

Effect of temperature on the formation of β -silicon carbide by hot isostatic pressing the pyrolyzed phenol resin–silicon composite

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Abstract

The aim of the present study is to investigate the effect of temperature on the formation of β -SiC below the melting point of silicon; and to develop a new technique that might be implied to convert the used polymeric materials to produce silicon carbide and to minimize the environmental problems caused by the gases formed during combustion of used polymeric products. In the first step, preforms were produced by pyrolysing phenolic resin and silicon powders at 850 °C, then HIPed at 1300–1400 °C, in second step. XRD peaks of β -SiC were observed at 1300 °C; and then these peaks were heightened with increasing the temperature. SEM photographs showed the formation of whisker and crystals of β -SiC in pores and matrix of the composite HIPed at 1400 °C. The increase in apparent density and Vickers micro-hardness of the composites; and the results of EDS and XPS analyses suggested that the formation of β -SiC was enhanced at higher temperatures.

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1. Introduction

Recently, increasing attention has been given to carbide materials due to their attractive properties. Among these materials, silicon carbide is a typical transition metal carbide with high melting point, high hardness, high abrasion resistance, good chemical resistance, good radiation resistance, good thermal conductivity, low thermal expansion coefficient, and high thermal shock resistance.^{1–7} 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 metals or hot gases, high temperature structural materials, and reinforcement in composites.^{8–11}

Phenolic resins have been widely used as coatings, adhesives, composites, etc. due to their excellent flame resistance, heat resistance, insulativity, dimensional stability and chemical resistance.¹² However, carbonized phenolic resin are usually highly microporous and are being used as filters, catalysis,

molecular sieves, gas absorbers and source of carbon for the synthesis of silicon carbide.¹³

Silicon carbide is a kind of covalent material with a tetrahedral structural unit similar to diamond. Due to its excellent properties, SiC has been applied in many important fields as an advanced functional material.¹⁴ Therefore, many efforts have been made to prepare silicon carbide by a variety of methods. Acheson process is mainly used for the production of silicon carbide on industrial scale, which involves a carbothermal reduction of sand by petrol coke at about 2400 °C. This method demands high temperature and long reaction time because both sand and petrol coke are solid, which limits the extent of reaction. Alternative methods include the sol–gel method by the thermal reduction of SiO₂/C material in a temperature range of 1250–1450 °C^{14–17} and the infiltration of pyrolyzed wood with silicon at a temperature beyond the silicon melting point.^{18,19} Ishihara et al.² have synthesized silicon carbide powders by the thermal reduction reaction at 1800 °C using silica and phenol resin as raw materials. Li et al.²⁰ have prepared silicon carbide by HIPing graphite in a silicon mold at 1700 °C for 2 h under a pressure of 100 MPa. Shi et al.¹ fabricated silicon carbide powders in a three-step process from silicon and phenol resin by heating at 1500 °C in Argon atmosphere.

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The aim of the present study is to investigate the effect of temperature on the formation of β -SiC below the melting point of silicon; and to develop a new technique that might be implied to convert the used polymeric materials to produce silicon carbide and to minimize the environmental problems caused by the gases formed during combustion of used polymeric products.

2. Experimental procedure

2.1. Starting materials

The average grain sizes of novolac-type phenol resin (PR-50590B, SUMITOMO BAKELITE Co., Ltd. Japan) and Si (FURUUCHI CHEMICAL Co., Ltd. Japan) powders are 35 and 1 μm , respectively. In order to maintain 1:1 atomic ratio between carbon and silicon atoms in the matrix, the calculated mass% ratio between phenol resin and silicon is 40:60. But considering the loss of carbon atoms due to evaporation and the formation of gaseous molecules during pyrolysis, the designed mass% ratio of phenol resin involved with Si powders is slightly larger than the calculated value, and is 44:56.

2.2. Sample preparation

Phenol resin of 44 g was dissolved in 16 ml of ethanol at room temperature and then mixed with Si powders to make slurry. The slurry was poured into Cu tubes with an inner diameter of 8 and 1 mm in thickness. The sealing was conducted by mechanical pressing the both ends of Cu tubes which allowed a small amount of gases formed during the pyrolysis to be released through tiny holes at the pressed ends. This incomplete sealing prevented the failure or ballooning of the tubes due to the increase in internal pressure with temperature.

In the first step, pyrolysis of the sealed mixtures was carried out in vacuum of about 15 mPa in an electric furnace. The specimens were heated from room temperature to 200 °C (at a rate of 5 °C/min), kept at this temperature for 60 min, and then heated to 850 °C (5 °C/min), kept at this temperature for 180 min. Cooling was also done in two steps, in the first step, cooled down to 450 °C (5 °C/min), and then to room temperature (in vacuum). These pyrolyzed phenol resin/Si composites with outer diameter (6–7 mm), comparable to the inner diameter of the Cu tube were obtained.

After the pyrolysis, the composites were taken out from the Cu tubes and wrapped with zirconia fabric (used to avoid the sticking of samples on inner surfaces of steel cases); and then enclosed in steel sheets (used for deep drawing). The edges of the steel sheets were welded to suppress the emission of gases from the composites completely. The steel containers were put into an alumina crucible and inserted in a HIP furnace (Kobelco, O2-Dr. HIP). The composites were HIPed at 1300, 1350 and 1400 °C for 10 min, in an Ar atmosphere of 50 MPa, in second step. The heating and cooling rates for all the temperatures were 10 °C/min. The HIPed composites were cut into pieces for analyses and tests.

