Formation of Silicon Carbide Whiskers from Organic Precursors Via Sol-Gel Method

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Abstract

Silicon Carbide (SiC) was synthesized by carbothermal reduction of silica precursor and carbon precursor. The silica precursor was obtained from tetraethoxysilane. Sucrose was used as carbon source. Tetraethoxysilane (TEOS) was hydrolyzed in acidic water (pH= 2). The molar ratio of TEOS-H2O-EtOH was taken as 1:8:2 in the sol-gel processing. Hydrolysed silica sol was polymerized with sucrose to incorporate carbon precursor into the silica network. The gel thus obtained was dried in an oven at 70oC and at 100oC. The solid mass obtained on drying was heat treated at 1000 °C in nitrogen atmosphere to obtain the black glass. It was characterized by FTIR, SEM and TGA. The black glass was further heated to 1500oC in argon to yield silicon carbide. this resulted in formation of β-SiC whiskers.

Introduction

Silicon carbide is probably the most widely used nonoxide ceramic material with attractive properties such as excellent mechanical strength chemical inertness and conductive thermal properties [1-3]. As a catalyst support, silicon carbide has application in several chemical reaction such as isomerization of linear saturated hydrocarbons [4], oxidation catalyst [5], selective oxidation of hydrogen sulfide into elemental sulfure [6], photo catalyst reaction [7]. Ledoux and co-workers developed a shape memory synthesis method to prepare porous silicon carbide materials [8-10] in which porous silicon carbide were produced by the reaction of gaseous silicon monoxide and the porous carbon template at temperature of 1200-1500 °C. Jinand Guo [11] prepared silicon carbide with surface area of 112 m²/g at temperature of 1250 °C by sol-gel method using Tetraethoxysilane as silicon source and self-prepared phenolic resin as carbon source and nickel nitrate as pore adjusting agent. Silicon oxycarbide (SiOC) are commonly known as Black Glasses. These are formed as an intermediate during low temperature carbothermal reduction reaction between silica and carbon precursors. At high temperature (T > 1300 °C) during carbothermal reduction, SiOC glasses undergo a phase separation leading to the crystallization of nano-sized SiC in an amorphous SiO_2 matrix [1,12-13]. In the same temperature range, a decomposition process may be active leading to the evolution of gaseous species and to a subsequent deterioration of the mechanical properties.

Manocha, et.al [14] reported studies on synthesis of black glass using sol–gel route with unmodified silicates as source for silicon and carbonaceous monomers as source for carbon. Following this route, the purpose is to introduce carbon containing organic groups in the molecular chain at the sol level during hydrolysis of TEOS and subsequent pyrolysis at different temperatures to give carbidic glass. Milonji, et.al [15] prepared SiC from silica sol with saccharose or activated carbon as external carbon sources. The effect of boric acid presence in the system on the surface characteristics of the SiC powders obtained has also been studied.

Experimental

Sol-gel processing and synthesis of SiC

TEOS was hydrolyzed with acidified water in presence of methanol solvent instead of ethanol (TEOS: H_2O: Methanol:: 1:8:2) (SSC1.25MeOH). Sucrose solution in water was added to silica sol. The TEOS: Sucrose molar ratio was taken as 1:1.25. Stirring was continued up to gellation. The product

was dried at 100 °C and cured at 180 °C. The resulting solid mass was heated to 1000 °C and 1550 °C in inert atmosphere.

In another set of experiments TEOS was hydrolyzed with acidified water in presence of ethanol (TEOS: H$_2$O: Ethanol:: 1:8:2) (SSC 1.25, SSC 1.25b, SSC1.25c) Sucrose solution was added in the silica sol. The TEOS: Sucrose molar ratio was kept as 1:1.25 like in previous. The gelled mass was dried at 100 °C, cured at 180 °C. Followed by heat treatment at 1000 °C and 1550 °C in inert atmosphere.

The products obtained were heated in air to remove excess carbon and treated with dilute Hydrofluoric acid to remove excess silica.

