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Clean and low-cost synthesis of high purity beta-silicon carbide with carbon fiber production residual and a sandstone



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ABSTRACT

The U.S. Department of Energy has initiated conversion of coal to solid materials, which can improve the coal-derived high-value product chain and decrease coal utilization related carbon dioxide emission. An integrated coal utilization technology was developed to respond to Department of Energy's call, which is extracting the molecules with desired molecular weight and structure in coal for carbon fiber production, then using carbon-rich residual from carbon fiber precursor extraction as carbon source to produce betasilicon carbide. For the first time beta-silicon carbide is synthesized from carbon fiber production residual and a sandstone. The synthesized beta-silicon carbide was characterized with multiple analytical techniques. The product exhibits good properties with its purity, density, and Vickers hardness reach the requirements of commercial silicon carbide. Specifically, the purity of the beta-silicon carbide obtained with the two inexpensive raw materials under argon atmosphere at 1600 °C reaches as high as 98%. It is the first time that the furnace-MS system was applied to analyze the gaseous products in coal-based beta-silicon carbide synthesis process. Also, a possible synthesis mechanism was proposed and confirmed with experimental results. The research further analyzed the environmental impact and proposed the possibility that the liquid wastes/byproducts generated during raw material treatment process can be recycled and efficiently reused as coagulants or desiccants when the developed betasilicon carbide synthesis process is applied in industry. This study provides a clean and low-cost approach for reusing waste residual from coal-based carbon fiber production and sandstone powder.

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1. Introduction

Coal has been used for generating electricity in power plants, which unfortunately may not be the best way to use the precious natural resource (Chen et al., 2016), especially considering the fact that people are increasingly concerned about the coal combustion associated CO₂ emission (Lai et al., 2018). Thus, people recently started to pay high attention to converting coal to solid materials,

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and among them are carbon fiber (Yang et al., 2016) and carbide (Liu et al., 2015), However, to the best knowledge of the authors, integrally producing both carbon fiber and carbide with coal have not been seen in literature. Therefore, according to the elemental composition characteristics of coal-rich in C and poor in H, and atom economy and energy saving principles, Fan's group proposed to produce both carbon fiber and carbide with high H:C and low H:C fractions in coal, respectively. Successful separation of the high H:C fraction from low H:C fraction in coal and preparation of carbon fiber with high H:C fraction were realized with ethanol and supercritical CO₂ (EtOH-SCC) (Liu et al., 2018) via extraction. This research was focused on the utilization of the EtOH-SCC extraction residual and sandstone in β -SiC synthesis.

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 β -SiC (3C–SiC) with a zinc blende crystal structure is synthesized at temperatures below 1700 °C. It can be utilized in many areas, including catalysis, ceramic manufacturing, coating, milling, and polishing (Chen et al., 2017). Also, β -SiC plays an important role in manufacturing semiconductors, solar cells, and optoelectronics due to its characteristics of the wide band gap, high electron mobility, and superior thermal conductivity(Gusev et al., 2016),(Pang et al., 2010),(Kamble et al., 2017).

Currently, Acheson process (Chen et al., 2018) is the main β -SiC synthesis method, which is started by mixing C-rich and Si-rich materials in an electric resistance furnace and followed by heating the mixture at given temperatures for a desired period (Makkee et al., 1998). The employed coal related C-rich raw materials include coal (Liu et al., 2015), coal tar pitch (Czosnek and Ratuszek, 2002), and metallurgical coke (Narciso-Romero et al., 1999), while coal related Si-rich raw materials are coal fly ash (Sulardjaka et al., 2011), coal gasification slag (Yin and Tang, 2011), and coal gangue (Xiao et al., 2015). Other C-rich and Si-rich raw materials are activated carbon and carbon black; and Si, SiO₂, carbosilane and methyltriethoxysilane, respectively. On one hand, the materials were successfully used for the synthesis of β -SiC. For example, the purity of β -SiC produced by coal gangue with carbon reached 76.01% (Xiao et al., 2015). Also, β -SiC synthesized with silica fume and brown coal semi-coke shows a purity of 90–91% (Anikin et al., 2016). On the other hand, the C concentration in the C-rich materials used in the conventional β -SiC is either too low or too high, which is not beneficial to β -SiC synthesis. Use of low C or high H:C raw materials such as coals only for β -SiC synthesis results in wasting a lot of valuable H, which is not desired for lowering the overall cost of β -SiC. Employing high C materials with relatively low activities such as activated carbon could lower β-SiC synthesis kinetics, which should also be avoided for β -SiC synthesis. Thus, the EtOH-SCC extraction residuals with reasonable H:C ratios were used in this research to overcome the shortcomings of the state-ofthe-art β -SiC synthesis technologies.

