

## Growth of silicon carbide nanowires on porous silicon carbide ceramics by a carbothermal reduction process

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Porous SiC ceramics with a high specific surface area are promising candidates for catalyst support applications and further fabrication of nanowire-reinforced composites. This study employed the carbothermal reduction process using a mixed powder bed consisting of low-purity SiO<sub>2</sub> and carbon black in order to grow SiC nanowires on phenolic resin-coated porous SiC ceramics. A nanowire grown at 1400°C in the absence of a metal catalyst additionally introduced from the outside had a diameter of 100 nm and a length of several tens of micrometres. The carbothermal reduction method for growing SiC nanowires on surfaces as well as inner pores of porous SiC substrates involves migration and liquid droplet formation of elemental Fe generated from the mixed powder bed into the surface and the pores of the SiC substrate. Subsequently, gaseous SiO and CO from the mixed powder bed as the intermediate for 1-dimensional SiC were offered to the neighborhood of the porous substrate, and then the growth of  $\beta$ -SiC nanowires on  $\alpha$ -SiC substrate occurred via a VLS mechanism.

**Key words:** silicon carbide, porous ceramics, nanowires, carbothermal reduction, powder bed technique.

### Introduction

Ideal porous materials should possess a high surface area and sufficient mechanical strength in order to be used under severe operating conditions [1]. However, a shortcoming of porous materials is their low mechanical strength, which restricts their effectiveness under a wide range of operating conditions. One of the most promising class of porous materials for industrial use are porous silicon carbide (SiC) ceramics, since they have a unique combination of good oxidation resistance and thermal-shock resistance as well as excellent mechanical and chemical stability at elevated temperatures [2].

Porous ceramics used as a gas filter with a high surface area should have high particulate filtration efficiency and good gas flow capability. Increasing the surface area of a porous material can be easily accomplished by increasing the open porosity. However, enhanced porosity can induce degradation of mechanical properties. Therefore, growth of a 1-dimensional structure on the inside pores and surfaces of porous substrates is expected to promote a much higher filtering efficiency resulting from an increased pollutant-substrate interface without a decrease in any of the mechanical properties.

During the past several years, a great deal of effort has been devoted to the synthesis of SiC nanowires. Numerous techniques have been developed, such as a

carbon nanotube-confined reaction [3, 4], arc discharge [5], laser ablation [6], chemical vapor deposition (CVD) via the vapor-liquid-solid (VLS) mechanism [7-11], a high-frequency induction heating process [12], and an advanced carbothermal reduction of silica xerogels [13]. However, most of these methods involve expensive starting materials (usually, metal organic materials are used), complicated equipment, time-consuming processes, low product yield and the need to introduce metal catalysts. These factors limit the application of nanowires and necessitate further study in each area in order to make the production of nanowires more economical.

This study employed a carbothermal reduction process using a powder mixture bed consisting of low-purity SiO<sub>2</sub> and carbon in order to grow SiC nanowires in the pores as well as on the surfaces of phenolic resin-coated porous SiC ceramics.

### Experimental Procedure

The SiC porous substrate with  $\beta$ -SiC as a neck composition between  $\alpha$ -SiC particles prepared by a Si melt infiltration method shows open porosity of 48% and a median pore diameter of around 12  $\mu$ m.

SiO, which served as the silicon source for silicon carbide nanowire growth on the SiC substrate, was generated by carbothermal reduction of commercial low-purity SiO<sub>2</sub> ( $\rho=2.45$  g/cm<sup>3</sup>,  $D_{50}=11.64$   $\mu$ m, Microsilica 971-U grade, Elkem Materials, Norway) containing Fe<sub>2</sub>O<sub>3</sub> (0.18 wt%). In order to supply volatile SiO and CO gases to the neighborhood of the SiC substrate, a powder mixture consisting of SiO<sub>2</sub> powder and carbon

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black ( $\rho=1.94 \text{ g/cm}^3$ ,  $D_{50}=5.11 \text{ }\mu\text{m}$ , Hi Black 5L, LG Chemical Co. Ltd., Korea) used as a bed were mixed in plastic bottles for 24h to increase the homogeneity. The powder mix ratio was 1:1 mass % of  $\text{SiO}_2$  to carbon black.