Characterization

The weight changes during pyrolysis in nitrogen were studied using Mettler Thermal Analysis system TA4000. The IR spectra were recorded using KBr pellet method on shimadzu made IR analyser (FT-IR 8300). X-ray diffraction studies were made on powdered samples using Rigaku X-ray diffractometer. CuKα radiation was used as an X-ray source. The microstructure of the samples was studied using scanning electron microscopy (Hitachi S3000N).

Results and Discussion

The dried gel samples were pale yellow in colour. The colour changed from pale yellow to brown to black with increase in temperature. On pyrolysis at 1000 °C, all samples resulted in fragmented,

shinning black, brittle and hard materials. Unreacted silica and carbon are also present in the samples. On further heating to 1550 °C, the material turned to black lump with outer surfaces green in colour. The green colour is due to the formation of silicon carbide whiskers and black lump is due to the formation of crystalline silicon carbide.

IR studies on Gelled and Pyrolysed Samples

The chemical transformation was studied using FTIR. This gave information about the backbone structure of siloxanes network as well as the organic group attached to it.

Figure 1 shows the IR spectra of dried silica gel, from this spectra we confirmed that the broad band around at 1000-1200 cm^{-1} is due to the formation of silica (-O-Si-O-) and another broad band around at 3200-3600 cm^{-1} is due to the Si-OH stretching frequency and O-H stretching frequency present in the sample. The peak at 960 cm^{-1} is assigned to Si-OH (or -OEt) stretching. The peak at 1600 cm^{-1} and 2360 cm^{-1} might be due to C-O stretching frequency corresponding to the moisture present in the sample. The bands at 457 cm^{-1} suggest the formation of ring structure of SiO$_4$ tetrahedron.