2.3. Properties and microstructural investigation

The density of the pyrolyzed and HIPed specimens was measured by Archimedes method. The microstructure of the polished specimens was observed using scanning electron microscopy (SEM; XL-30 ESEM Series, FEI Company Ltd., Japan) and the energy dispersive spectrometer (EDS), equipped to the SEM, was used to carry out the elemental analyses. The crystalline structure was observed by X-ray diffraction (XRD-6000S Shimadzu Co. Ltd., Japan), which was performed with Cu irradiation (1.54060 Å) at a scanning rate of 2 °/min, in 2θ range between 20° and 80°. Chemical states of atoms in the composites were investigated by X-ray photoelectron spectroscopy (XPS; ESCA-1000, Shimadzu Co. Ltd., Japan) with Mg K α irradiation (1.253 keV). Since the specimens were exposed to air, their surfaces were removed by Ar⁺ ion milling for 5 min, before the XPS analyses. Vickers microhardness of matrices of the composites was measured by using Vickers microhardness tester (HMV, Shimadzu Co. Ltd., Japan). A load of 9.807 N was applied for 30 s.

3. Results

3.1. Apparent density and Vickers microhardness

Fig. 1 shows that the apparent density and Vickers microhardness (HMV) of the composites increases with temperature. The rise in density may be attributed to the HIPing process. The maximum apparent density (2.75 g/cm³) was obtained at 1400 °C, which is 88.71% of the bulk density of SiC (3.1 g/cm³). The rise in HMV may be attributed to the densification and enhancement in the formation of SiC at higher temperatures. The maximum HMV (16.1 GPa) was achieved at 1400 °C and is less than the hardness of bulk SiC (28 GPa).

3.2. Microstructure

Fig. 2 shows the cross-sectional SEM photographs of the pyrolyzed and HIPed composites. The matrices of composites are composed of spherical micropores and particles with diameter ranging from several μm to several 10 μm . The voids result from the degradation of polymer components and resulted in the low apparent densities of the composites.

Fig. 3 shows more precise microstructure of the matrices containing particles and pores. The particles (B, D, F and H) are embedded in the pores and matrices of the composites.

Fig. 3(e and f) shows the formation of whisker and crystalline β -SiC in the composite HIPed at 1400 °C (Fig. 3(d)).

In order to obtain the further information of materials, which constitute particles, crystals and the surrounding matrix, EDS analyses were carried out. The EDS analyses showed that the peak of C in the matrices (A, C, E and G) of the composites decreases with temperature, while there is a very little change in the peak height of Si (Fig. 4). This fact shows that the matrices are composed of silicon and carbon. EDS analyses of particles (Fig. 5) showed that the peak height of carbon decreases with temperature, which means that some reactions took place that

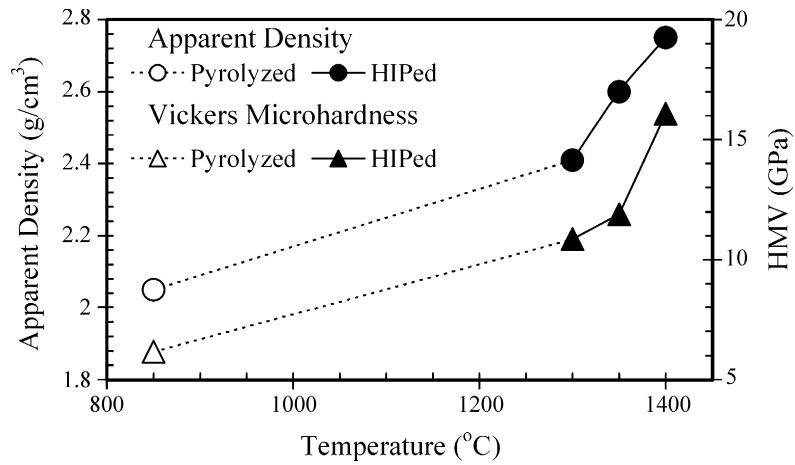


Fig. 1. Effect of temperature on the apparent density and Vickers microhardness.

consumed the carbon at higher temperature, because the loss of carbon during HIPing is difficult due to closed system. The atomic percentage of Si and C in the crystal (H) is almost 1:1, which shows that the crystals are composed of silicon carbide.

3.3. Analysis of crystalline structure

XRD spectra obtained from pyrolyzed and HIPed composites are shown in Fig. 6. The XRD spectrum of composite pyrolyzed at 850 °C did not reveal the formation of SiC (Fig. 6(a)). On the

other hand, low peaks of SiC were observed at 1300 °C. And then these peaks were heightened at high temperatures, because the formation of SiC was enhanced at higher temperatures. The peaks at $2\theta = 28.4^\circ, 47.3^\circ, 56.1^\circ$ belong to (1 1 1), (2 2 0) and (3 1 1) planes of cubic crystalline silicon.²¹ XRD peaks around $2\theta = 35.6^\circ, 41.4^\circ, 60.0^\circ$ and 71.8° are (1 1 1), (2 0 0), (2 2 0) and (3 1 1) belong to cubic silicon carbide (β -SiC), respectively.^{7,14} Other peaks of Si and β -SiC are also indexed in Fig. 6. The peaks of carbon were not observed in XRD profile, which means that amorphous carbon exists in the pyrolyzed and HIPed specimens.

