

Synthesis of Silicon Carbide from Silicon and Activated Carbon through Mechanical Milling and Heat Treatment

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Abstract - Silicon carbide (SiC) has been synthesized using a simple method without any additional additives. The synthesis has been carried out by mixing silicon powder with activated carbon powder with 1:1 molar ratio using High Energy Milling (HEM) for 40 hours. After milling, heat treatment was applied with and without argon as the inert gas. The sample was held for 2 hours at maximum temperature of 1300°C (without argon) and 1100°C (with argon) followed by natural cooling down to room temperature. XRD, FTIR, and SEM investigation were carried out toward sample before and after heat treatment. From XRD profiles, silicon was the only phase detected in the sample before heat treatment indicating no reaction occurred between silicon and carbon during milling. After heat treatment without argon, mixed silica phases in form of cristobalite and quartz were detected. It was estimated that all carbon had been burnt becoming carbon dioxide and the remaining silicon oxidized becoming silica. The β -SiC phase was obtained after heat treatment under argon gas atmosphere. However, silicon and silica phases were still detected. All FTIR results support the XRD data in general. SEM images show that after milling for 40 hours, spherical particles with a size of about 250 nm were formed from a mixture of silicon and activated carbon. Flakes of silica were formed after heat treatment without argon. Spherical particles with diameter of below 200 nm were observed after heat treatment under argon atmosphere and according to the XRD result, these particles were a mixture of β -SiC, silicon, and silica phases.

Index Terms - Silicon carbide, silicon, activated carbon, mechanical milling, heat treatment.

INTRODUCTION

Silicon carbide (SiC), also known as carborundum, has outstanding characteristics such as has wide band-gap, high melting point, high thermal conductivity, high hardness, low thermal expansion, low density, good optical and electronic properties, excellent oxidation resistance and chemical inertness [1]–[3]. SiC is widely applied in power devices [1], military, and aerospace engineering [2]. In nuclear industry, SiC can be used as a coating material of the Tri-Structural Isotropic (TRISO) fuel system for the Gen-IV High Temperature Gas-cooled Reactor (HTGR) fuel [4], and as a candidate material for the Accident Tolerant Fuel Cladding (ATFC) in the advanced light water reactor (LWR) [5].

Many methods are known for synthesizing SiC, for instance and chemical vapor deposition [6], [7], polycarbosilane pyrolysis [8], [9], carbothermal reduction [10], sol-gel [11], and sonochemistry [12]. All of the mentioned synthesis methods have a common issue of being low yield, uneconomical, and not feasible for mass production. Mechanical milling has been expected to become a promising method for mass production of SiC. Synthesis of SiC using high energy ball mill have been previously reported [13]–[17] with some challenges with regards to the dead corner effect, bigger particle size, and agglomeration.

In this work, silicon carbide was synthesized from its elemental components with a simple mechanical milling followed by heat treatment. Here, the challenges have been tried to be resolved by the use of activated carbon and toluene as well as the implementation of heat treatment after the mechanical milling. The phase composition and morphology of sample before and after heat treatment were investigated.

EXPERIMENTAL PROCEDURE

Mixing Process

The starting powder used in this experiment was silicon powder (Merck, 99% purity, <150 μm particle size) and activated carbon powder (Merck, 90% purity, <100 μm particle size) with 1:1 molar ratio. The activated carbon was selected as the carbon source because of its highly developed porosity and large surface area [18]–[20] which is useful for physical adsorption of silicon particles during milling process. This adsorption was expected to assist the solid state reaction between silicon and carbon. The mechanical milling process has been carried at room temperature using a shaker-type high energy ball mill apparatus to achieve more homogeneity. The balls are made of carborundum with a diameter of about 5 mm and the vial is made of tungsten carbide. The powder to ball ratio was 1:10. Toluene has been used as a milling medium to prevent oxidation, to further increase the mobility of the sample powder, and to reduce the dead corner effect. The total milling time is 40 hours with every 90 minutes of milling interspersed with 30 minutes of stopping for cooling the milling apparatus.

After milling, the slurry was placed on a petri dish and dried with an oven at 100°C for 4 hours. The dried sediment was then crushed manually into powder using mortar agate.

Heat Treatment

Heat treatment was done via pressureless sintering with two different sintering mechanism. The first sintering mechanism was carried out by using furnace apparatus without using inert gas with high heating rate of 50°C/min and 2 hours holding time at maximum temperature of 1300°C. The second sintering mechanism was carried out under argon atmosphere with quiet low heating rate of 3°C/min. At maximum sintering temperature of 1100°C, it was held for 2 hours and followed by a cooling process down to room temperature in the furnace by continuously flowing the argon gas.