Fig 2 shows the IR spectra of co-polymers heated at 1000 °C. The broad band around 1000-1200 °C disappeared because there is reaction between silica and carbon precursors, but some of the free silica is present in the sample. The peak at 1080 cm^{-1} is due to the Si-O vibration in Si-O-Si. A peak at 820 cm^{-1} along with that at 670 cm^{-1} suggest that at least some of the silicon atoms are bonded to carbon atoms. The peak at 960 cm^{-1} is assigned to Si-OH (or -OEt)
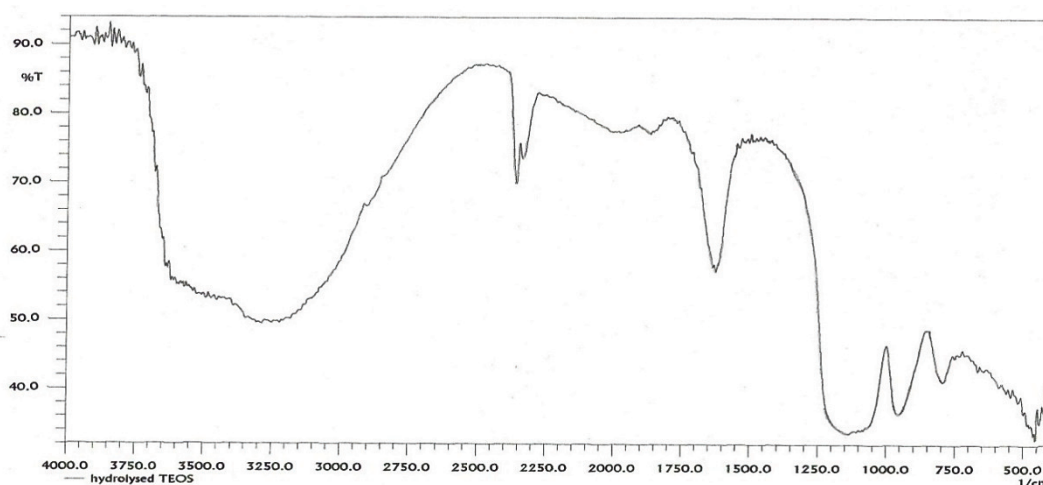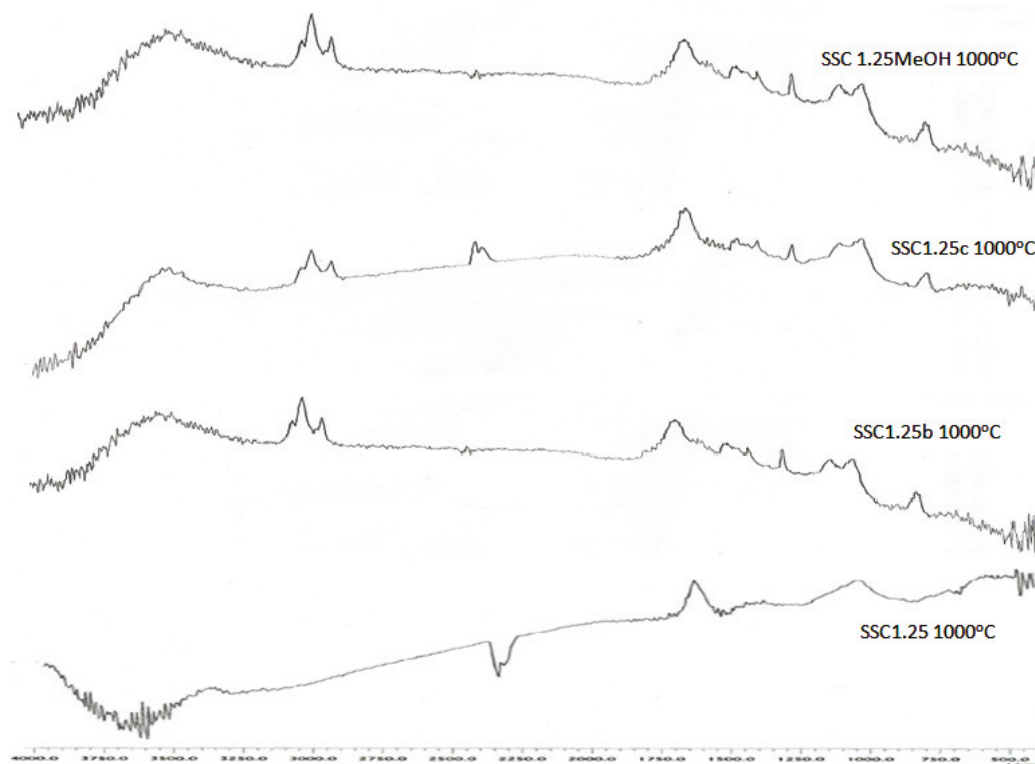