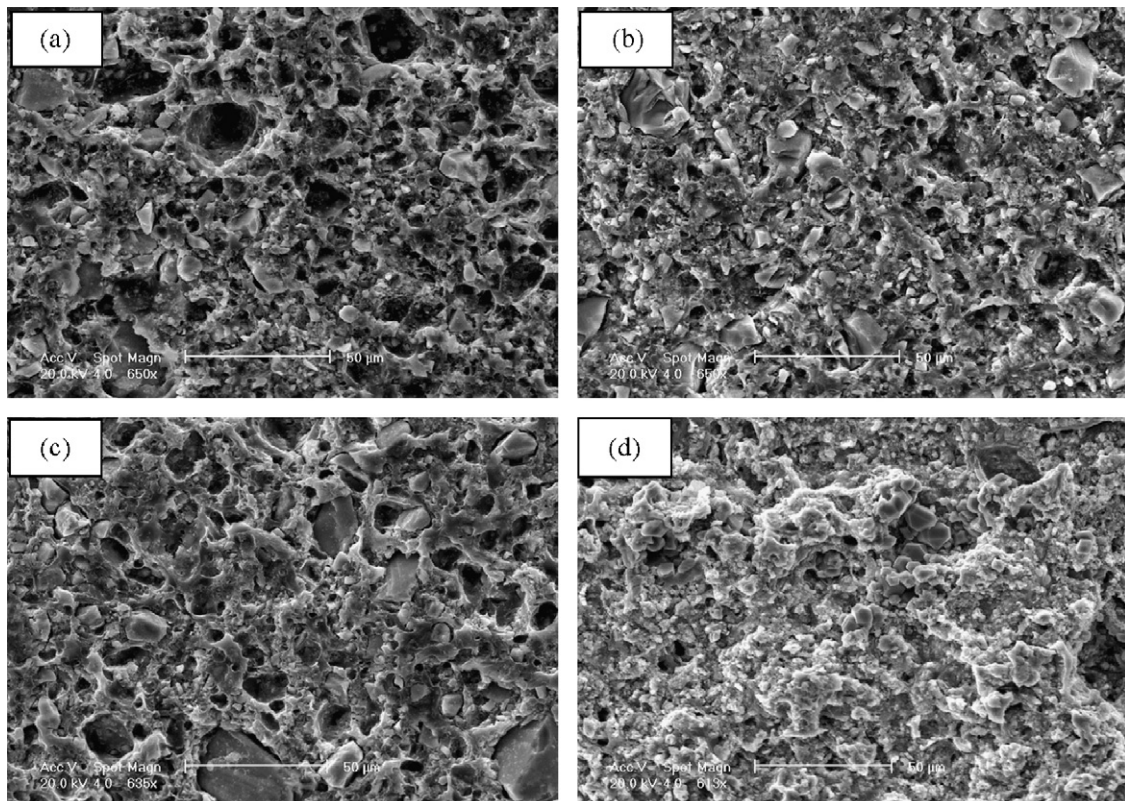


Fig. 2. SEM micrographs of the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