2. Experiments

2.1. Residual and sandstone powder preparation

The residual was obtained from EtOH-SCC extraction of Powder River Basin (PRB) coal as previously reported (Liu et al., 2018). Liquid tar was used for high-value carbon fiber synthesis (Liu et al., 2018). The solid residual needed to be treated prior to its use as a C resource for β -SiC synthesis for this research. The residual was washed with ethanol to extract remained liquid tar and then dried under vacuum at 60 °C for 12 h to remove the ethanol, followed by cooling the particles to room temperature and crashing them to <250 µm. The residual was then leached with a 5 M HCl and heated at 75 °C for 48 h to remove metallic impurities, followed by cooling, filtering, and washing it with deionized water, drying under vacuum at 60 °C for 12 h. The cleaned residual was used for β -SiC proudction.

The sandstone samples were obtained from Plumbago Creek silica sand deposit located in the Albany County of Wyoming. The sandstone was ground to fine powders (75 μ m). The obtained sandstone powder was then treated with the 1.2 M HCl to eliminate metallic impurities. The treatment processes include dissolving, filtering, washing with deionized water, and drying under vacuum at 60 °C for 12 h.

2.2. β -SiC synthesis

The mixtures of cleaned residual and sandstone powder were carbonized within 1300-1600 °C with holding times of 1-3 h

under Ar flow (50 ml/min) to synthesize β -SiC. A mass spectrometer (MS, HPR-20, HIDEN) was connected to the high-temperature horizontal tube furnace (HTRH-Carbolite) to detect gaseous species generated during SiC synthesis process. During the reaction process, the gaseous products were identified and recorded by the molecular mass/mass number (m/z) signal of the MS. The obtained β -SiC products were treated at 850 °C for 6 h under air atmosphere to remove unreacted carbon. The schematic diagram of the experimental set-up for the synthesis of β -SiC is shown in Fig. 1. The flow diagram of the experiment including all procedures is shown in Fig. 2.

2.3. Characterization of residual, sandstone powder and β -SiC products

2.3.1. Chemical properties characterization of residual, sandstone powder and β -SiC products

The elemental analysis of the residual was performed by using an elemental analyzer (vario MACRO cube, Elementar), and the oxygen content was calculated by the subtraction method. An inductively coupled plasma mass spectrometry (ICP-MS, NexIon 350, PerkinElmer) was operated to determine the composition of treated sandstone powder and ash of treated residual. A nine-point calibration curve from 0 to 100 ng/L was created for each analysis. Residual was dried at 105 °C overnight to remove moisture, then calcined at 550 °C for 6 h to obtain ash sample. For each test, 0.03 g sample was mixed with 0.24 g lithium metaborate (BLiO₂) and heated at 1100 °C for 5 min in the air atmosphere. The obtained glass-like mixture was then fully dissolved by 5 wt% nitric acid (HNO₃). The dissolved solution was diluted with deionized water to obtain the testable sample for ICP-MS tests. The purity of the obtained β-SiC was determined with ICP-AES following the method of CAP-017P.