The porous SiC substrate was dipped into a mixture solution consisting of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Kanto Chemical Co. Inc., Japan) and phenolic resin (resole type, Kolon Chemical Co. Ltd., Korea) of 1 to 1 in a weight fraction in order to improve the wettability of the phenolic resin for the porous SiC material. The resin-coated substrate was dried at  $80^\circ\text{C}$  for 24h and then heated at  $350^\circ\text{C}$  for 1h in air to remove other impurities. The resin-derived carbon on both the surfaces and the pores of the substrate acts as nucleation sites for the SiC growth reaction with the SiO species generated from the mixed powder beds consisting of  $\text{SiO}_2$  and carbon.

The powder bed was placed on a BN-coated graphite plate and then the phenolic resin-coated SiC substrate was put on the powder bed mixture in a box furnace chamber with a graphite heater. After evacuation of the furnace chamber to about  $1 \times 10^{-2}$  Torr (1.33Pa), a high purity (99.99%) argon gas was introduced at a constant pressure of 0.1 MPa and a flow rate of  $2 \text{ L/minute}^{-1}$ . Heat treatment was carried out at 1300 to  $1600^\circ\text{C}$  for 1h using a one-step heating cycle in the furnace with increasing increments of  $10 \text{ K/minute}^{-1}$ . The sample was cooled at the fastest permissible rate allowed by the water chiller equipment.

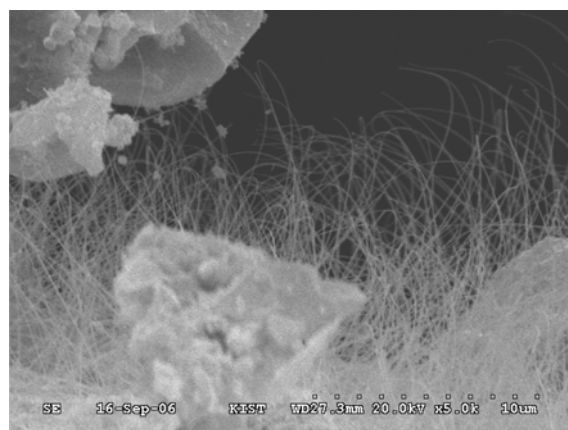
The morphologies of various SiC nanowires grown on both surfaces and inside pores of SiC substrates were observed by scanning electron microscopy (SEM, Hitachi, S-3000H, Japan). Phase identifications of specimens treated at various temperatures were determined by X-ray diffractometry (XRD, Rigaku, D/max-2C, Japan) using  $\text{CuK}\alpha_1$  radiation (wavelength  $1.54056 \text{ nm}$ ), an operating voltage of  $40 \text{ kV}$  and a current of  $30 \text{ mA}$ . XRD patterns of the sample were obtained in the  $2\theta$  range between  $20$  and  $80^\circ$  with a step of  $0.01^\circ$  and a scan speed of  $5^\circ \text{ minute}^{-1}$ . The detailed structural features and chemical compositions of the SiC nanowires were further determined at  $400 \text{ kV}$  by high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-4010, Japan) equipped using an energy dispersive X-ray (EDX) system.