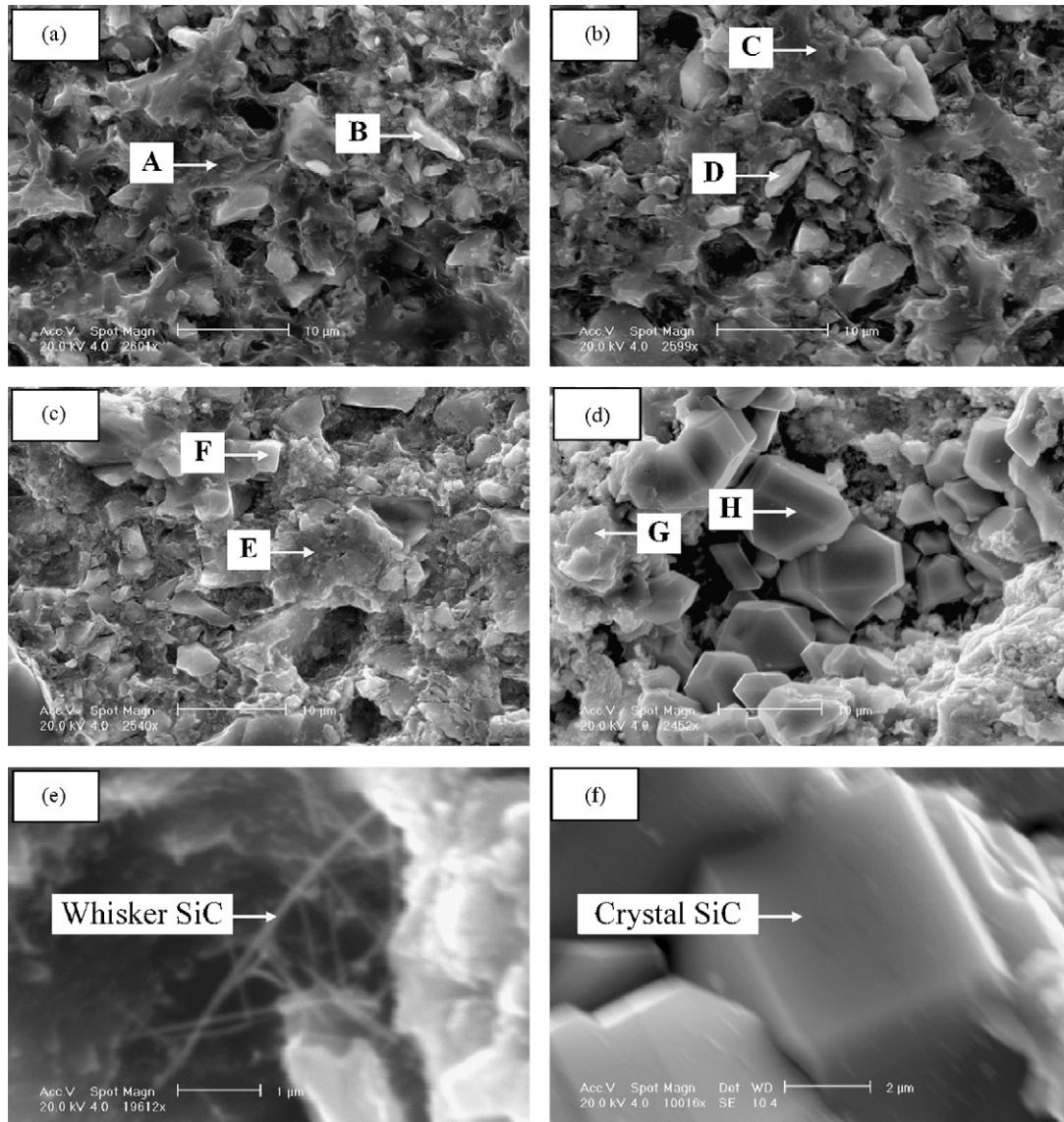


Fig. 3. Enlarged SEM images of the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C, (e, f) whisker and crystalline SiC formed in the composite HIPed at 1400 °C.

3.4. X-ray photoelectron spectra investigations

3.4.1. Silicon

XPS spectra of Si $2p^{3/2}$ electrons obtained from the pyrolyzed and HIPed specimens are shown in Fig. 7. The highest peak around 99.00 eV corresponds to Si. The spectra are broadened towards higher energies indicate that Si atoms are bound with other atoms. The peak in the range 101.19–100.44 eV corresponds to SiC, whose existence in cubic form was also observed in XRD analyses of HIPed composites but could not be observed in the pyrolyzed composite (SiC might be amorphous). It is reasonable to consider that XPS spectra for Si $2p^{3/2}$ have a range with nearly the same intensity from 101.50 to 103.50 eV where chemical state of Si varies continuously from mono-oxide to fully oxidized state of dioxide. Peak between 102.90 and 103.60 eV belongs to SiO₂. The peak in the range

101.70–102.70 eV corresponds to the deposited thin layer (about 300 nm) of silicon monoxide.²² The formed SiO and SiO₂ may be amorphous because XRD spectra of the composites did not reveal their crystalline existence. The peak height of silicon decreases and that of SiC increases with temperature, which is in agreement with XRD results.

3.4.2. Carbon

XPS spectra of C 1s electrons obtained from pyrolyzed and HIPed composites are broadened towards high-energy side and have several peaks (Fig. 8). The peak from 284.05 to 284.25 eV originated from carbon and the peak around 283.0 eV is considered to be attributed to C 1s in SiC. The formation of SiC was also observed in XRD analyses of the composites and XPS spectra for Si 2p electrons.

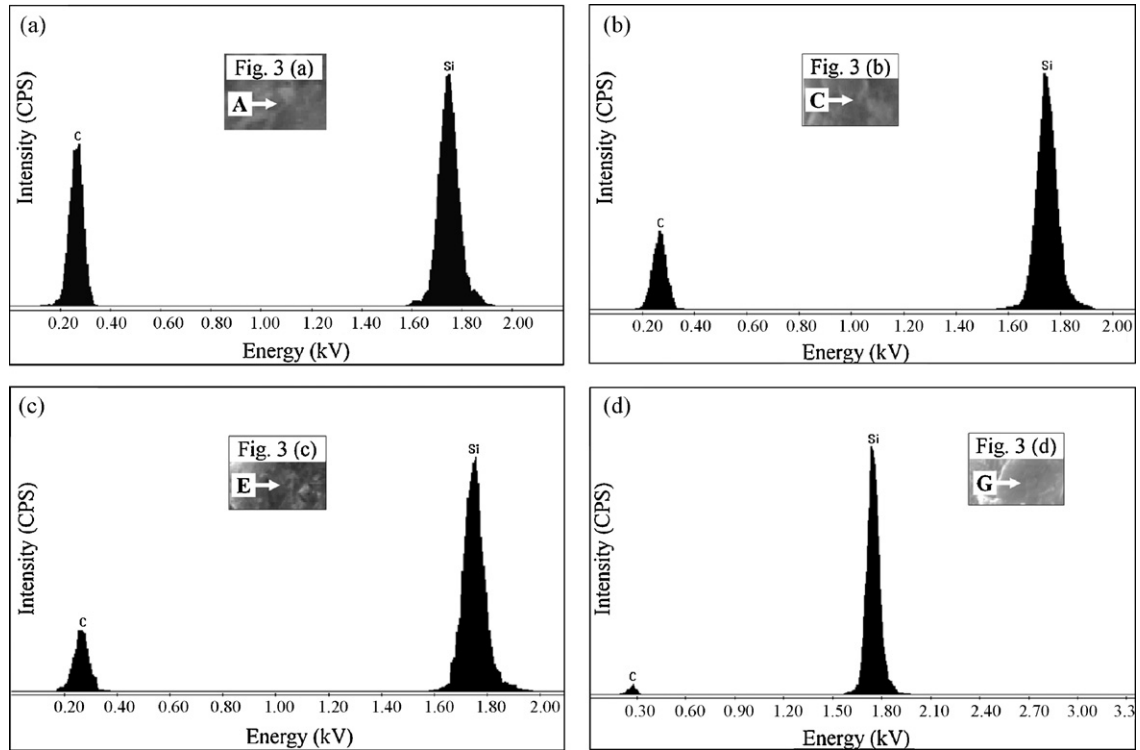


Fig. 4. EDS analyses of the matrices of the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

The peak between 285.07 and 285.11 eV is assigned to hydroxyl (R–OH)²³ and between 286.24 and 286.65 corresponds to carbonyl (>C=O). These results suggest that the peak height of SiC increases with temperature and the

various organic compounds with different functional groups formed during pyrolysis and HIPing; and these gaseous molecules were deposited on the inner surfaces of the closed pores.