2.3.2. Qualitative characterization of residual, sandstone powder and β -SiC products

Powder X-ray diffraction (XRD) tests were performed on a Rigaku X-ray diffraction system using Cu K α 1 radiation ($\lambda = 1.54056$ Å) at 40Kv and 40 mA. The sample was placed on a zero diffraction Si holder and was scanned from 10° to 90° (2 θ) with a 5°/min scanning rate at room temperature. The samples were also identified by Fourier transform infrared spectrometer (FTIR, Nicolet iS FT-IR) with a resolution of 4 cm⁻¹. A spectrofluorometer (Fluorolog-3, Horiba Scientific) was adopted to explore the photoluminescence (PL) of the synthesized β -SiC materials. The



Fig. 1. Schematic diagram of experimental set-up for synthesis of silicon carbide. [(1) high-temperature horizontal tube furnace, (2) mass spectrometer, (3) computer, (4) temperature controller, (5) mass flow controller power supply/control module, (6) Argon cylinder, (7) mass flow controller]



Fig. 2. Flow diagram of experiment.

excitation wavelength of 320 nm was applied to obtain PL spectra of β -SiC materials and recorded in the wavelength range of 400 nm-550 nm.

2.3.3. Physical properties characterization of residual, sandstone powder and β -SiC products

Textural properties of samples were determined from the nitrogen adsorption/desorption at -196 °C using a Quantachrome Autosorb-iQ unit. Prior to measurement, samples were degassed under vacuum at 300 °C for 6 h to remove humidity and preadsorbed gases before exposure to the nitrogen (N₂) gas. The specific surface area was calculated from N₂ isotherm data using the BET model, and the total pore volume and average pore diameter were evaluated. Microhardness of β-SiC was tested by a hardness tester (Mitutoyo HM-123) following ASTM E 384-17 standard. The density of synthesized β-SiC material was determined by a Mettler Toledo balance (ML204T/00) equipped with a density kit (ML-DNY-43). The morphologies of β-SiC product samples were studied on a scanning electron microscope (SEM, FEI company, Quanta 250) and a transmission electron microscope (TEM, FEI, Tecnai G2 F20 S-TWIN).

2.3.4. Thermogravimetric analysis of β -SiC products

The oxidation behavior of β -SiC powders was evaluated by using a thermogravimetric analyzer (TGA, SDT-Q600, TA instruments). Around 15 mg β -SiC sample was loaded onto an alumina sample holder and heated from room temperature to 1400 °C under air flow.

3. Results and discussion

3.1. Properties of untreated/treated residual and sandstone samples

The results of the ultimate analysis of treated residual obtained by elemental analysis and the ash composition are listed in Table 1. The residual contains ~6.15% ash. The concentrations of Si, main metal elements and rare earth elements (REEs) in the residual and its ash are shown in Table 2. The amounts of Si, Ca, K, Mg, Na and

Table 1

Ultimate analysis data and ash content of treated residual.

Sample	Elementa		ash			
	С	Н	0	Ν	S	(wt% db)
Residual	76.09	4.78	17.14	1.28	0.71	6.15

REEs account for 2.156%, 0.14%, 0.012%, 0.033%, 0.005% and 0.001% in the residual, respectively. While Si in residual primarily exists in the form of SiO₂, the other metallic impurities account for less than 2 wt%, which means it is effective to use 5 M HCl solution to remove metallic impurities. In addition, treated residual contains 76.09% C. an indication of its high quality as a C source for β -SiC synthesis. The crystal phase characteristics of the ashes in original and treated residuals are presented in Fig. 3. Prior to acid solution treatment. the major phases in the ash of the residual are quartz (SiO₂) and kaolinite (AlSiO₅(OH)₄). After the pretreatment with HCl solution, XRD pattern of the ash in the residual as shown in Fig. 3 (b) only shows the peaks of SiO₂. Thus, the 5 M HCl solution can effectively eliminate metallic impurities under the given operating conditions. Fig. 4a-b shows XRD patterns of original and 1.2 M HCl leached sandstone powders, respectively. These patterns clearly show that CaCO₃ was removed from the original sandstone sample. After leached by HCl solution, the concentration of SiO₂ in sandstone powder increased, which is also confirmed with the ICP-MS results shown in Table 3. The treated sandstone powder contains up to 96.75% SiO₂ and was used as a Si source in the β -SiC synthesis process.