Composition and Morphology Investigation

The phase composition was checked using X-ray diffraction technique (PANalytical Empyrean) with Cu-K α (1.5418 Å) selected as the source. Fullprof program was used to define the phase composition and the crystallite size. To check the functional groups and compounds formed at the end of the process, identification has been carried out using the FTIR method, namely the Fourier Transformation Infra-Red Spectrometer (Bruker Tensor 27, KBr method). Information on particle size and morphology has been observed using SEM with a magnification process up to a scale of 30,000.

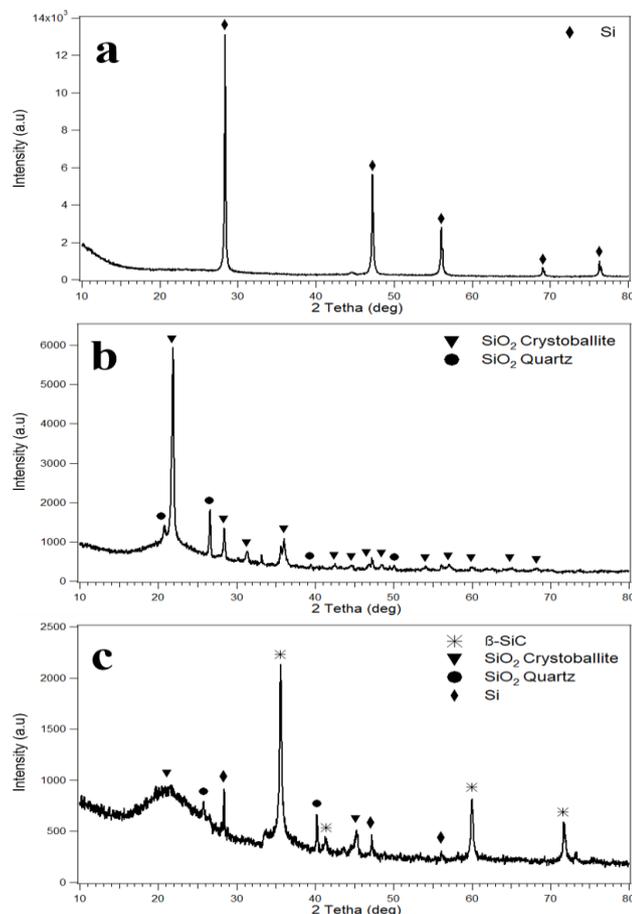


Figure 1

XRD profile of (a) sample before heat treatment, (b) after heat treatment without argon, (c) after heat treatment with argon

RESULT AND DISCUSSION

Phase Composition

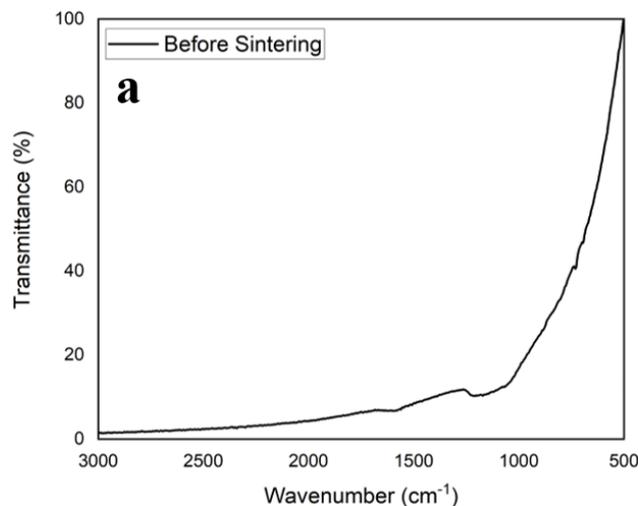
Fig. 1a very clearly shows that the powder milled for 40 hours has not shown any other phases formed beside the silicon phase indicating no solid state reaction occurred between silicon and carbon during milling process. As far as the accuracy of the apparatus is concerned, impurity phase from neither the balls nor the vial has been detected. The absence of other phases during the milling process is very likely due to the relatively low mechanical energy due to the low frequency and relatively light mass of the SiC balls. Insufficient milling duration and a fairly long stopping period might also have contributed. Previously, a similar work reported no formation of SiC after milling for 24 hours at 400 rpm [14] while other work reported a complete formation of SiC after milling for 60 hours at 600 rpm using planetary ball mill with 1:15 sample to ball (steel) ratio [17]. Other work reported that the SiC synthesis was completed after 300 hours of milling in a vibrating ball mill machine with sample to ball (sapphire) ratio of 1:6 [13]. The use of extreme powder to ball (steel) ratio of 1:67 was reported giving complete formation of SiC after 15 hours of milling time [16]. However, considering that the carbon being used was activated carbon which contains pores, it was very possible that the silicon occupied those pores during milling process. In other words, silicon was physically adsorbed into the activated carbon.

