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SYNTHESIS AND CHARACTERIZATION OF SILICON CARBIDE NANO POWDER BY SOL GEL PROCESSING

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Abstract: *SiC nano particles with mono dispersed distribution were synthesized by using of silicon alkoxides and phenolic resin as starting materials. After synthesis of sample, characterizations of the obtained powder were investigated via Fourier Transform Infrared Spectroscopy (FTIR) with 400-4000 cm*$^{-1}$*, X-ray Diffractometry (XRD), Laser Particle Size Analyzing (LPSA), Si*^{29} *NMR analysis, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). FTIR and Si*^{29} *NMR results of the gel powder indicated that Si-O-C bonds were formed due to hydrolysis and condensation reactions . FTIR results showed a very strong peak for heat treated powder at 1500°C after carbon removal which is corresponded to Si-C bond. Obtained pattern from X-ray diffractometry showed that the final products contain* β*-SiC phase with poly crystalline planes and little amounts of residual carbon. PSA results showed that the average particles size were 50.6 nm with monosized distribution. Also microstructural studies showed that the SiC nano powders have semi spherical morphology with mean particles size of 30-50 nm and also there are some agglomerates with irregular shape.*

Keywords: *Nano materials; Particulates and Powders; Carbides; Nanostructures; Sol-gel Chemistry; Microstructure*

1. INTRODUCTION

Silicon carbide is one of the most important carbide materials because of its unique properties. Silicon carbide is known as an important non-oxide ceramic with high melting point (2827 °C), high hardness, high wear resistance, low thermal expansion coefficient, good chemical resistance and good thermal conduction in ceramic industry [1-3]. These properties make silicon carbide an attractive candidate material for many applications such as grinding materials, polishing paste, wear-resistant materials, catalyst supports, filters for molten metal or hot gases, high-temperature structural materials, and reinforcement in composites [4-8].

Industrially used low cost silicon carbides are produced by reactions between silica or silicon and carbon (usually cokes) at 1400 – 1800 °C. This process involves gas-solid reactions and produces coarse particles so that they must be ground and classified in required sizes. Even after such processing, the resulting silicon carbide powder is not adequate to the relevant application [9, 10]. To obtain high-performance SiC ceramics, powders with a narrow particles-size distribution are required [11].

Some of these methods have disadvantages. For example, CVD process is a high cost and low efficiency method and Si metals direct carbonization will leave high amount of impurities in final powder. So, using an appropriate method is required for SiC particles synthesis.

Sol Gel method has been established as a novel process for nano particles synthesis with several outstanding features, such as high purity [12], high chemical activity, improvement of powder sinterability, possibility for particles mixing at molecular scale and etc. A sol gel process using metal alkoxides has been widely applied for the synthesis of ideal powders; homogeneous, size and shape controlled [13]. Aelion et al. were among the first to investigate the kinetics of hydrolysis and condensation of TEOS. The rate and extent of the hydrolysis reaction were found to be influenced by the strength and concentration of the acid or base catalyst while temperature and solvent were of secondary importance [14].

The aim of this research is to produce the producing of nano sized silicon carbide powder by a novel sol gel chemical processing rout. In this study we developed a sol gel processing to produce phenolic resin-TEOS hybrid gel with hydrochloric acid (HCl) as the catalyst, and to synthesize SiC nano powder by carbothermal reduction of the obtained gel.

2. MATERIALS AND METHODS

The silicon source used in this research was tetraethyl orthosilicate (TEOS Merck) and the carbon source was phenolic resol (Resitan RIL 1002). Also ethanol (99.99% Merck) was used as solvent and hydrochloride acid (HCl 3.5% wt. Merck) as catalyst. The sol was prepared by mixing 20gr phenolic resin, 25 ml water and 15 ml ethanol and then 35 ml TEOS was added to solution. pH was controlled during mixing by gradually addition of 0.05 mole HCl as catalyst. Then the alcohol removed from sol by heating at 40 °C. During temperature increasing and aging due to the condensation phenomena the particles were joined together and formed polymeric gel containing siloxane bonds with carbonaceous phase in its structure. The derived gel was aged in oven for 24 hr at ambient temperature and was dried at 110 °C to form xerogel. The gel was pyrolized at 700 °C for 1 hr and then was heat treated at 1400 and 1500 °C in an electric furnace with Ar flow.