3.2. β -SiC synthesis process and reaction mechanism study

After the pretreatment, a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder was prepared and used for synthesizing β -SiC. To monitor reaction progress during the β -SiC synthesis process, the mixtures were heated to different targeted temperature points in the range of 1300 °C to 1600 °C and the XRD patterns of these products are shown in Fig. 5. It clearly shows that

Table 2

Concentrations of Si, main metal elements and REEs in treated residual and its ash.

Sample	Si (wt%)	Al (wt%)	Fe (wt%)	Ca (wt%)	K (wt%)	Mg (wt%)	Na (wt%)	REEs (wt%)	Total (wt%) ^a
Ash of treated residual	35.073	0.002	0.001	2.281	0.190	0.529	0.084	0.021	100
Treated residual	2.156	0	0	0.14	0.012	0.033	0.005	0.001	6.15

^a wt% based on oxides.



Fig. 3. XRD patterns of (a) ash of original residual and (b) ash of treated residual.



Fig. 4. XRD patterns of (a) sandstone powder and (b) treated sandstone powder.

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Concentrations of SiO_2 and metal oxides in treated sandstone powder.

Treated sandstone powder	Al	Fe	Ca	К	Mg	Na	Si	Total
wt % on an oxide basis	1.276	0.464	0.580	0.812	0	0.232	96.75	100

the intensities of quartz (SiO₂) peak decrease when the increase in temperatures from 1300 °C to 1500 °C. Quartz (SiO₂) is stable or is in the form of crystalline silica below 870 °C. The conversion from quartz (SiO₂) to cristobalite (SiO₂) starts below 1000 °C (Chaklader and Roberts, 1961), and the intensities of peaks represent cristobalite (SiO₂) increases with temperatures in the range of 1300–1600 °C. The peaks representing β -SiC start to appear when the temperature reaches 1600 °C and these peaks can be clearly noticed in Fig. 6a. The peak intensity of β -SiC is continuously enhanced with the increase in holding time within 0–60 min. On the other hand, the intensities of quartz and cristobalite SiO₂ peaks decrease with holding time, and the peaks disappear at 60 min.

Within 60–180 min, the XRD peak intensity of β -SiC remains the same as shown in Fig. 6b. Based on these results, 1600 °C and holding times of 60–180 min were used for conducting subsequent synthesis tests and determining other optimal conditions for further improving the quality of β -SiC.

The phase changes during the β -SiC synthesis process were studied by XRD and analyzed thoroughly. The gaseous byproducts released during the reaction process were also monitored and recorded by an integrated furnace-MS system to study the reaction mechanism. The results are presented in Fig. 7. Fig. 7 (a) shows the evolution of gas species below 1600 °C, while Fig. 7b shows MS record of the whole reaction processes including those in



Fig. 5. XRD patterns of products synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: $10 \degree C/$ min; heating temperature range: $1300\degree C - 1600\degree C$; holding time: $0 \min$].

temperature-ramp and isothermal periods. When the heating rate is $10 \,^{\circ}$ C/min and reactants are hold at $1600 \,^{\circ}$ C, the major gaseous species released are H₂, CH₄, H₂O, CO, and CO₂. Similar to coal

pyrolysis process, C2 and C3 species are released during β -SiC synthesis process in the temperature range of 400-800 °C. However, the yields of C2 and C3 species are much lower than those of other gaseous species. As reported by Dong et al. (2017), H₂O is released from ~100 °C to 1600 °C. The H₂O peaks appear at 100-200 °C and 800 °C. The first peak at 100-200 °C results from the release of physically adsorbed water. The second peak less noticeably at ~800 °C can be attributed to the deoxygenation reaction of treated residual. H₂ is regenerated within a broad temperature range, 500–1600 °C. CO, another gaseous byproduct, leads to three peaks as shown at ~550 °C, 800 °C, and 1600 °C. Evolution of CH₄ happens between 400 °C and 900 °C. An intensity curve for m/z = 44 was also recorded by the integrated furnace-MS unit, which belongs to CO₂ that formed in the range of 400–600 °C. The existence of SiO that widely accepted as an intermediate during SiC synthesis was confirmed by other researches (Dong et al., 2017),(Han and Li, 2005). SiO is another intermediate appearing initially at ~925 °C (Gardner, 1974) and its generation rate increases significantly above 1100 °C (Dong et al., 2017).

