Synthesis and Structural Analysis of Silicon Carbide from Silica Rice Husk and Activated Carbon Using Solid-State Reaction

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Abstract. Synthesis of Silicon Carbide (SiC) has been performed using a solid-state reaction method. We used silica and activated carbon as raw materials. The silica was synthesized from silica rice husk using an alkali extraction and a sol-gel method. The purified silica was then mixed with the activated carbon at the same ratio, homogenized, and then cold pressed into pellets by adding polyvinyl alcohol to glue them perfectly. The pellets were then sintered in a vacuum of a high-temperature furnace in an inert arc-furnace at 1200, 1300, and 1400 °C for 6 hours. The samples were characterized for their particle size, surface area, phase composition, microstructure, and resistivity. The XRD data analysis showed that the samples are dominated by the SiC phase in the form of 3C-SiC and 6H-SiC, CO (Carbon (II) oxide), and SiO₂ phases. The weight fractions of SiC samples were respectively fallen to 68, 98, and 69% for 1200, 1300 and 1400 °C sintering temperatures.

Keywords: Silicon carbide, silica rice husk, activated carbon, solid-state reaction

1. Introduction
Silicon carbide (SiC) is one of the most widely used non-oxide ceramics for many industrial applications because of its attractive high-temperature properties, such as high strength, high hardness, and high wear and thermal shock resistance. It also possesses an excellent chemical oxidation resistance. The silicon carbide’s performance under such extreme conditions is expected to enable significant improvements to a variety of applications. Nanostructured SiC has shown to exhibit superior properties (greater elasticity and strength) compared to the bulk SiC. It also shows the potential applications in light emitting diodes and UV Photodetectors due to a higher light-emission efficiency [1]. There is a significant interest in the synthesis of nanostructured SiC including nanospheres, nanowires, nanorods and so on as novel functional materials for a nanoscale engineering [2]. In normal conditions, the synthesis of SiC is difficult due to oxidation of carbon and silica at a high temperature. In contrast, the synthesis of phase-pure of sub-micron-sized of βSiC powder has been achieved from its constituent elements namely carbon and silicon to form SiC can occur at a
temperature as low as 900 °C. The phase-pure SiC can be formed only at the temperatures of 1200 °C and above [3].

Recently, Zhang et al. [4] reported the direct synthesis of nanostructured silicon carbide (SiC) materials using a pulsed laser deposition technique. Kawamura et al. [5] showed that β-type cubic SiC could be prepared from a Si and fullerene powder mixture or α-Si and amorphous carbon (carbon black) powder mixture by the Na flux method at 900-1000 K. Kriener et al. [6] presented a study of mainly hexagonal boron-doped 6H-SiC , without any indication of a cubic 3C phase fraction, by means of X-ray diffraction, and resistivity measurements. Walter et al. [7] used solid-state reactions in the Al-Si-C at a sintering temperature of 1450 °C for 8 hours under a vacuum condition in a graphite furnace. Andrievski [8] reported that amorphous SiC nanoparticles have been synthesized by using a low-pressure microwave plasma, inductively coupled plasma to synthesis β-SiC nanopowders, carbothermic reduction to synthesis α-SiC nanocrystals. The amorphous SiC particles were synthesized from tetramethylsilane precursor at room temperature and a low precursor partial pressure using argon as carrier gas. However, all these methods are expensive and require special equipment.

In this paper, we reported a synthesis of SiC using polyvinyl alcohol to prevent sticking the precursors. Due to its scarce availability in nature, SiC ceramics must be synthesized. The industrially high demand of SiC raw material takes intensive attention to produce a renewable material at a low cost. The rich silica content in the rice husk ash is one of prospective low cost and renewable starting materials in synthesizing SiC due to its desired silica and carbon-activated contents. A simple approach to synthesized SiC nanoparticles by using a solid-state reaction at the temperatures of 1200, 1300, and 1400 °C and characterized their mechanical properties. A novel synthesis route resulting high purity SiC but at a low cost is addressed in this study.