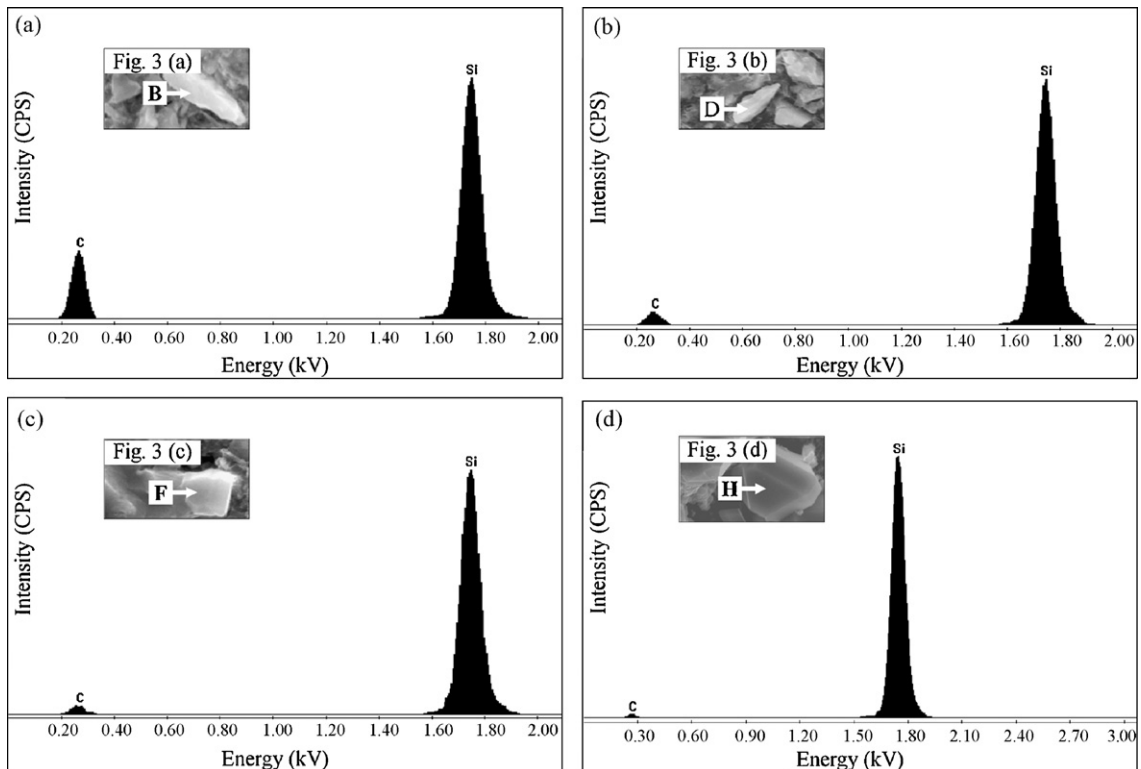


Fig. 5. EDS analyses of particles in the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

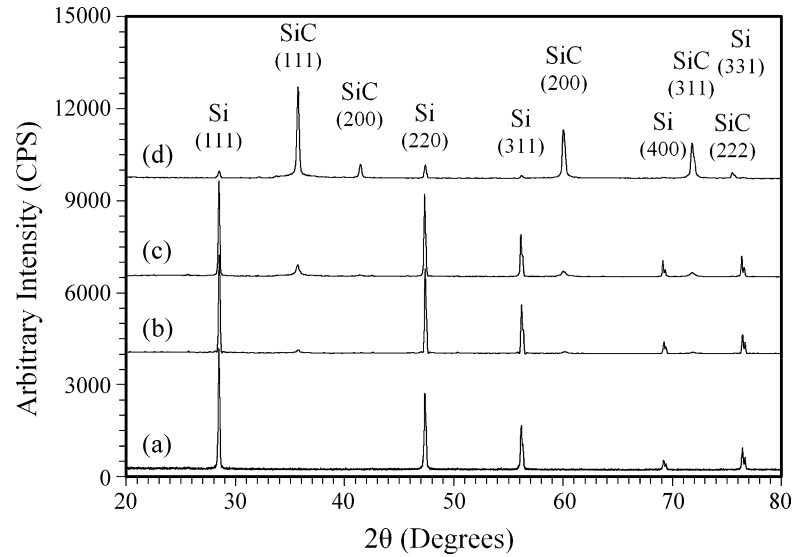


Fig. 6. X-ray diffraction spectra obtained from the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