Therefore, both synthesis temperature and holding time have significant effects on the formation of β -SiC. Generally speaking (Weimer et al., 1993), SiC synthesis reaction based on petroleum coke and pure silica is

$$3C(s) + SiO_2(s) \rightarrow SiC(s) + 2CO(g).$$
(R1)

However, the mechanism of synthesizing β -SiC with EtOH-SCC



Fig. 6. XRD patterns of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [Heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: (a) 0 min-60 min, (b) 60 min-180 min].



Fig. 7. Online furnace-MS analysis of gaseous species released during β-SiC synthesis process. [(a) temperature-ramp period from room temperature to 1600 °C, heating rate: 10 °C/ min; (b) temperature-ramp period from room temperature to 1600 °C and isothermal for 5 h at 1600 °C].

extraction residual and sandstone has not been reported. The EtOH-SCC extraction residual mainly contain C, H, and O. H₂ and CO should be major products when the residual was heated to high temperatures within Ar, as observed and shown in Fig. 7. Accordingly, the main reactions occurring the residual and sandstone based β -SiC should be

 $SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$ (R2)

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g).$$
 (R3)

It was confirmed by elemental analysis that EtOH-SCC extraction residual contains a certain amount of H element and the MS result shows that H₂ is observed in a wide temperature range from 500–1600 °C. SiO₂ can be reduced by H₂ to form SiO and H₂O when the temperature is higher than 925 °C (Gardner, 1974). Also, both H₂ and H₂O are detected by MS when the temperature is higher than 925 °C as shown in Fig. 7, a confirmation of R2. The reaction rate of R2 increases with temperature (Gardner, 1974), which can simultaneously increase H₂ consumption and of SiO. The generated SiO is an important intermediate for the formation and growth of SiC (Dong et al., 2017). SiO can then react with C at 1600 °C to produce SiC and CO as shown in R3. EtOH-SCC extraction process plays an important role in increasing the porosity of residual whose surface area is 128 m²/g, which is much higher than that of raw PRB coal $(3.36 \text{ m}^2/\text{g})$ (Tan et al., 2019) and thus benefits the improvement of reaction rate of heterogeneous reaction between C(s) and SiO(g) or acceleration of β -SiC production. In the studied β -SiC synthesis, H₂ released from EtOH-SCC extraction residual during heating process plays a critical role in accelerating β -SiC production, which is fundamentally different from the coke (C) and SiO₂ based β -SiC synthesis pathway. The schematic diagram showing the β-SiC formation mechanism is shown in Fig. 8.

3.3. Properties of the synthesized β -SiC

3.3.1. Surface area, porosity and density analysis

Fig. 9 shows N₂ adsorption-desorption isotherms of β -SiC samples and Table 4 presents the textural properties of raw materials and β -SiC products. The surface area of β -SiC synthesized with the

holding time of 60 min is 101.6 m²/g, and it increases to ~108 m²/g and barely changes when the holding time extended from 120 to 180 min. The average pore diameter and total pore volume show opposite trends. The β -SiC samples obtained with the holding times of 120 and 180 min exhibit similar average pore diameter -~5.5 nm, and total pore volume -0.15 cm^3 /g, which are lower than that of β -SiC synthesized with 60-min isothermal period, 6.3 nm and 0.16 cm³/g, respectively. The surface areas of β -SiC samples synthesized in this research are much higher than that of the SiC sample from another research, 21.75 m²/g (Y. Liu et al., 2017), resulting from much small average pore diameter (5.5 nm) of the β -SiC synthesized in this research. From the density test, the true density for SiC powder (1600 °C, 180 min) is 3.15 g/cm³, which is very close to the density of β -SiC which is 3.16 g/cm³ shown in the CRC Handbook of Chemistry and Physics.