2. Materials and Methods

The synthesis of Silicon Carbide was prepared by solid-state reaction methods using the raw material of SiO₂, activated carbon, and PVA. The SiO₂ was synthesized from silica rice husk using an alkali extraction and sol-gel method with a purity of up to 99.45 % [9] as the main material. In this method, solid powders of starting materials with particular molar mass ratios were mixed, homogenized, and then cold pressed into pellets with the addition of polyvinyl alcohol to stick perfectly. The pellets were then sintered in a vacuum of the high-temperature furnace in an inert gas at the temperatures of 1200 °C, 1300 °C, and 1400 °C for 6 hours. The samples were then characterized by using powder X-ray diffractometer (XRD) with Cu Kα₁ with 2θ between 20° to 80° (wavelength 1.5406 Å), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX), and resistivity by using a four-point probe method (I-V meter).

3. Results and Discussion

The phase identification of as-prepared samples was carried out based on XRD patterns. The most common polytypes of SiC presently being developed for electronics are 3C-SiC, 2H-SiC, 4H-SiC, and 6H-SiC that shown in the schematic cross-section (Figure 1) [10].

Figure 2 shows the typical XRD pattern of samples prepared at 1200, 1300, and 1400 °C for 6 hours. The sintering temperature and duration affect the intensity of the material and tend to reduce the intensity when surpassing its melting point [11]. Therefore, we noted that the crystalline structures and diffraction peaks intensity were mainly depended upon the increasing temperature.

The XRD data analysis showed that the samples have a dominant phase of SiC in the form of 3C-SiC and 6H-SiC structure. We also found a weak intensity of CO (Carbon (II) oxide), and SiO₂ phases. This composition is a good agreement with the EDX data. In the sample sintered at 1200 °C, four phases were observed, i.e., 6H-SiC, 3C-SiC, CO, and SiO₂ with the PDF number of 01-073-6302, 01-073-1708, 01-076-2378, and 01-070-2540 respectively. It is found the appearance of several peaks identified as a 6H-SiC phase. The 6H-SiC peaks appear at diffraction angle 2θ of 25.92°, 27.25°, 35.35°, 45.56°, 49.36°, 56.48°, 59.72°, 62.60°, and 71.56°. We also observed three peaks belong to 3C-
SiC. The 3C-SiC observed at $2\theta$ of 35.35°, 59.72°, and 71.56°. Minor peaks found showing CO phase at $2\theta$ of 29.62° and 31.53°. We found SiO$_2$ phase exists at $2\theta$ of 21.57°, 51.92°, and 53.52°.

![Figure 1. The schematic cross-sectional depiction of SiC atomic crystal structure. After [10].](image)

Meanwhile, the sample sintered at 1300 °C shows three phases exist, i.e., 6H-SiC, 3C-SiC, and CO. It was also observed that two weak peaks represented the CO phase, while reducing SiO$_2$ intensity. The shoulder is associated with stacking faults, which serves as a common feature of SiC material, demonstrating the crystalline nature of the sample prepared at the temperature of 1200 °C [4]. Increasing temperature up to 1400 °C provides to increase the 6H-SiC and reduce 3C-SiC. On the other hand, a SiO$_2$ increase significantly. The refinements gave the cell constant falls to $a = 4.3480$ Å, which was consistent with the reported value in the literature ($a = 4.3480$ Å, AMCSD, No. 001791). The weight fraction of SiC which were sintered at 1200, 1300, and 1400 °C reached 68, 98, and 69% respectively. All samples have also been analyzed for the particle size, particle morphology, and distribution using a scanning electron microscope (SEM) which is depicted in Figure 3.