## Results and Discussion

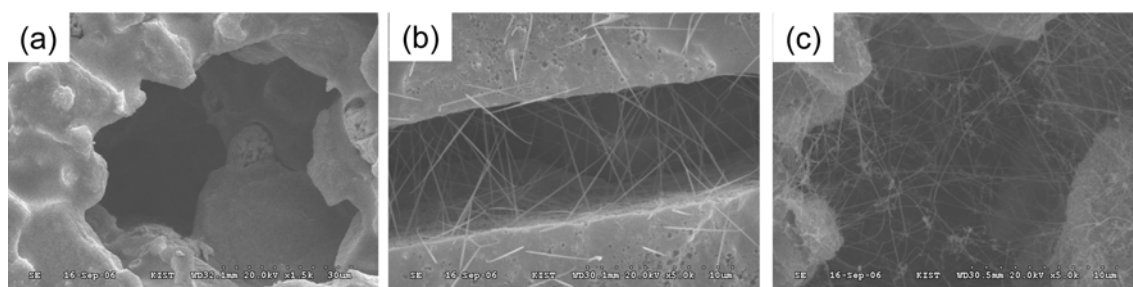
According to the scheme of this study, efficient growth of SiC nanowires requires the conversion of  $\text{SiO}_2$  not to SiC solid but to SiO vapor. It also requires that the SiO generated should interact with the carbon-carrying species in the solid and vapor phases which will enable the growth of SiC in a 1-dimensional structure [14].

Figure 1 shows an SEM image of the surface of a porous SiC ceramic heat-treated in the carbothermal reduction system using a mixed powder bed consisting of  $\text{SiO}_2$  and C at  $1400^\circ\text{C}$  for 1h in argon. It is noteworthy that well-defined and straight nanowires grew on the surface of the substrate. This means that SiC nanowires grown on a SiC ceramic surface can enhance the filtering efficiency for fine detrimental particles by increasing the adsorption area.

Figure 2 shows SEM images for the inner pores of the porous SiC ceramics heat-treated at various temperatures for 1h in Ar by the carbothermal reduction process using a mixed powder bed. Generally, porous SiC ceramics prepared by Si melt infiltration show excellent mechanical strength due to the  $\beta$ -SiC as a neck composition and the residual Si content which is located between the SiC particles. In order to achieve better mechanical properties and greater oxidation resistance, the residual Si is partially oxidized to  $\text{SiO}_2$  under oxidative conditions such as those used for the initial substrate in this study. Additionally, the  $\text{SiO}_2$  phase on



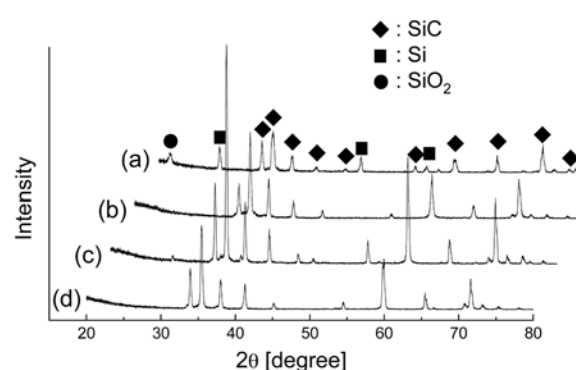
**Fig. 1.** SEM image of the surface of a porous SiC substrate heat-treated at  $1400^\circ\text{C}$  for 1h in argon.



**Fig. 2.** SEM images of pores in porous SiC substrates heat-treated at (a)  $1300^\circ\text{C}$ , (b)  $1400^\circ\text{C}$  and (c)  $1500^\circ\text{C}$  for 1h in argon, respectively.

the SiC substrate assists in the interaction with homogeneously coated carbon resulting from the phenolic resin under the carbothermal reduction condition, which accelerates the kinetics for the growth of SiC nanowires. However, it is desirable that the modification of the pore structure for porous ceramics is avoided above 1600 °C because structural collapse induced by the reaction of Si and SiO<sub>2</sub> with resin-derived carbon and thermal decomposition of  $\beta$ -SiC. SiC nanowires were grown at 1400 and 1500 °C (Fig. 2(b)) and (Fig. 2(c)), but no reaction was found in the sample treated at 1300 °C (Fig. 2(a)). This indicates that the reaction between SiO gas and solid carbon derived from the phenolic resin required for the SiC nanowire growth is no longer possible at 1300 °C. Nanowires grown at 1400 °C have straighter and cleaner surfaces than those formed at 1500 °C. This may be due to a smaller pressure drop during the filtering operation. Additionally, SiC nanowires can be successfully grown in the pores as well as on the surfaces of the porous SiC substrates by carbothermal reduction using the mixed powder bed technique. It is noteworthy that all wires can be grown across the pores. This can provide SiC ceramics with enhanced mechanical properties and a high specific surface area for catalyst supports.