3.3.2. Phase analysis

Crystallinities of the synthesized β -SiC samples were assessed with powder XRD. Fig. 10 shows the XRD patterns of β -SiC samples synthesized with a heating rate of 10 °C/min and held at 1600 °C for 60–180 min. All the characteristic diffraction peaks corresponding to (111), (200), (220), (311), (222) planes of β -SiC (JCPDS Card No: 29–1129) appear in Fig. 10. Another weak shoulder peak at around 2 θ = 33.6° marked as SF results from the stacking faults (SF) on the (111) plane in β -SiC crystals (Dong et al., 2014),(Li and Guo, 2018),(Zhang et al., 2016). The XRD results reveal that β -SiC is the only phase in these SiC powder samples, which indicates that the synthesized silicon carbides have high β -SiC purities. The purity of β -SiC powder is about 93%. With further treatment by the acid mixture of HNO₃ and HF to eliminate metallic impurities and unreacted SiO₂, the purity of β -SiC products.

3.3.3. FTIR analysis

FTIR spectra for β -SiC materials obtained at 1600 °C with different holding times (60min, 120 min, 180min) are displayed in Fig. 11. All the β -SiC samples display a strong band at around 785 cm⁻¹associated with its stretching vibration. The observation is consistent with that reported in literature within the absorption



Fig. 8. Schematic diagram showing the formation mechanism of β-SiC.



Fig. 9. Nitrogen adsorption-desorption isotherms of β-SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: 60 min, 120 min, 180 min].

Table 4 Surface area, average pore diameter and total pore volume of raw materials and β -SiC prepared with different holding times.

No.	Sample name	BET surface area [m ² g ⁻¹]	Average pore diameter [nm]	Total pore volume [cm ³ g ⁻¹]
1	Treated residual	126.0	3.9	0.12
2	Treated Sandstone powder	170.1	3.7	0.15
3	1600 °C, 60 min	101.6	6.3	0.16
4	1600 °C, 120 min	108.1	5.4	0.15
5	1600 °C, 180 min	108.7	5.5	0.15



Fig. 10. XRD patterns of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/ min; heating temperature: 1600 °C; holding time: 60 min, 120 min, 180 min].

band of 860-760 cm⁻¹ (Nikkam et al., 2014). Along with XRD results, the FTIR spectra further confirm the formation of β -SiC. The peak intensities of the Si–C band become higher when the holding time β -SiC increases from 60 min to 120 min, although they show almost no change with the continuous increase in holding time.

3.3.4. Photoluminescence analysis

The PL spectra of β -SiC powder samples are provided in Fig. 12. The samples were excited with light from a xenon source with an excitation wavelength of 320 nm at room temperature. In Fig. 12, β -SiC powder samples show similar PL spectra, and all samples exhibit two light emission peaks at wavelengths of 436 nm and 526 nm, corresponding to the band gaps of β -SiC at 2.84 eV and 2.36 eV, respectively. The band gap at 526 nm (2.36 eV) is attributed to (β)3C–SiC as previously reported (Brillson et al., 2002),(Van Dorp et al., 2009). The peak (2.84 eV) around 436 nm shows a blue shift compared to the band gap (2.36eV) of 3C–SiC, which can be attributed to the structural defect (Li and Guo, 2018),(Prakash et al.,



Fig. 11. FTIR spectra of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: 60 min, 120 min, 180 min].

2015). Along with XRD and FTIR results, PL analysis further confirms the formation of (β)3C–SiC.

3.3.5. Antioxidation ability analysis

Antioxidation ability of β -SiC was evaluated by TGA. β -SiC powder samples synthesized with a heating rate of 10°C/min 1600 °C with different holding times were heated from 25 °C to 1400 °C under air with the flow rate of 100 ml/min. The oxidation data in terms of the relative mass changes with temperature for different samples during the whole oxidation period are given in Fig. 13. The TGA curve for β -SiC sample synthesized with a holding time of 60 min shows a significant weight loss within 600-900 °C and this weight loss is attributed to the oxidation of unreacted carbon. The other two samples did not show significant weight losses, which means that all carbons were consumed due to the use of longer sample holding times at 1600 °C. Also, all the TGA profiles show weight increases in higher temperature ranges, resulting from the β -SiC oxidization by O₂ in the air under high temperature and the formations of SiO₂ and SiO. Specifically, one sample was oxidized at 900 °C, whereas the oxidations of the other two β -SiC



Fig. 12. Photoluminescence spectra of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: 60 min, 120 min, 180 min].