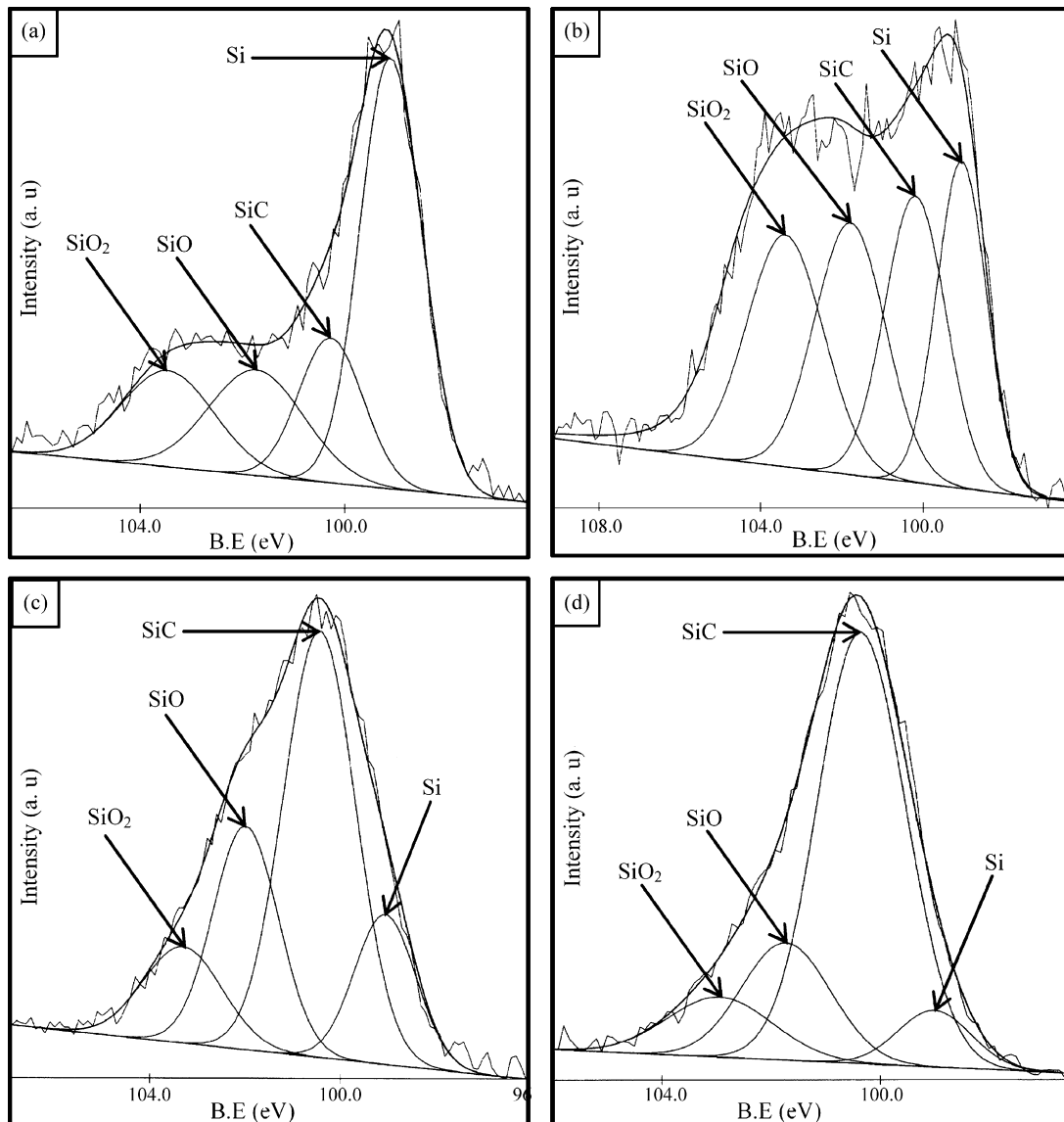


Fig. 7. XPS spectra of Si $2p^{3/2}$ electrons obtained from the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