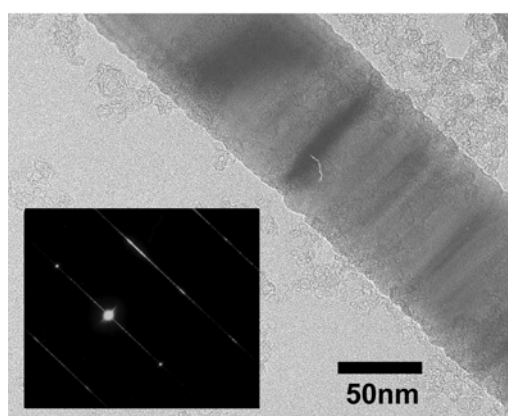
Figure 3 shows the XRD patterns of the nanowires grown on the porous SiC substrates heat-treated at various temperatures for 1 h in an argon atmosphere. There are main phases of  $\alpha$ - and  $\beta$ -SiC in all the XRD patterns. The sample without a 1-dimensional structure treated at 1300 °C shows residual Si and SiO<sub>2</sub> peaks similar to the initial substrate. However, all the SiO<sub>2</sub> peaks disappeared and the residual Si phase practically vanished when the temperature was increased above 1400 °C. This indicates that SiO<sub>2</sub> on the SiC substrate surface reacted with the phenolic resin-derived carbon under the carbothermal reduction conditions and then all the SiO<sub>2</sub> phase was consumed to generate SiO gas. The residual Si solid may react with the coated carbon solid to form an SiC layer on the SiC substrate. The



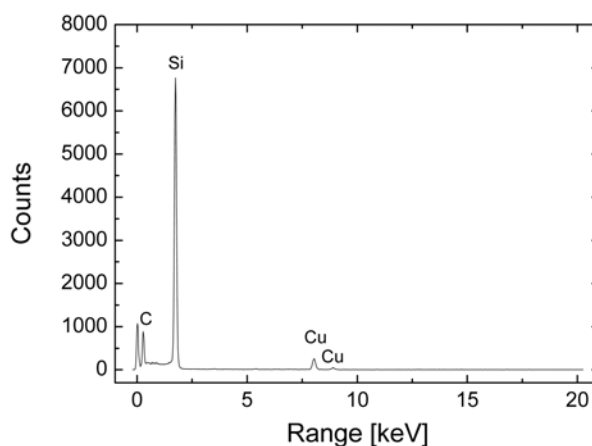
**Fig. 3.** XRD patterns of porous SiC substrates with SiC nanowires on their surfaces and in the pores heat-treated at various temperatures of (a) 1300, (b) 1400, (c) 1500 and (d) 1600 °C for 1 h, respectively.

solid-gas reaction which occurs directly between gaseous the SiO and solid carbon tends to show a 1-dimensional structure with a high density of stacking faults. The product formed by the solid-solid reaction tends to be a film with a low density of stacking faults.

To examine in more detail the structure and chemical composition of a  $\beta$ -SiC nanowire core grown at 1400 °C for 1 h in Ar, high-resolution transmission electron microscopy (HRTEM) combined with energy dispersive X-ray (EDX) analysis was performed, and is shown in Fig. 4. Generally, nanowires have a smooth surface which helps to improve wetting and increase the adhesive strength in reinforced materials. This wire has about a diameter of about 100 nm and a relatively smooth surface roughness. A key characteristic was that no amorphous SiO<sub>2</sub> layer was formed on the outer layer of the  $\beta$ -SiC nanowire. No evidence of oxygen or other impurities was found in the EDX spectrum (Fig. 4(b)). The inset image in Fig. 4(a) shows the corresponding selected area electron diffraction (SAED) pattern obtained from the same sample. The SAED shows bright spots as well as streaks, indicating a single crystalline nature with some defects. These stacking faults are generally thought to originate from thermal stress dur-



(a)



(b)

**Fig. 4.** The (a) HRTEM micrograph and (b) EDX spectrum of a SiC nanowire core grown at 1400 °C for 1 h in Ar. Inset in (a) is the SAED pattern of the identical sample.