Fig. 13. TGA profiles of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: 60 min, 120 min, 180 min].

samples started at 1100 °C. Consequently, β -SiC products isothermally held at 1600 °C for 120 min and 180 min have similar antioxidation abilities, and thus more stable in air than the β -SiC held for 60 min. Therefore, longer holding time is beneficial to the improvement of the properties and qualities of produced β -SiC, according to the result of XRD and FTIR and TGA tests. Based on its strong antioxidation ability under high temperature and high surface area characteristics, β -SiC could be promising catalyst support for heterogeneous reactions (Cuong et al., 2014) and a candidate for high temperature electromagnetic wave absorption (C. Liu et al., 2017).

3.3.6. Microstructural analysis

SEM observations with different magnifications were conducted for the β -SiC products synthesized with isothermal holding times of 120 min and 180 min at 1600 °C to investigate their morphology and microstructure as shown in Fig. 14. The low-magnification SEM images or Figs. 14a–1 and 14b-1, exhibit that the β -SiC materials are consisting of particles below 100 µm. SEM image of β -SiC synthesized with an isothermal holding time of 180 min shows smaller average particle size than that of β -SiC synthesized with an isothermal holding time of 120 min, resulting from cracking of large particles into small ones with the increase in reaction time. Fig.s 14a-2 and 14b-2 show the surface characteristics of the β -SiC particles. Open porosity can be seen on the surface of the β -SiC particles in both samples. The high porosity values are related to the high surface areas of the synthesized β -SiC product. The high porosity could be induced by the gaseous species released during the pyrolysis of residual with inherently high porosity. β -SiC in this research also shows a Vickers hardness of 2240 kg/mm², and it is comparable to commercial products and researches conducted by Suresh (2200 kg/mm²) (Suresh et al., 2008) and Yamamoto (2200 kg/mm²) (Yamamoto et al., 2005).

The TEM image in Fig. 15a and selected-area transmission electron diffraction (SAED) image in Fig. 15b reflects the microstructural of synthesized β -SiC. The SAED pattern indicates that the β -SiC product is a polycrystalline material with high crystallinity. It shows three concentric diffraction spot rings centered on a bright central halo. The concentric rings represent three typical lattice planes of β -SiC sequentially indexed to be the (111), (220) and (311) crystal planes of β -SiC (JCPDS Card No: 29–1129). The results of XRD, FTIR, PL, and SAED, β -SiC was successfully synthesized from EtOH-SCC extraction residual of PRB coal and sandstone powder.

3.4. Environmental impact

Currently, SiC is industrially produced through Acheson process that occurs at as high as 2500-3000 °C and needs as long as 7 days for reactions and 7 days for cooling, thus SiC production process itself is energy intensive. Also, the carbon needed for industrial SiC production is supplied in the form of coke whose manufacturing is energy intensive. Thus, the overall industrial SiC production process is very energy intensive. The environmental emissions resulting from the Acheson process based SiC production are obviously high, resulting from the pollution characteristics of the coking process. The new SiC production technology uses the residual or waste from a new carbon fiber production technology(Liu et al., 2018) for providing the needed carbon resource of SiC, which is a pollution avoiding strategy for the perspective of obtaining carbon resource context. Moreover, the residual is more reactive with SiO₂ than coke is and thus entails the low reaction temperature and energy consumption characteristics of the new SiC production technology.

The environmentally friendly characteristics of the new SiC preparation technology is clear when we look at how the environmentally concerned elements in coal are used or controlled during the SiC production process. The most important element is carbon and thus the mainly concerned environmental issue is CO₂. CO₂ emission control is the major driving force for developing the integrated carbon fiber(Liu et al., 2018) and subsequent carbide production technology. Both carbon fiber and subsequent carbide production need carbon. The integrated technology is designed to extract the carbon in smaller molecules in coal for carbon fiber production(Liu et al., 2018), while the carbon-rich residual from coal extraction or larger molecules in coal becomes an ideal carbon source for carbide. Using the carbon in coal for producing two highvalue carbon materials is a smart way of using and fixing carbon in coal from the perspective of atom economy. Also, considering the fact that the energies needed for the carbon materials (actually all the materials) will be provided via renewable resources such as solar energy or solar-derived electricity. The new SiC production process is less intensive in energy consumption than the state-ofthe-art SiC manufacturing processes, the carbon footprint of the new SiC production technology should be smaller than those of conventional SiC synthesis processes, and much smaller than the combustion-based coal utilization technologies in which carbon is emitted and then captured with a large amount of energy. As a