Fig. 1. IR spectra of dried silica

Fig. 2. IR spectra of a) SSC 1.25, b) SSC 1.25b, c) SSC 1.25c and d) SSC 1.25MeOH co-polymer heated at 1000 °C.
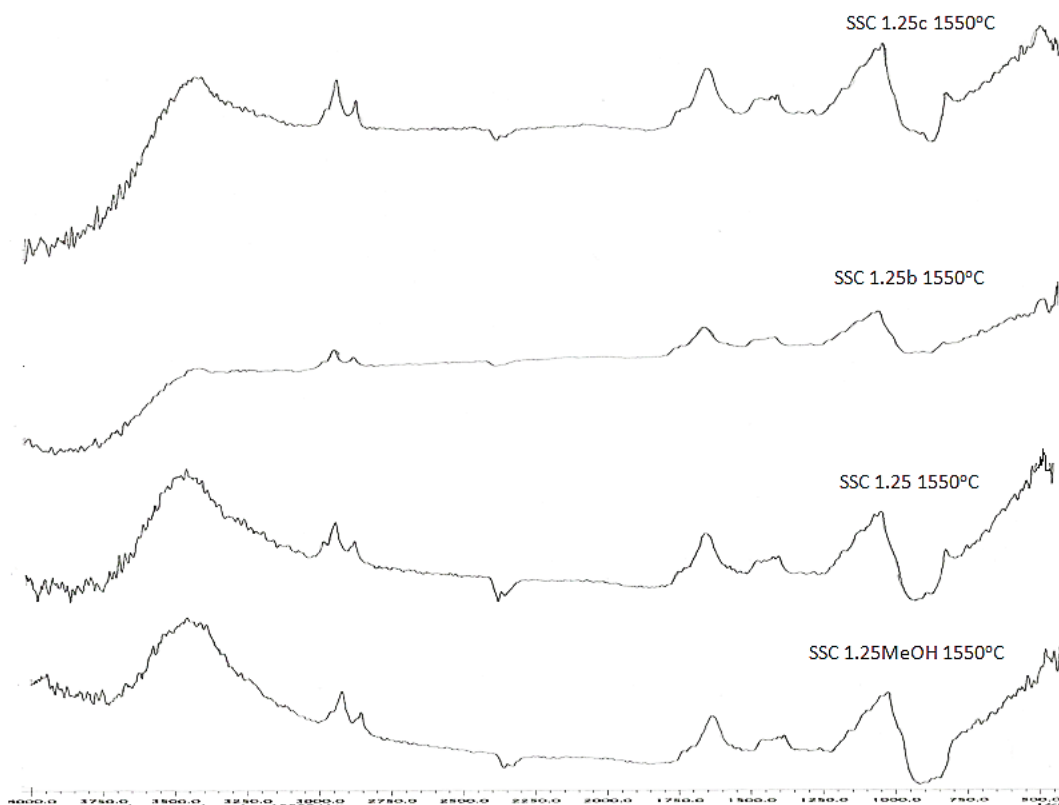

Fig. 3. IR spectra of a) SSC 1.25MeOH, b) SSC 1.25, c) SSC 1.25b and d) SSC 1.25c co-polymer heated at 1550 °C.

stretching. The peak around at 2900 cm^{-1} is due to the methylene group (–CH$_2$- strong asymmetric stretching) in organic molecule (*i.e.* sucrose molecule). The peaks between at 3200-3600 cm^{-1} are assigned to absorbed water and silanol groups present in all the samples. There is evidence of C-O bonds in heat treated samples which have vibrational bands between the ranges 1600-1800 cm^{-1}.

Figure 3 also shows the IR spectra of co-polymers heated at 1550 °C. On pyrolysis of the samples to 1550 °C, the bands at 960 cm^{-1} disappeared while those at 457 cm^{-1} suggest the presence of some amount of SiO4 tetrahedron. The peaks at 669 cm^{-1} and 850 cm^{-1} are due to the Si-C bonding. A small peak at 2920 cm^{-1} is observed in the pyrolysed samples. These may be due to the carbonaceous materials (*i.e.* C-H bonding in methylene group) as a result of cracking of hydrocarbon group in sucrose. From this IR spectrum, we confirmed that a small proportion of free carbon and free silica are present in the sample.

Thermal analysis of Pyrolysed samples

Figure 4 shows TGA curves in nitrogen of the dried sample of silica gel. In the case of silica gel, it exhibits weight loss mainly in two temperature ranges. Major weight loss occurs in the first temperature range up to 400 °C. This is attributed to evolution of absorbed water, residual solvents and on-going condensation reaction amongst silanol groups.

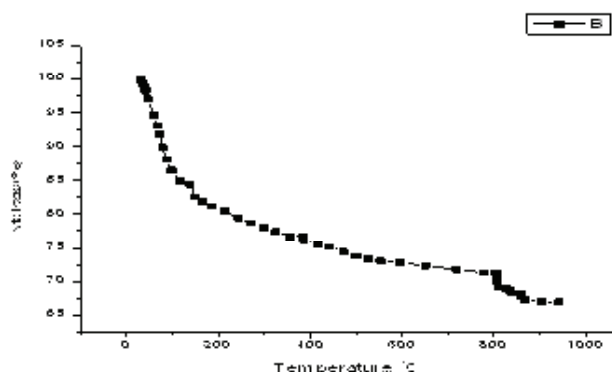Fig. 4. TGA graph of dried silica gel

The second weight loss is observed in the temperature range 700-900 °C, which is due to the sintering of material to a compacted silica structure. In case of hybrid organic-inorganic gels *i.e.* Fig 5 and 6 the TGA graphs of co-polymers at 1550 °C and 1000°C respectively The first weight loss was observed at 50-100 °C, is attributed to evolution of