The FT-IR analysis was done by using SHIMADZU 8400s instrument at 400-4000 cm^{-1}. NMR results by the ^{29}Si MAS spectra were obtained using a 11.7 T Varian Unity 500 spectrometer with a 7 ms 90° pulse and a delay time of 60s. HORIBA LB550 instrument was used for particle size distribution measurements. All phase analyses were done by using X-ray PHilips xpert diffractometer with Cu-kα radiation (λ=1.45 A°). The formation and morphology of SiC nano particles were studied by LEO 1455VP scanning electron microscopy (SEM) and PHilips CM200 transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectrum of the gel powder. As it can be seen, a broad band at 3200 cm^{-1} corresponded to molecular water hydrogen-bonded to each other and to (Si-OH) groups. Siloxane bonds (Si-O-Si) which are formed by complete hydrolysis and condensation reactions of Silicon alkoxides are presented at 498, 800, 1090 cm^{-1}. The bands observed around 2920 cm^{-1}, (1200-1456) cm^{-1} and 1593 cm^{-1} respectively were related to (C-H) bonds of methylene, (C-C) and (C-O) bonds, and (C=C) double bonds as well as aromatic loops which all are corresponded to phenolic resin bonds. It is noteworthy that there is a peak related to (Si-O-C) bonds at 754 cm^{-1} which

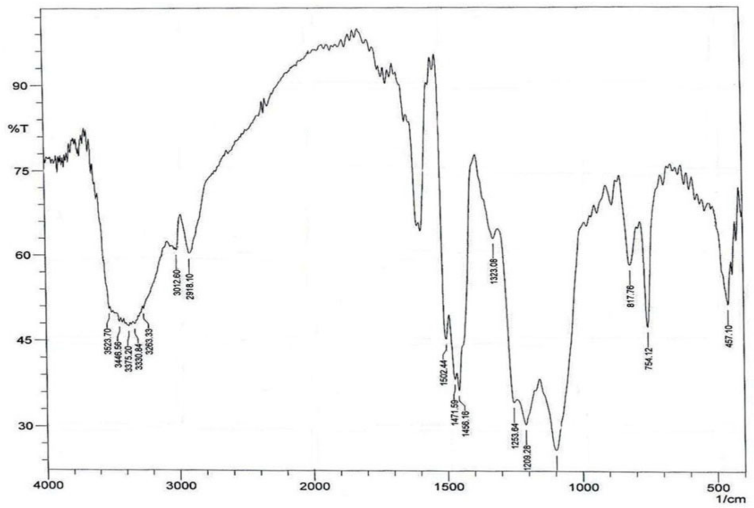

Fig. 1. FT-IR spectroscopy pattern of the Gel powder.

is formed from phenolic resin carbon atoms connections with hydrolyzed and condensed TEOS (Si-O) bonds at molecular levels [15].

In the current work, Si^{29} MAS NMR analysis was performed on samples which are shown in figure 2. Resonance peaks of gel powder containing carbon and silicon phases were examined during these analyses. These peaks were in the form of Q^n (n=2, 3, 4) in which n is the number of Si-O-Si bonds. In the other word, Q^n is microstructure of silicon atom in $Si(OSi)_n(OR)_{4-n}$ units which is $Q^2[Si(OSi)_2(OR)_2]$, $Q^3[Si(OSi)_3(OR)]$ and $Q^4[Si(OSi)_4]$. Also R is related to hydroxyl groups (OH^-) or methylene groups ($-C_2H_5$). Si^{29} MAS NMR will give a wide range signals between -75 and -125 ppm which are corresponded to three different part with chemical transmission amounts of about -90 to -98 ppm, -98 to -105 ppm and -105 to -115 ppm belong to Q^2, Q^3 and Q^4 regions. Figure 2 shows Si^{29} MAS NMR spectrum of synthesized gel powder in the presence or absence of carbon phase. As it can be seen, the present signal of Q^4 in figure 2-a is in the range of -111.1 ppm which exhibits a high resonance intensity and signifies large number of silicon bonds which are formed during gelation process.