**Table 1.** BET surface areas of porous SiC ceramics treated at various temperatures for 1h in Ar

Temperature [°C]	1300	1400	1500	1600
BET surface area [m <sup>2</sup> /g]	18.72	43.68	54.51	Structural collapse

ing the growth process [15, 16]. Since the SAED streaks are always perpendicular to the stacking fault planes {111}, the main growth direction of the nanowires can be assumed to be parallel to the <111> direction.

A well-accepted mechanism of nanowire growth via the gas-phase reaction is the so-called vapor-liquid-solid (VLS) process, which results in the formation of spherical particles on the tips of nanowires [17]. In the EDX spectrum for the tip of the nanowire grown at 1400°C, an Fe metal tip at the end of nanowire was detected, so a simple model is proposed to explain the growth of nanowires. The Fe element acts as a catalyst for the growth by the VLS mechanism. Catalyst particles for the growth of the nanowires are considered to originate from the iron oxide that exists in the SiO<sub>2</sub> of the mixed powder bed, since the iron oxide could be reduced to iron by carbon black powder in the bed under carbothermal reduction reaction conditions. Elemental irons can be evaporated from the bed and then migrate on the SiC substrate. Resin-derived carbon on the SiC fliter surface may further diffuse into the migrated iron to form an Fe-C alloy. The liquid Fe-C alloy has a large accommodation coefficient and is a preferred site for incoming SiO and CO vapors released during the carbothermal reduction process. When Si and C atoms are supersaturated in the Fe-C liquid,  $\beta$ -SiC nanocrystals nucleate at the liquid-solid interface and could be expected to grow along the preferred orientation.

Table 1 shows the BET surface areas of porous SiC ceramics treated at various temperatures. The sample grown at 1300°C without nanowires shows a BET surface area of 18.72 m<sup>2</sup>/g. When the temperature was increased above 1400°C, however, the surface area suddenly increased along with the carbothermal reduction reaction. The surface area of the sample grown at 1400°C was two times greater than the surface area of the sample grown at 1300°C. The surface area increased with increasing temperature up to 1500°C, which is in a good agreement with the SEM observations shown in Fig. 2. However, investigation of the surface area of the sample treated at 1600°C was insignificant since structural degradation of the porous SiC substrate occurred due to the thermal decomposition of the  $\beta$ -SiC organizing necks of the SiC substrate. Consequently, the porous ceramics embedded with high specific surface area nanowires synthesized by the carbothermal reduction process between 1400 and 1500°C using a mixed powder bed system are promising candidates for catalyst support applications in terms of procedure cost and simplicity.

## Conclusions

The possibility of introducing  $\beta$ -SiC nanowires into porous SiC ceramics opens new opportunities for further fabrication of nanowire-reinforced composites. Moreover, porous ceramics embedded with high specific surface area nanowires are promising candidates for catalyst support applications. It is proposed that the growth of  $\beta$ -SiC nanowires follows the VLS mechanism in the absence of a metal catalyst introduced from the outside. These nanowires are about 100 nm in diameter and several tens of micrometres in length. The carbothermal reduction method for the growth of SiC nanowires on surfaces as well as inner pores of porous SiC substrates was modified as follows: (i) migration and liquid drop-let formation of the Fe element from mixed powder bed onto the surfaces and the pores of the SiC substrates; (ii) supplying gaseous SiO and CO generated from the mixed powder bed as an intermediate to the neighborhood of the porous substrate for the growth of SiC nanowires; and (iii) growth of  $\beta$ -SiC nanowires on  $\alpha$ -SiC substrate via the VLS mechanism. The BET surface area of the SiC ceramic containing  $\beta$ -SiC nanowires grown at 1400°C was two times greater than that of the ceramic grown at 1300°C.

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