As previously mentioned, considering the heating process without using argon gas and with a fairly high heating rate of 50°C/min, the oxidation process cannot be avoided. Here in Fig. 1b, it can be seen that the dominant crystallite phase formed was a mixture of silica phases (SiO₂) in the form of cristobalite and quartz. This is very likely because all carbon had been burnt completely forming carbon dioxide (CO₂) and the remaining silicon was oxidized becoming silica. A similar phenomenon was also occurred in other previous work [13]. Cristobalite and quartz has identical chemical formula, which is SiO₂, but with different crystal structure. In fact, cristobalite is a polymorph of quartz group resulted from further reaction between quartz and oxygen. In nature, cristobalite is stable at around 1500°C, but it can be crystallized at considerably lower temperature around 890-900°C [21].

Fig. 1c shows the XRD profile pattern of sample after heat treatment with argon gas which was flushed previously into the heating chamber to remove the oxygen. Here, β-SiC phase with sharp peaks was clearly detected. However, the cristobalite and quartz as well as silicon were also still detected. Assuming that in the milling process most of the silicon particles filled the pores inside the activated carbon, then the heating process carried out in a relatively pure argon gas atmosphere encouraged an atomic interdiffusion mechanism between silicon and carbon to form β-SiC at a relatively low temperature. This is also supported by the relatively low heating rate of 3°C/min which enabled the formation of stable phases [22]. Meanwhile, the presence of other phases such as cristobalite and quartz, apart from the possibility that the oxygen impurity in the argon gas oxidized the uncovered silicon. This suggests the need of inert gas with very high purity. The remaining detected silicon phase was due to the relatively lower sintering temperature of 1100°C. A higher annealing temperature is probably needed to achieve complete formation of SiC via heat treatment under a high purity of inert gas atmosphere.

IR-Spectrum Measurement

Fig. 2a shows the FTIR spectrum of sample before heat treatment. No absorption peak was observed. This indicates that no chemical bond was formed after milling process for 40 hours. This is in accordance with the XRD result in Fig. 1a with only silicon phase detected.



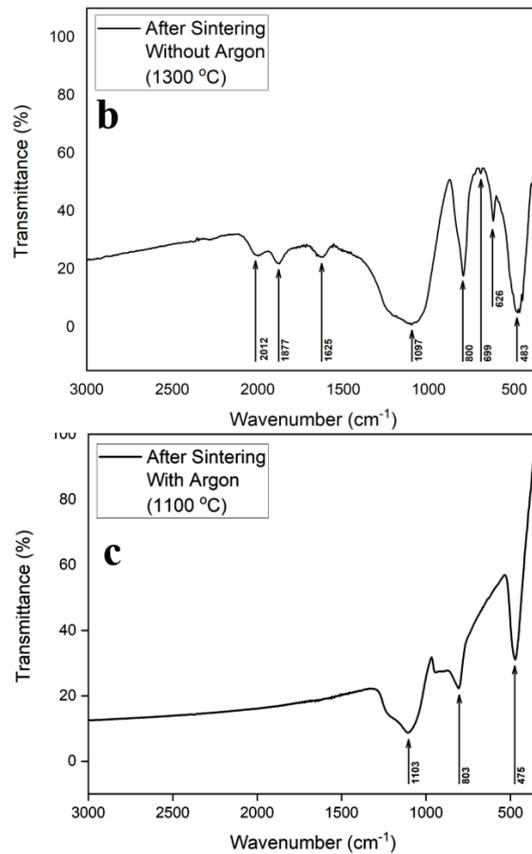


Figure 2.

FTIR spectrum of (a) sample before heat treatment, (b) after heat treatment without argon, (c) after heat treatment with argon

A quartz-like FTIR spectrum was observed in the sample after heat treatment without argon gas as shown in Fig. 2b. The peaks detected are at wavenumber of 1877, 1625, 1097, 800, 699, and 483 cm^{-1} [23], [24]. Absorption peak at 1097 cm^{-1} and 800 cm^{-1} correspond to the Si–O–Si asymmetric and symmetric stretching vibration of silica functional group respectively [24]–[26]. The mixed Si–O–Si and O–Si–O bending mode was represented with the peak at a wavenumber of 483 cm^{-1} [23]. The other remaining peaks detected also belong to the silica functional group as well as the amorphous silica which is suitable with the XRD result in Fig 1b which only silica phases in form of cristobalite and quartz were formed.

A chemical bond between silicon and carbon was observed from the FTIR spectrum of the sample after heat treatment under argon atmosphere as shown in Fig. 2c, represented with an absorption peak at a wavenumber of 803 cm^{-1} with a shoulder at around 1000 cm^{-1} which is the transversal and longitudinal optic vibration mode of Si–C bond in β -SiC [13], [16], [17], [27]. This also justified the β -SiC phase observed in Fig. 1c. The other two peaks detected at wavenumber of 1103 cm^{-1} and 475 cm^{-1} are similar with the peaks in Fig. 2b which correspond to the Si–O–Si stretching vibration and mixed Si–O–Si with O–Si–O bending mode of silica functional group respectively.