In frequency ranges of -102.4 ppm and -92.3 ppm, Q^3 and Q^2 silicons are observed, respectively, which indicates that during condensation stage OH and methylene ($-C_2H_5$) bonds are still presented on the surface of siloxane bonds. Figure 2-b shows NMR spectrum resulted from TEOS xerogel containing carbon phase. As it is observable, the signal presented at -111.1 ppm was shifted to -108.6 ppm due to the presence of Q^4 structural units which is related to formation of Si-O-C complex bonds and their effects on $Si(OSi)_4$ chemical transmissions. This finding could also be supported by FTIR spectrum(see figure (1)). On the other hand, the decrease in peaks intensity of Q^2 and Q^3 structural units is also observable within the spectrum obtaind from the sample containing carbon phase. Hence, one can conclude that presence of carbon phase in sample could change xerogel structures containing $Si(OSi)_4$ during sol-gel process and, moreover, that carbon phase is incorporated into the $Si(OSi)_4$ structure at molecular level.

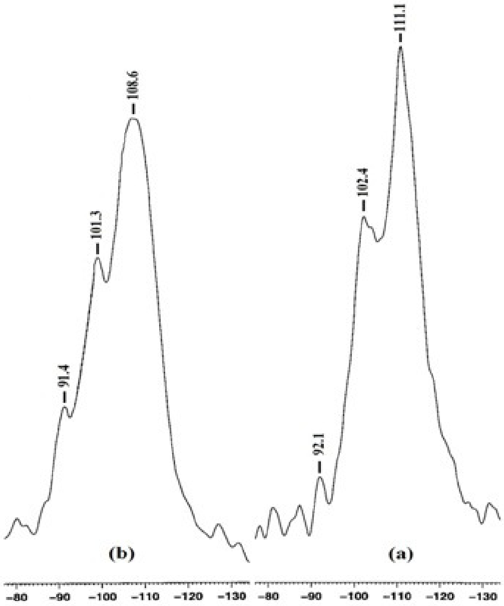

Fig. 2. ^{29}Si MAS-NMR spectra of the gel powder (a) without carbon phase and (b) with carbon phase

Figure 3 shows the X-ray diffraction patterns of powders heat treated at 700, 1400 and 1500 °C for 1 hr with a heating rate of 10 °C/min under Ar atmosphere. As it is observable in this figure, the

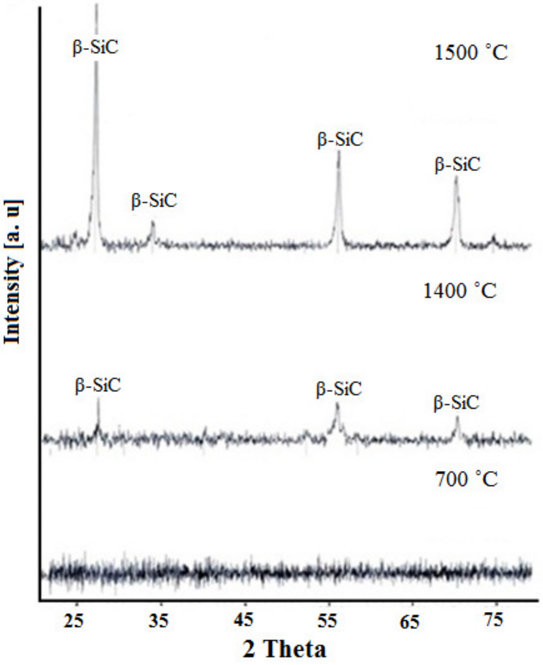

Fig. 3. X-ray diffraction patterns of powders heat treated at 700, 1400 and 1500 °C for 1 hr.

pyrolyzed gel at 700 °C for 1 hr is an amorphous siliceous structure contains carbon which called organic carbide glass. This product contains very high surface area powders which are SiC nanosize precursors. After heating at 1400 °C, the β-SiC nuclei formation begins and the peaks have low intensity because of SiC formation at low reaction rate at this temperature. After increasing the heating temperature to the 1500 °C, the SiC formation reactions promote and the peaks intensities increase. So it reveals that at the same time, reaction will promote with increasing temperature. Thus it seems that according to this process the best heating temperature for SiC synthesis is 1500 °C.

Figure 4 indicates FTIR spectrum of heat treated powder at 1500°C. The XRD analysis results could be confirmed by FTIR data. Final powder analysis after carbon removal resulted in a very strong peak emerged at 800 - 900 cm^{-1} which is corresponded to the Si-C bond. A weak peak presented at 1000-1200 cm^{-1} belongs to small fraction of (Si-O) bonds.