absorbed water and others volatiles. And the second weight loss was observed at 500 °C, is attributed to excess carbon present in the samples after heating at 1000 °C and 1550 °C. After removing free carbon, there is a presence of free silica and silicon carbide (Table.1).
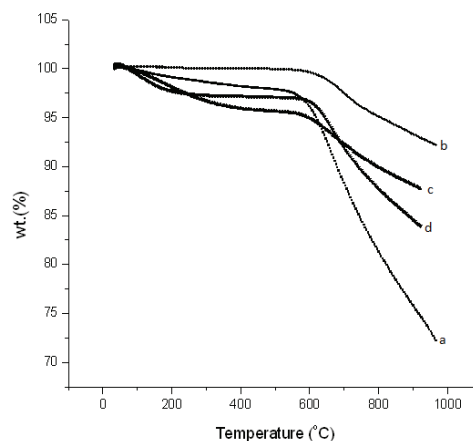

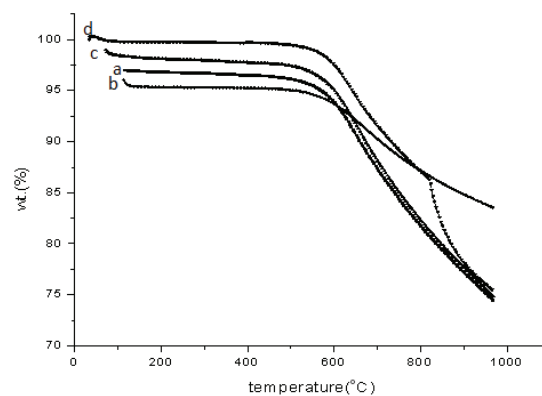Fig. 5. TGA graph of a) SSC 1.25c b) SSC 1.25b, c) SSC 1.25 and d) SSC 1.25MeOH co-polymer heated at 1000 °C.

Fig. 6. TGA graph of a) SSC 1.25MeOH, b) SSC 1.25, c) SSC 1.25b and d) SSC 1.25c co-polymer heated at 1550 °C.

Table 1
% of free silica, free carbon and silicon carbide of the sample SSC1.25MEOH, SSC1.25b, SSC1.25c and SSC1.25 after heated at 1550 °C

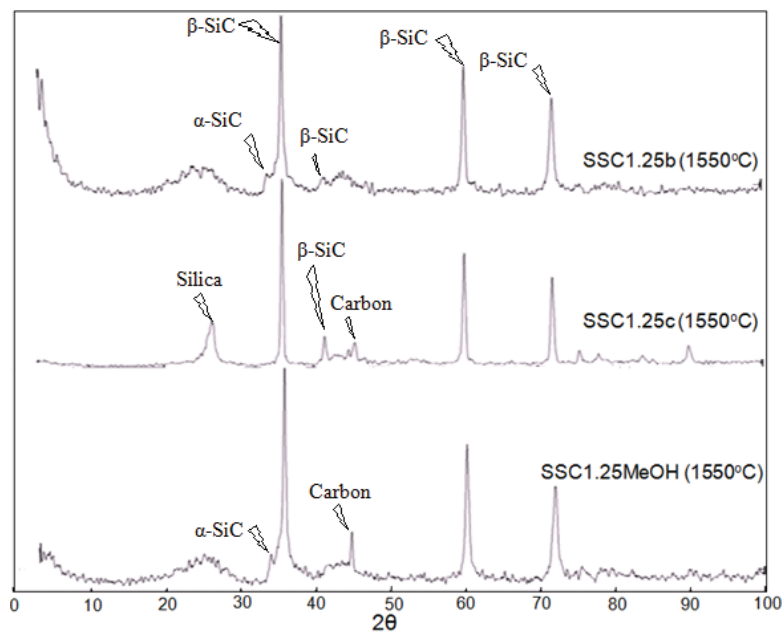| Sample Name	% of Free Silica	% of Free carbon	% of silicon carbide
SSC1.25MeOH	17.2	25.53	57.27
SSC1.25b	13.66	25.13	61.21
SSC1.25c	09.27	24.5	66.23
SSC1.25	16.64	16.45	66.91

