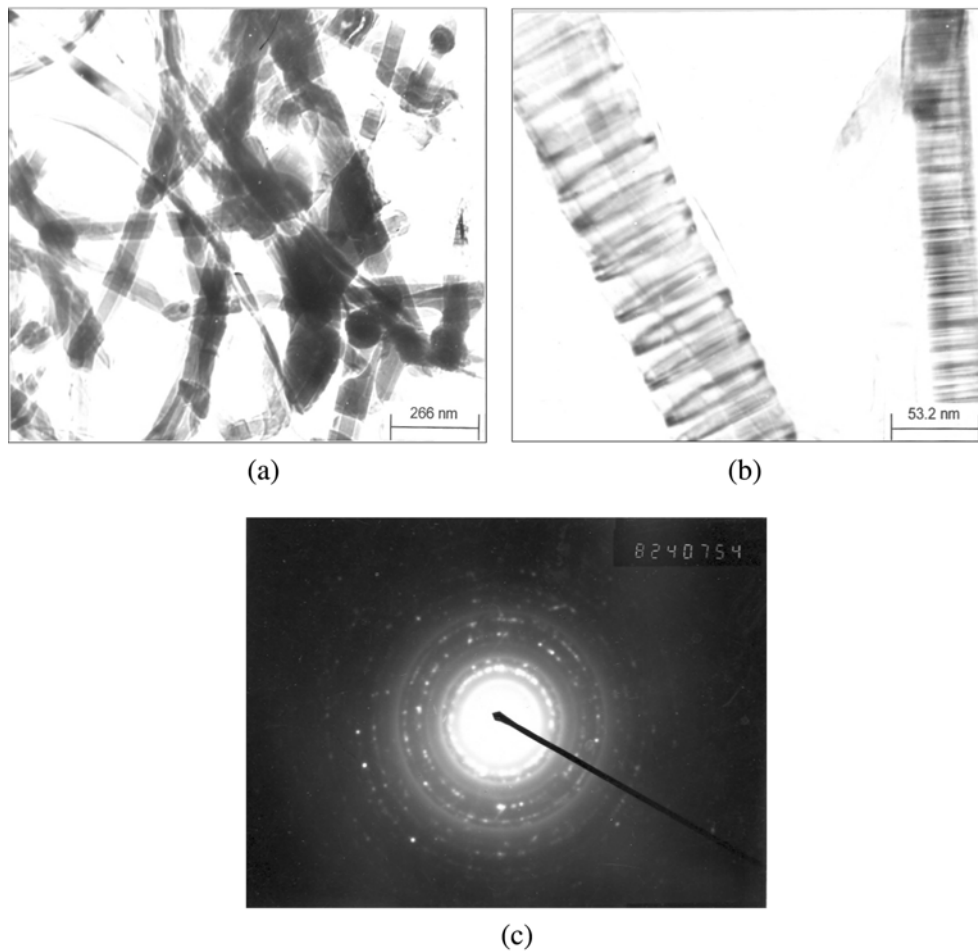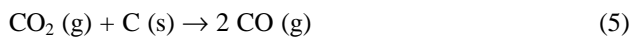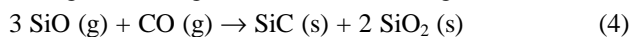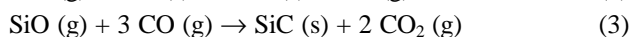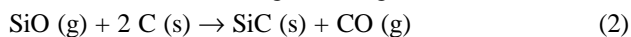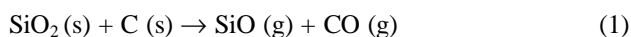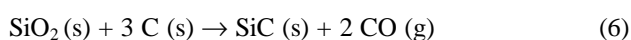
(a)

(b)

(c)

Fig. 4. Transmission electron micrographs of the pyrolyzed (HTT = 1400°C) products derived from (a) silica impregnated coconut fibres with TEOS (b) silica impregnated coconut fibres with MTEOS (c) selected area diffraction pattern of SiC_W synthesised from silica impregnated coconut fibres with MTEOS.

the sol-gel process has helped in bringing silica and carbon together because the coconut fibres could be impregnated effectively with the sol, which is in the liquid form. The carbothermal reduction of silica takes place through the following reactions.

$$SiO_2 \,(s) + C \,(s) \rightarrow SiO \,(g) + CO \,(g) \qquad (1)$$
$$SiO \,(g) + 2 \,C \,(s) \rightarrow SiC \,(s) + CO \,(g) \qquad (2)$$
$$SiO \,(g) + 3 \,CO \,(g) \rightarrow SiC \,(s) + 2 \,CO_2 \,(g) \qquad (3)$$
$$3 \,SiO \,(g) + CO \,(g) \rightarrow SiC \,(s) + 2 \,SiO_2 \,(s) \qquad (4)$$
$$CO_2 \,(g) + C \,(s) \rightarrow 2 \,CO \,(g) \qquad (5)$$

The overall reaction is

$$SiO_2 \,(s) + 3 \,C \,(s) \rightarrow SiC \,(s) + 2 \,CO \,(g) \qquad (6)$$

Reaction (1) is the rate-controlling step and it is an important step because it initiates the process [16, 25]. The sol-gel process adopted in the present investigation makes the reaction faster than the reaction between silica and the carbon powders, which are generally used in the carbothermal reduction of silica because the nanoparticles of silica are synthesised through sol-gel technique [26] and hence can react faster than the macro/micro particles of silica. Further, the silica obtained through sol-gel process led to the formation of SiC at 1400°C without employing any catalyst since it can react effectively with carbon due to its small size. The impregnation of coconut fibres with silica was made easy through sol-gel technique because sol, which is in liquid form could be absorbed by the fibres. The alkyl group in MTEOS also helps in the carbothermal reduction of silica because the carbon produced during the heating of MTEOS derived gel according to the following reaction [27]

$$\equiv Si - CH_3 + \equiv Si - CH_3 \rightarrow \equiv Si\text{–}CH_2\text{–}Si\equiv + C + 2H_2$$
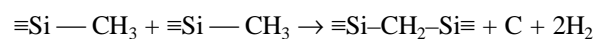
is expected to be amorphous carbon which helps in the formation of carbon monoxide (CO) as explained in equation 5 and CO is an important component in the carbothermal reduction of silica as seen from equations 3 and 4.

4. Conclusions

The present investigation shows that coconut fibres, an agro-waste can be effectively impregnated with silica using silicon alkoxides and pyrolyzed at 1400°C to get needle like fine silicon carbide whiskers having diameter in the range of 20–80 nm. The sol-gel technique, adopted in the present investigation helped in bringing carbon and silica in close contact, which resulted in the formation of SiCw at 1400°C without employing catalysts.

Acknowledgements

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