Morphology Investigation

Fig. 3a shows a SEM image of the sample after milling for 40 hours. An interesting thing was observed that the milling process had formed particles with a size of about 250 nm which are dominantly spherical. The spherical particles were formed from a mixture of silicon and activated carbon because activated carbon has relatively large pores so that it was very possible for silicon to fill those pores. Moreover, toluene was used as the milling media. In addition to being useful for preventing silicon from oxidation, toluene also encourages better mobilization of fine particles so that the physical adsorption mechanism was very likely to be realized. As seen in Fig. 1a, it was confirmed that only the silicon phase was detected while activated carbon only contributed as a background because it was amorphous.

Fig. 3b is a SEM image of the sample after heat treatment without using argon gas. At maximum temperature of 1300°C, all activated carbon was estimated to be burnt completely forming CO_2 gas while the uncovered silicon particles underwent oxidation forming silica and appeared as flakes.

As explained in Fig. 3a, assuming that the silicon particles had filled the pores inside the activated carbon, then, heat treatment in an inert gas atmosphere and with a low heating rate of 3°C/min had given sufficient time for the atomic interdiffusion of silicon and carbon to occur and form silicon carbide. Fig. 3c is a SEM image showing particles which are still a mixture of phases as shown in Fig. 1c, namely the β -SiC with small traces of silicon and silica in form of cristobalite and quartz. This is supported by the XRD measurement result as shown in Fig. 1c. The particles appeared homogeneous with diameter below 200 nm, smaller than the particle size before heat treatment in Fig. 3a, and also relatively smaller compared to other works [13], [16], [17].

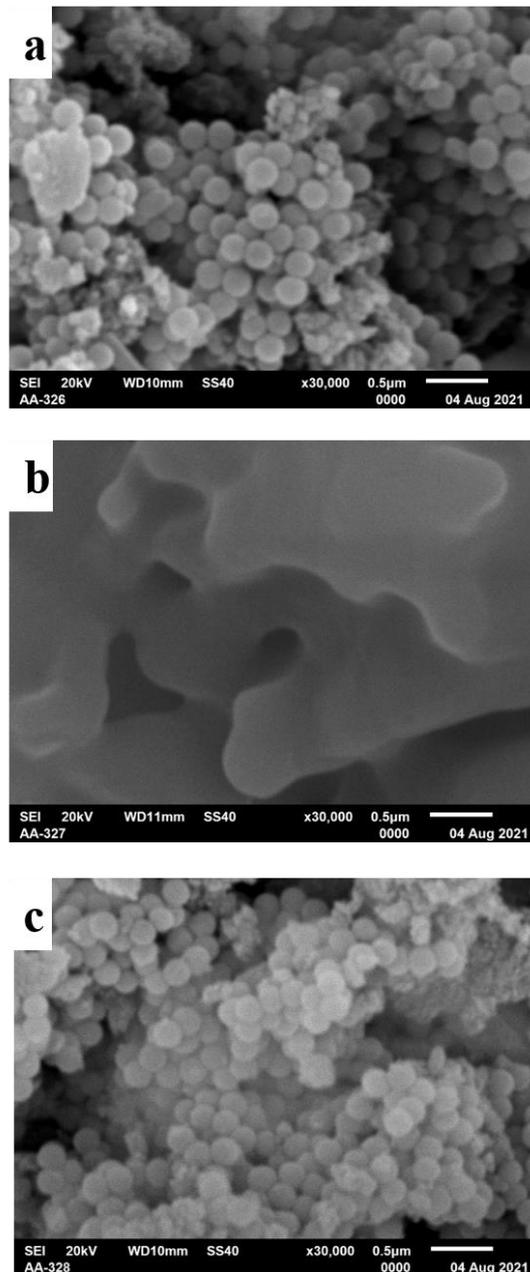


Figure 3.

SEM image of (a) sample before heat treatment, (b) after heat treatment without argon, (c) after heat treatment with argon

CONCLUSION

In this work, β -SiC has been synthesized through a mechanical milling of silicon and activated carbon powder followed by a heat treatment process under argon gas atmosphere. The formation of β -SiC phase at relatively low temperature was possible because silicon particles had been physically adsorbed into the pores inside the activated carbon during milling process, so that heat treatment under inert gas atmosphere allowed an effective atomic interdiffusion between Si and C. The formed silica phases in form of cristobalite and quartz are very likely related to the uncovered silicon outside the pores of activated carbon which reacted with oxygen as a part of the argon gas impurities. The process of forming the β -SiC phase is estimated to be more effective if the sintering temperature is higher and under a high purity inert gas atmosphere.

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