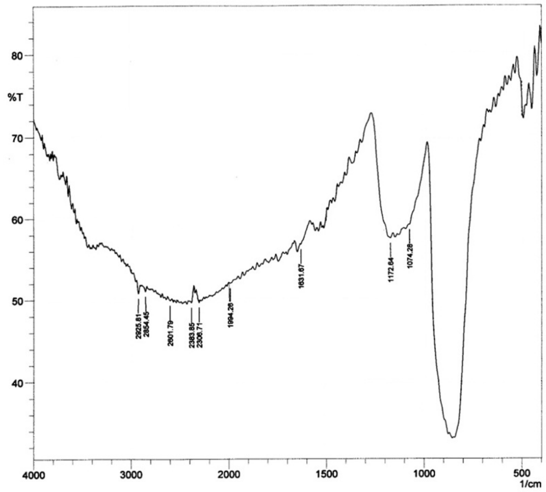

Fig. 4. FTIR spectroscopy of heat treated powder.

Figures 5 and 6 show the particle size distribution curves of the powders heat treated at 1400 and 1500 °C for 1 hr, respectively. At temperatures less than 1500 °C, the nucleation of β-SiC promotes slowly because the SiC formation reaction occurs based on solid-gas mechanism. First all SiO_2 particles convert to the SiO gas phase and react with the solid carbon to produce SiC particles. By temperature raising, the reaction rate of SiO gas increases and consequently results in SiC formation reaction rate improve. So it can be seen that the particle size distribution increases with temperature elevation. From these figures it could be concluded that the particles have a narrow size distributions.

Figure 7-a shows SEM image of gel powder synthesized at mentioned conditions. As it is shown, agglomerates sizes which are formed by TEOS and phenolic resin precursors are about (80-100) nm and have irregular morphology.

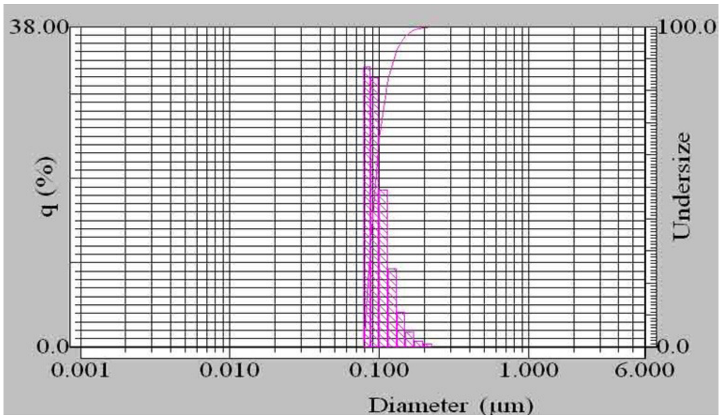

Fig. 5. Particle size distribution curve of the powder heated at 1400 °C for 1 hr.

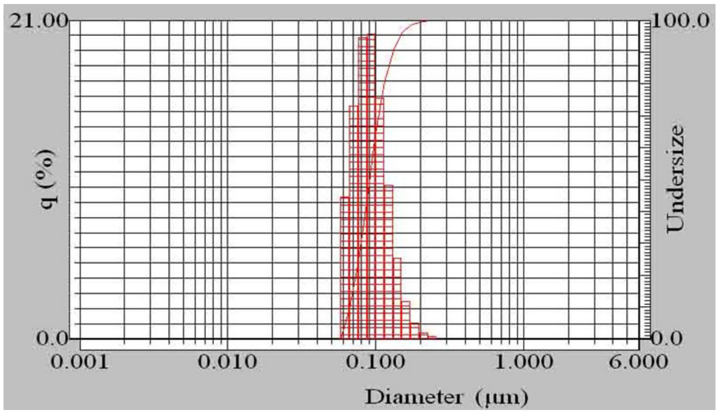

Fig. 6. Particle size distribution curve of the powder heated at 1500 °C for 1 hr.