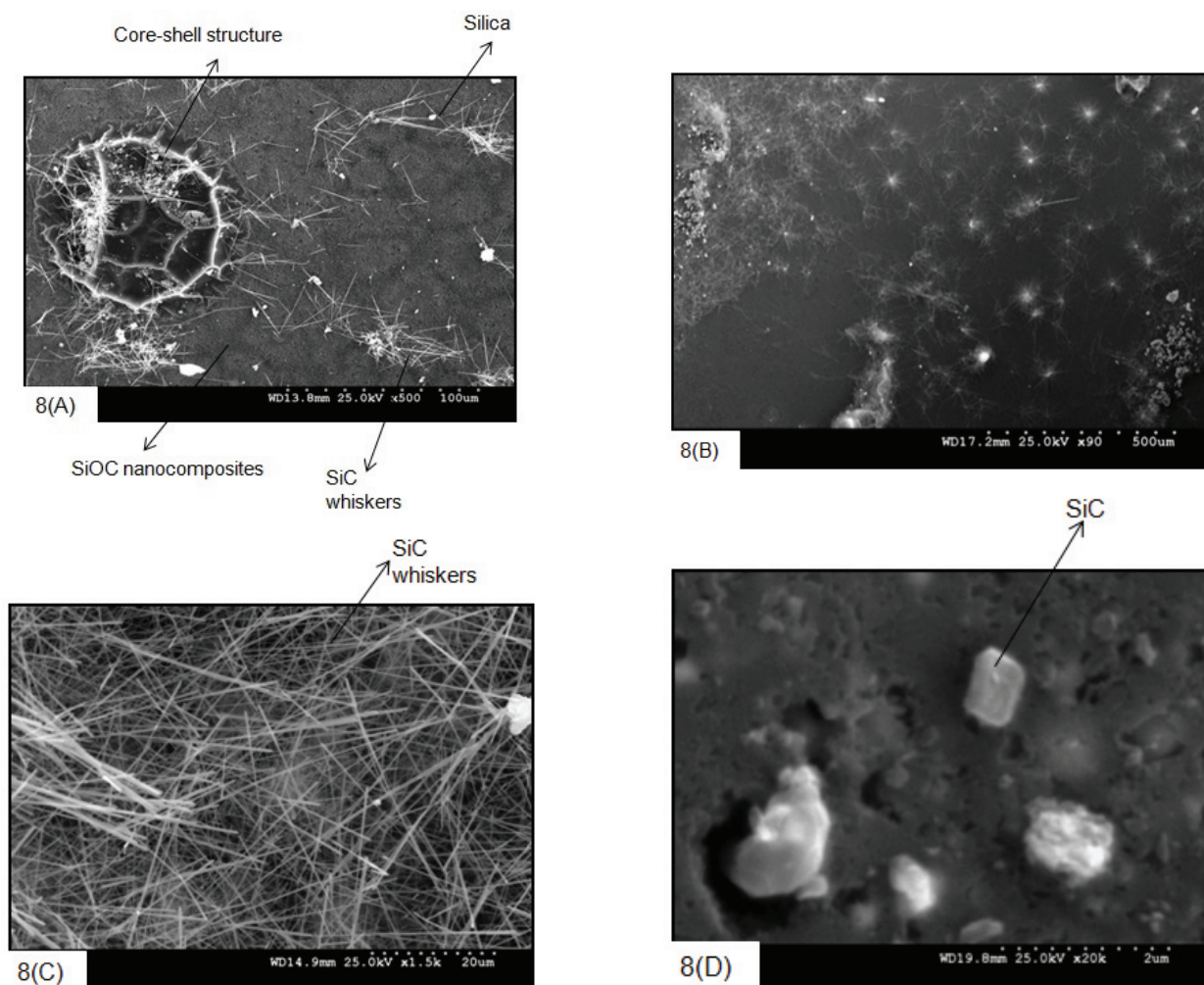Fig. 7. XRD graph of SSC 1.25b, SSC 1.25MeOH at 1000 °C and 1550 °C