![Figure 2. X-ray diffraction pattern from SiC sintered at 1200, 1300, and 1400 °C.](image)
It is seen that activated carbon of charcoal yielded as platelets with the size of ~50 \( \mu \text{m} \) (Figure 3a), while purified silica tends to agglomerate as shown in Figure 3b. The size of the agglomerate is ~60\( \mu \text{m} \). A typical SiC plate-like grain is shown in Figure 3c. On the selected area indicated by red lines, showing that the plate like grains comprises by a stacked vertically thin plates. The particle morphology of SiC were examined using three different pellets. The morphology of the particles change following the increase of in the sintering temperature. The size of individual thin plates in each case show a relatively constant of ~0.5 \( \mu \text{m} \) (Figure 3c).

![Figure 3. SEM images of (a) activated charcoal, (b) purified silica, (c) SiC at 1200 °C, (d) SiC at 1300 °C, and (e) SiC at 1400 °C.](image)

![Figure 4. EDX results of (a) activated charcoal, (b) purified silica, (c) SiC sintered at 1200, (d) 1300 °C, and (e) at 1400 °C.](image)
Like those above, the agglomerates also contained whiskers in almost all cases. However, the morphology of the whiskers changed from free, sharp-edged whiskers at temperature 1300 °C and blunt-type whiskers at 1400 °C. The processing temperatures of 1300 and 1400 °C is close to partial sintering. Figure 3e indicates the fusion of many whiskers or individual thin sheets to form a large grain of ~5 μm. The continuous formation of such grains increases the overall grain size. A similar observation was reported for a SiC synthesis by Johnson et al. [12]. These authors reported that as soon as SiC forms on the surface of the carbon primary particles, the primary particles begin to grow by sintering. The SiC particles resemble to the carbon precursor which have a tendency to grow significantly at higher temperatures, because of increased sintering. The similar grains were not observed for other synthesis conditions, confirming that the fusion of particles is uniquely a high-temperature process and not a process-dependent factor. These fused particles are assumed to decrease the surface area of the particles, which eventually results in the reduction of the reactivity.

![Images of I-V meter results](image1.png)  ![Images of I-V meter results](image2.png)  ![Images of I-V meter results](image3.png)

Figure 5. I-V meter results of SiC at (a)1200, (b)1300, and (c)1400 °C.

The resistivity of SiC which were sintered at 1200 °C (Figure 5a) and 1300 °C (Figure 5b) shows an ohmic relation [13]. The calculated resistivity falls to 9.8 Ω cm and 138.3 Ω cm respectively. On the other hand, the SiC which sintered at 1400 °C (Figure 5c) exhibit a non-ohmic behavior with average resistivity falls to 38.55 Ω cm. The resistivity of semiconductor materials such as Si and Ge were $10^{-3}$-10$^2$ Ω cm [13]. The three samples of SiC being studied show a resistivity in the range of a semiconductor. By comparing the purity of the samples obtained from the XRD analysis and resistivity, we may conclude that resistivity is strongly affected by SiC fraction of the samples.

4. Conclusion

The synthesis of Silicon Carbide has been done by using solid state reaction methods using the raw material of SiO$_2$, activated carbon, and PVA under vacuum condition. The SiO$_2$ was synthesized from silica rice husk using alkali extraction and sol-gel method with a purity of up to 99.45%. It was shown that the samples are dominated by SiC in the form of 3C-SiC and 6H-SiC structure. We also found a minor impurity of CO (Carbon (II) oxide), and SiO$_2$ phases within a good agreement with the EDX characterization. The weight fraction of SiC which were sintered at 1200, 1300, and 1400 °C respectively achieved of 68, 98, and 69%. The morphology of the particles has changed according to the sintering temperature. The EDX data show that the carbon atom concentration (at %) is approximately 82.81 %, 50.20%, and 64.18% and the silicon atom concentration varies from 01.24%, 16.00 and 12.90%. According to the resistivity, the obtained SiC belongs to the semiconductor. The resistivity of SiC at the 1200 °C and 1300 °C show an ohmic behavior ranged from 9.8 Ω cm to 138.3 Ω cm. We noted that the resistivity is strongly affected by its purity of the samples.

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