Fig. 14. SEM images of β-SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: (a) 120 min, (b) 180 min].



Fig. 15. (a) TEM image and corresponding (b) SAED pattern of β -SiC synthesized with a mixture of 50 wt% treated residual and 50 wt% treated sandstone powder. [heating atmosphere: Ar; heating rate: 10 °C/min; heating temperature: 1600 °C; holding time: 180 min].

matter of facts, the new coal utilization technology can use or directly fix 40-50% carbon in coal in forms of solid carbon fiber and carbide. Also, the hydrogen and the remaining 50-60% carbon is mainly converted into syngas that can be subsequently used for producing organic chemicals or solid materials such as polymers, and consequently fixing the carbon unfixed during carbon fiber and carbide production processes. Combusting 1 ton of coal typically releases 2–2.5 tons of CO₂. Therefore, the superiority of the new SiC production technology in alleviating CO₂ emission is out of the question. Furthermore, other environmentally concerned elements especially heavy metals including Hg and As are removed during the pretreatment process of the coal extraction residual prior to its use for carbide production. The pretreatment can be used for very efficiently removal of the environmentally concerned heavy metals. The liquid wastes/byproducts generated during raw material treatment process can also be recycled and reused efficiently when the developed β -SiC synthesis process is applied in industry. After residual treatment, the used leaching solution contains AlCl₃ and FeCl₃ that can be used as coagulant for water treatment. Further, after sandstone treatment most of the acid is consumed, and the pH value of wastewater is around 6–7. The wastewater contains a certain amount of CaCl₂ that can be recycled and reused as desic-cant. The liquid wastes/byproducts also have economic value in this proposed technology. Thus, the SiC produced with the new technology should be environmentally safe or friendly.

4. Conclusions

Extracting PRB coal with ethanol and supercritical CO_2 to produce carbon fiber precursor and using the solid residual as carbon source to synthesize beta-silicon carbide is a novel and integrated technology for coal utilization. For the first time, β -SiC powders were successfully synthesized by reacting sandstone powder with EtOH-SCC extraction residual of PRB coal in Ar atmosphere at 1600 °C. The obtained β -SiC product shows good properties with its purity, density, and Vickers hardness being up to 98%, 3.15 g/cm³, and 2450 kg/mm², respectively. The β -SiC also exhibits good antioxidation ability in air when the temperature is lower than 1100 °C. A possible reaction mechanism was also proposed for the synthesis process and confirmed by the experimental results. The success in synthesizing β -SiC with the residual of coal-based high-value carbon fiber precursor production and sandstone powder opens a new and clean pathway for utilization of coal in generating value-added products with less or much less carbon footprints, which benefits both coal and carbide industries from the perspectives of cost reduction and environmental protection. Commercialization of the new technology will lead to a win-win scenario for the economy and environment.

Declaration of interest

None.

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Nomenclature

REEs: rare earth elements

- EtOH-SCC: ethanol and supercritical CO2
- β -SiC (3C–SiC): cubic silicon carbide
- PRB: Powder River Basin
- M: mol/L
- MS: mass spectrometer
- ICP-MS: inductively coupled plasma mass spectrometry
- ICP-AES: inductively coupled plasma atomic emission spectroscopy
- XRD: X-ray diffraction
- FTIR: Fourier transform infrared spectrometer
- PL: photoluminescence
- BET: Brunauer-Emmett-Teller
- SEM: scanning electron microscope
- TEM: transmission electron microscope
- TGA: thermogravimetric analyzer
- SAED: selected-area transmission electron diffraction