Fig. 8. A) is of SSC 1.25, 8(B) is of SSC 1.25 MeOH, 8(C) is of SSC 1.25 b, 8(D) is of SSC 1.25 c at 1550 °C
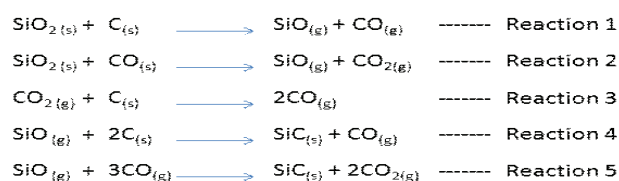
XRD Studies

Figure 7 shows XRD scans of the pyrolysed samples of sucrose-TEOS co-polymers. The powder X-ray diffractogram of black glass obtained at around $2\theta = 22°$ (d= 0.35-0.45 nm) characteristic of an amorphous silicate structure. Unordered carbon also exhibits similar broad band in this range. Therefore, the broad band at 2theta = 22° at 1000 °C may be due to combined amorphous carbon and amorphous silica structures and hence of siliconoxycarbide family. XRD of the samples heated at 1550 °C shows development of crystalline phases in amorphous black glass. The major peaks of the samples at diffraction angles $2\theta = 35.7°$, 41.4° 60.1°, 71.9°, 75.4°, 90° are attributed to the (111), (200), (220), (311), (222), (400) planes of the cubic β-SiC phase. At the same time shoulders near the (111) plane of β-SiC ($2\theta = 35.7°$) indicate the existence of the hexagonal polytypes α-SiC.

Surface Morphology Studies

Figure 8 is SEM micrograph of samples heat treated at 1550 °C. It shows sample is covered by SiC whiskers and small amount of crystalline SiC particle as well as carbon. But after removing free carbon (Fig. 9), SEM graphs show the crystalline SiC particle present in the inner side of the sample. From this fig. 9 we concluded that there is formation of SiC whiskers and crystalline SiC particle and also there is a small proportion of free carbon and free silica. The diameter of SiC whiskers is about ~100 nm.

Some micro cracks are also found on the carbon shell of carbonized powder. These pores may be caused by the large amount of gas produced in the decomposition of sucrose resin shell at 300-450 °C in N_2 atmosphere. When this process is finally finished, the sucrose shell of precursor powder is completely converted into carbon. The powder / whisker ratio as well as whiskers morphology can be explained via the conventional vapour-liquid-solid (VLS) mechanism, in which the suggested reactions listed below, take place. Firstly, SiO_2 component was reduced by carbon (carbon network from sucrose) to generate the gaseous components, SiO and CO (Reaction 1). CO, the product of the first step, can also react with SiO_2 to form gaseous SiO and CO_2 (Reaction 2). Then CO_2 reacted with the surrounding carbon network to produce CO according to Reaction 3. Finally the ultimate product, β-SiC, was obtained from the gaseous SiO, CO and the carbon network through the Reaction 4 and 5. All these reactions can make a circle to continue the synthesis process from the starting steps.