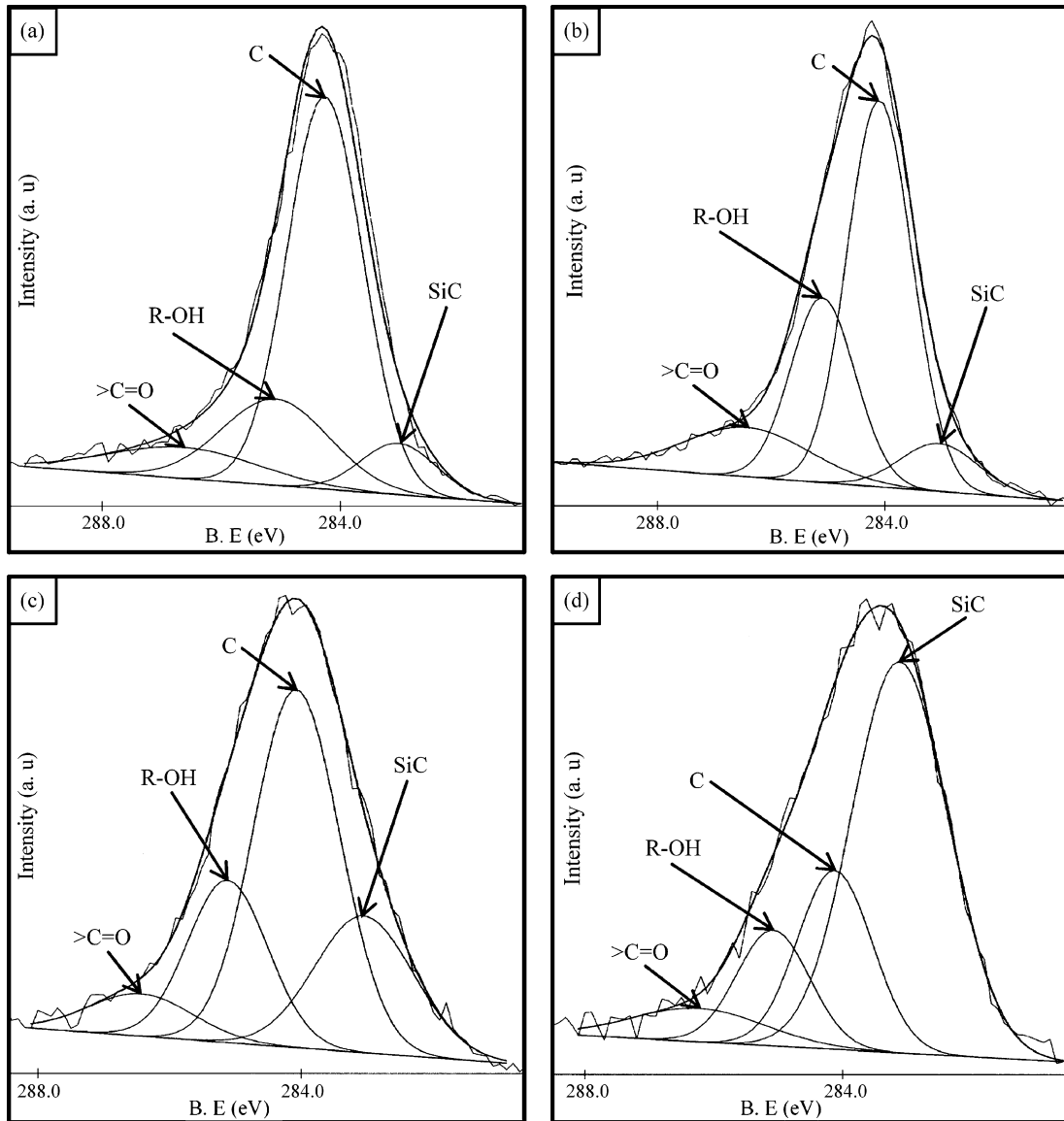


Fig. 8. XPS spectra of C 1s electrons obtained from the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

3.4.3. Oxygen

The XPS spectra of O 1s electrons obtained from the pyrolyzed and HIPed specimens revealed the presence of three peaks corresponding to hydroxyl (R–OH) or carbonyl (>C=O) group between 531.70 and 531.88 eV, SiO (532.50 eV), SiO₂ between 533 and 534 eV (Fig. 9). The formation of gaseous compounds caused the formation of pores and those gaseous compounds which trapped in closed pores were deposited on the inner surfaces of pores.

4. Discussion

Fig. 10 shows a relationship between the change in Gibbs free energy and temperature for formation of various compounds. The change in Gibbs free energies of CO and SiO are very closely related to each other (Fig. 10). The pyrolysis of phenol resin yields CO and other gases, and XPS

analyses also suggested the formation SiO, SiO₂ and SiC. In addition, SEM analyses showed the porous structure of the composites. Li et al.²⁰ have prepared silicon carbide by HIPing graphite in a silicon mold at 1700 °C for 2 h, under a pressure of 100 MPa and Shi et al.¹ fabricated silicon carbide powders in a three-step process from silicon and phenol resin by heating at 1500 °C in Argon atmosphere.

It is generally considered that SiC is formed by the reaction of gaseous silicon monoxide (SiO) and carbon monoxide (CO) or carbon (C) in the carbothermal reduction. However, the reaction of SiO and CO becomes thermodynamically favorable when the partial pressure of CO is greater than 0.027 MPa and the temperature is higher than 1300 °C.¹⁴ In addition, in the presence of pores in the composite bodies, carbothermal reactions could occur producing SiO and CO species; and when these gaseous species were entrapped in the porous structure, with P_{SiO}/P_{CO}