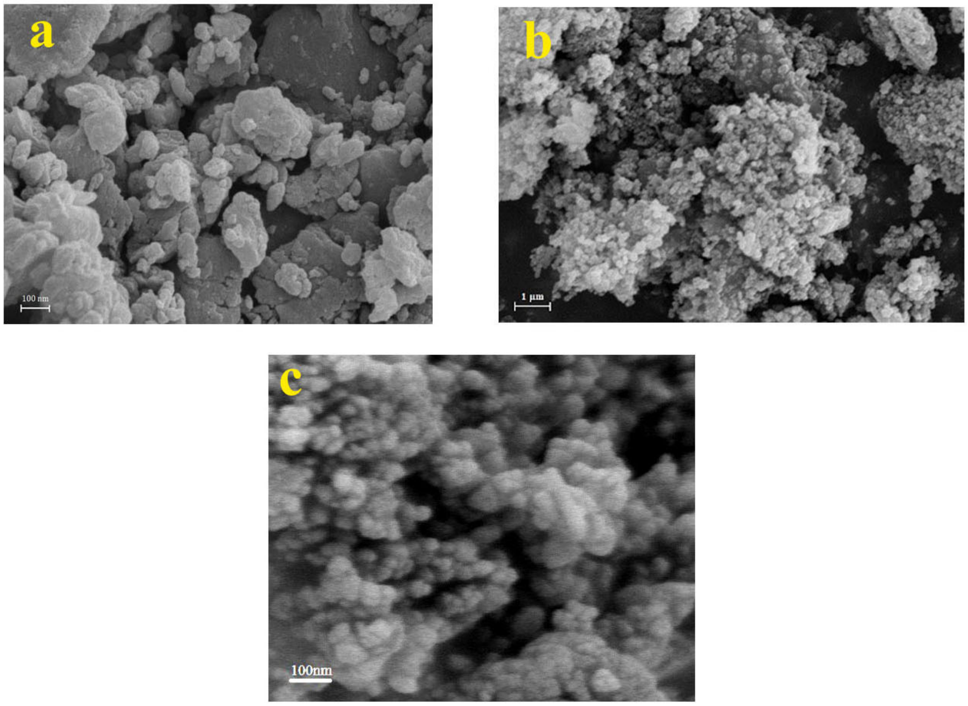

Fig. 7. SEM/SE images of (a) gel powder (TEOS + phenolic resin), (b) pyrolized powder at 700°C(c) synthesized powders at 1500°C for 1hr

Figure 7-b indicates SEM image of pyrolized powder at 700°C. According to this figure, it could be observed that after the removal of the volatile materials, precursor particles form a nearly monosized structure with semi spherical morphology. Figure 7-c shows SEM image for synthesized powder at 1500°C for 1 hr. As it can be seen in this figure, the produced formed agglomerates size is estimated to be less than 100 nm with irregular morphology.

Figure 8 shows transmission electron micrograph (TEM) of the powder heat treated at 1500 °C for 1 hr. According to this figure, the mean size of the particles is between 30-50 nm with semi spherical morphology. Their diffraction patterns indicates three perfect diffraction rings correspond to the (311), (220) and (111) planes of cubic SiC [16].

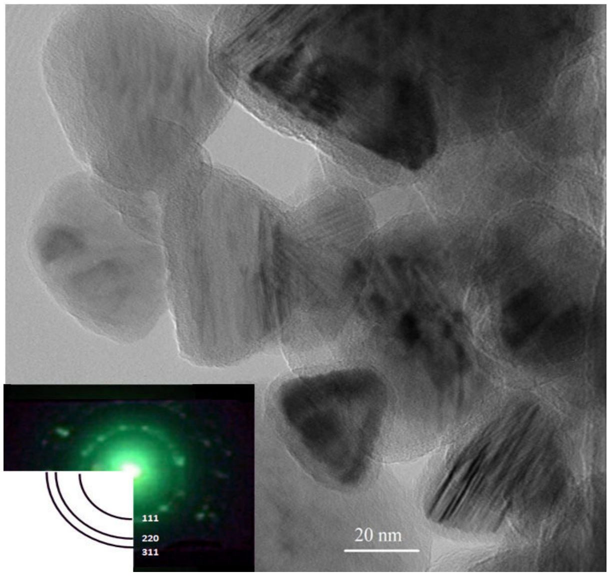

Fig. 8. Transmission electron micrograph of the powder heat treated at 1500 °C for 1 hr.

4. CONCLUSION

According to the results obtained in this work, it can be concluded that in the sol gel chemical synthesis of nano SiC particles, the pH and heat treating temperature are the main important factors which control the process. From Si-O-C bonds formation peak shown in FTIR spectrum it can be concluded that TEOS and phenolic resin precursors were mixed efficiently at molecular level in the sol. The XRD studies of nano sized SiC particles showed that the nucleation of β-SiC phase starts from 1400 °C and the growth completes at around 1500 °C. The scanning electron microscopy revealed that the sizes of formed agglomerates are less than 100 nm and their morphology is irregular. Finally transmission electron micrographs showed that the morphology of the particles is semi spherical and their sizes are in the range of 30-50 nm.

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