$$SiO_{2(s)} + C_{(s)} \longrightarrow SiO_{(g)} + CO_{(g)} \quad \text{------- Reaction 1}$$

$$SiO_{2(s)} + CO_{(s)} \longrightarrow SiO_{(g)} + CO_{2(g)} \quad \text{------- Reaction 2}$$

$$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)} \quad \text{------- Reaction 3}$$

$$SiO_{(g)} + 2C_{(s)} \longrightarrow SiC_{(s)} + CO_{(g)} \quad \text{------- Reaction 4}$$

$$SiO_{(g)} + 3CO_{(g)} \longrightarrow SiC_{(s)} + 2CO_{2(g)} \quad \text{------- Reaction 5}$$

The overall reaction is as follows

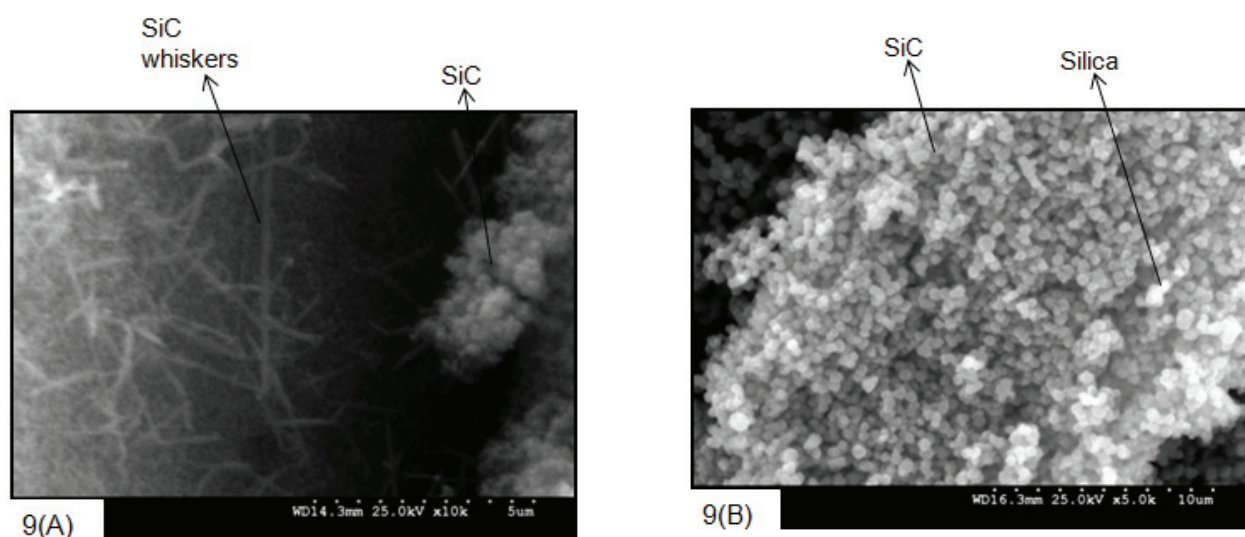$$SiO_{2(s)} + 3C_{(s)} \longrightarrow SiC_{(s)} + 2CO_{(g)}$$

9(A)

9(B)

Fig. 9. (A), (B) is of SSC 1.25 and 9(C), (D) is of SSC 1.25b at 1550°C after removing free carbon

On the other hand, carbon particle obtained upon $C_{12}H_{22}O_{11}$ decomposition are at a molecular level comparable with silica particles. As a results much finer SiC powder are produced.

Conclusion

Silicon oxycarbide and silicon carbide are formed following organic-inorganic hybrid gels routes starting from unsubstituted silicate and carbon monomers. From Sol-gel process gives a wider scope to add carbon containing organic molecules in the silicate network structure at sol stage. The pyrolysis of such organic-inorganic gels occurs mainly over two temperature ranges characteristic of condensation reactions and decomposition/ rearrangement reactions in carbonaceous materials. At 1000 °C, the material is black shining brittle, hard glass. At 1550 °C, crystalline silicon carbide phase are found to be formed in the amorphous black glass, the extent of structure development being dependent on the ratio of the reactant, especially, Sucrose and TEOS ratio. The black material so obtained exhibits good resistance towards oxidation.

Acknowledgment

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