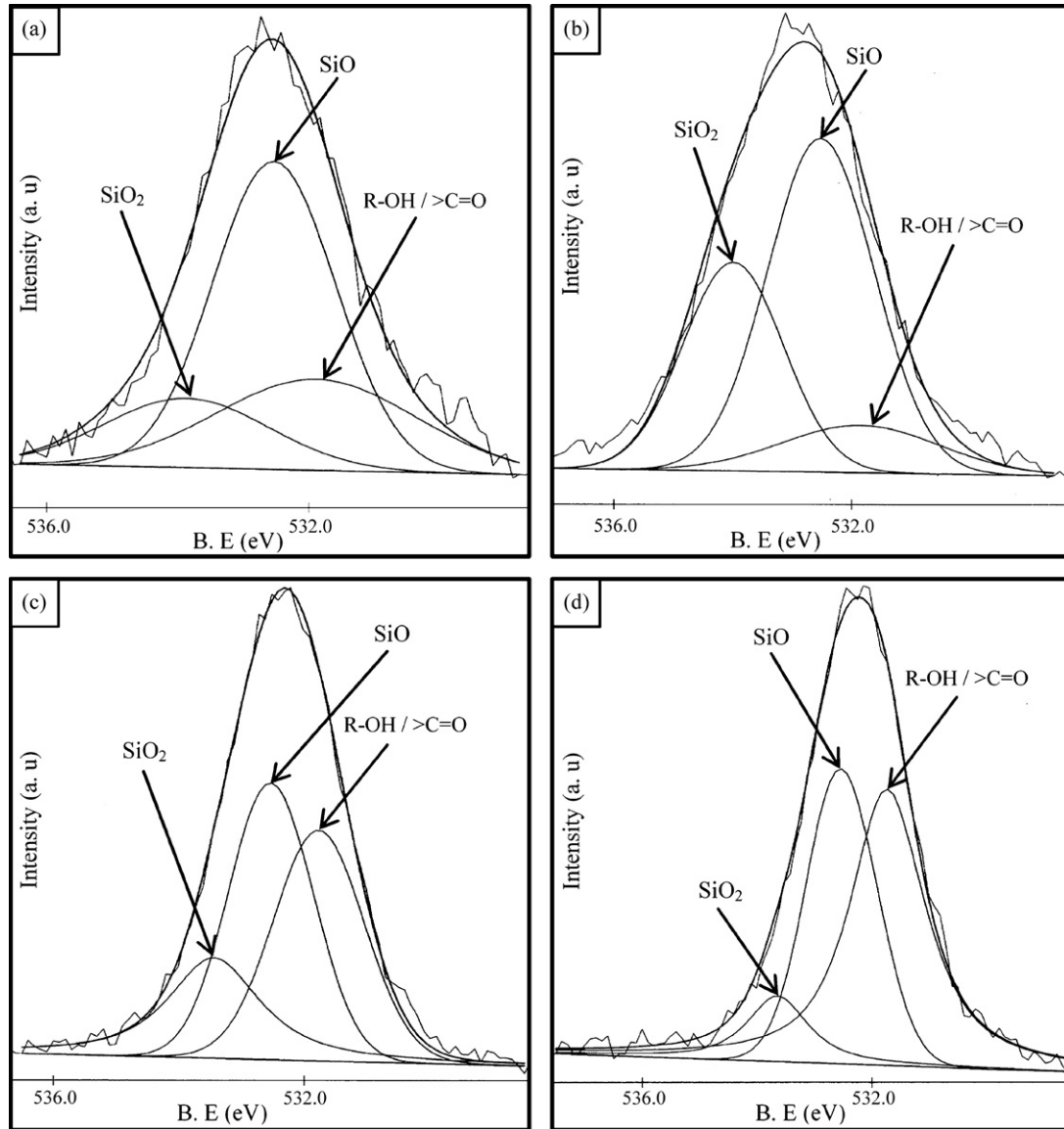


Fig. 9. XPS spectra of O 1s electrons obtained from the specimens (a) pyrolyzed at 850 °C, (b) HIPed at 1300 °C, (c) HIPed at 1350 °C, and (d) HIPed at 1400 °C.

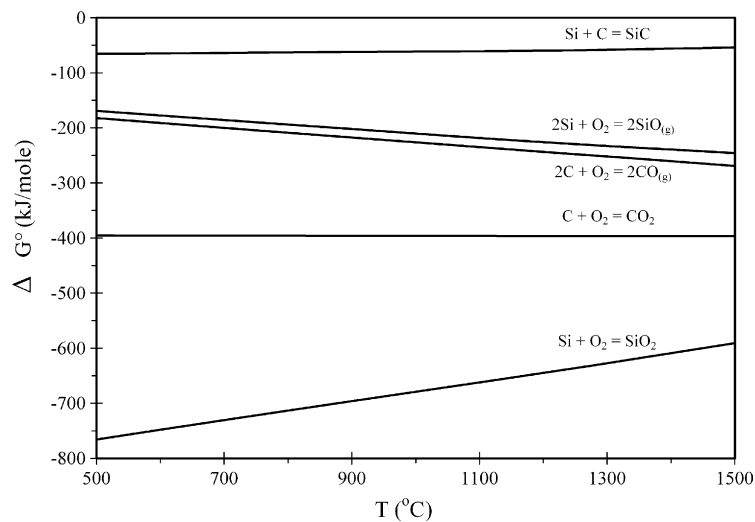
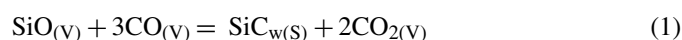


Fig. 10. Change in Gibbs free energy with temperature for the formation of various compounds.

ratio higher than one, SiC whisker particles could be produced. The reactions involved in this step can be summarized as:²⁴



Hence, the overall reaction is:



Considering the above discussion and from our experimental results of XRD, EDS, SEM, XPS analyses and change in Gibbs free energy, we suggest that the formation of SiC whisker particles might be by the carbothermal reactions of SiO and CO, as given by Eq. (3). In addition, the formation of β -SiC was enhanced at higher temperatures below the melting point of silicon. Hence, SiC might be nucleated by the reaction of SiO and CO, and gradually grown to crystals.

Therefore, the current paper describes a novel, simple and cost effective method for the fabrication of β -SiC from commercially available phenol resin and silicon powders.

5. Conclusions

Two-step process was used to investigate the effect of temperature on the formation diamond structure silicon carbide. Pyrolyzed composites were obtained by heating the novolac-type phenol resin and silicon powders at 850 °C in vacuum, and then these composites were HIPed at 1300, 1350 and 1400 °C for 10 min, in an Ar atmosphere of 50 MPa. The matrices of the HIPed composites were composed of amorphous carbon, cubic Si and β -SiC. The results showed that β -SiC was nucleated by the reaction of gaseous SiO and CO molecules, and then grown to larger ones (several μm in size). The crystal growth of β -SiC particles with facets and the formation of whisker β -SiC were observed at 1400 °C. The formation and growth of β -SiC in addition to the densification of matrices by HIPing led to the increase in hardness at higher temperatures below the melting point of silicon. This new technique might be implied to convert the used polymeric materials to produce silicon carbide and to minimize the environmental problems caused by the gases formed during the combustion of used polymeric products.

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