Fabrication of SiCf/SiC composites through hybrid processing via chemical vapor infiltration, electrophoretic deposition, and liquid silicon infiltration

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ABSTRACT

The present work demonstrates the effectiveness of a novel hybrid process comprising chemical vapor infiltration (CVI), electrophoretic deposition (EPD), and liquid silicon infiltration (LSI) techniques for the successful fabrication of low-porosity SiCf/SiC composites. For this purpose, fiber/matrix interphase dual coating layers of BN and SiC were coated onto SiC fabrics using CVI. A ceramic matrix consisting of SiC and carbon black nanoparticles was then infiltrated into the fine voids of the fabrics using EPD. Finally, LSI was performed to obtain dense microstructures with low porosities by filling the remaining small gaps and reacting Si with C to form SiC. Microstructural results observed by scanning electron microscopy revealed a dense structure with no damage to the fibers. The experimental density was found to be 2.62 g/cc, with an open porosity of 0.55. The room-temperature flexural strength was evaluated to be 111 MPa, and the composites displayed little fiber pull-out.

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1. Introduction

Fiber-reinforced ceramic matrix composites (CMCs) in general and SiCf/SiC composites in particular have been recognized as potential candidates for many widespread applications owing to their typical properties such as low density, high specific strength and hardness, excellent nuclear radiation tolerance, oxidation resistance, and thermal shock resistance [1–5]. These applications include high-performance brake discs, high-temperature heat exchangers, structural components for solar receivers, nuclear reactors, hypersonic aircraft, and space reentry vehicles. At present, many researchers are investigating the fast and efficient fabrication of CMCs because their use has been limited by various fabrication problems.

In general, during the fabrication of CMCs, coating of the weak fiber/matrix interphase, infiltration of the ceramic matrix phases, and the selection of fiber preforms play decisive roles in determining CMC properties. To fabricate high-density and low-porosity CMCs, voids in the fiber preforms are essentially infiltrated by a matrix phase after coating with a suitable interphase. For this purpose, a wide range of manufacturing techniques are being actively developed. These techniques are categorized into three types based on the type of precursor phase used: gas phase, liquid phase, and solid phase or ceramic methods [4]. The gas-phase method includes chemical vapor infiltration (CVI) techniques; liquid-phase methods include precursor infiltration and pyrolysis (PIP) and liquid silicon infiltration (LSI) and/or reactive melt infiltration (RMI) methods, whereas solid-phase or ceramic methods include slurry infiltration (SI), nano-infiltrated transient eutectoid (NITE), hot pressing (HP), and electrophoretic deposition (EPD)-based techniques. Each technique has its own advantages and disadvantages [4–11].

LSI has been demonstrated to be an effective technique for fabricating C/SiC and SiCf/SiC composites. Low fabrication costs, low residual porosities, short fabrication times, and ease of near-net-shaping are the main advantages of the LSI method. From an industrial point of view, this method is economically more viable despite having disadvantages such as the presence of residual silicon and fiber damage, which may limit composite performance. To overcome these drawbacks, the composites are coated with weak interphase layers such as PyC, BN, or SiC using the CVI method. To reduce the residual silicon and increase the SiC content in the final product, researchers infiltrate a slurry containing sources of both carbon and SiC into the preforms using a brush and/or vacuum before LSI. However, the reliability of the composites prepared by these methods is always a problem. In past years, much research has focused on the use of CVI and LSI techniques for the fabrication of long fiber-reinforced CMCs since their existence from longer times [12–16].

Alternatively, EPD-based techniques have several advantages, such as precise controllability of the
composition, a simple, completely automated deposition apparatus, and fast and even growth rates. Several successful attempts have been made to use EPD-based techniques for the fabrication of SiC/SiC since their exploration from mid-1990s. In particular, there has recently been a significant boost in the use of EPD-based techniques for fabricating various CMCs. However, these studies are limited to the fabrication of relatively small-sized composites, and there are still some challenges [9,17–21].

By using only one fabrication technique, it is very challenging to achieve high density and low porosity. To overcome the problems associated with each fabrication method, researchers have developed hybrid techniques by combining the above-mentioned techniques [9,16,21–27]. The fabrication efficiency can be improved significantly by using a novel hybrid processing technique comprising CVI, EPD, and LSI, thus taking advantage of each method. EPD can be performed after coating with CVI to infiltrate the matrix phase and then LSI can be implemented. From an industrial point of view, there is also a need to develop an economically viable fabrication technique for manufacturing relatively large-sized samples. The purpose of this work is therefore to develop a hybrid technique using EPD together with CVI and LSI for the fabrication of relatively large-sized (15 × 6 cm²) high-density and low-porosity SiC/SiC composites.

2. Materials and fabrication

With regard to the fabrication of SiC/SiC composites, a hybrid processing technique comprising CVI, EPD, and LSI was used in the present work. As a first step, CVI was performed on SiC fabrics. For this purpose, commercially available two-dimensional plain-woven Tyranno SA3 SiC fabrics (Ube Industries, Japan) cut into planar 15 × 6 cm² dimensions were used as the reinforcements. The SiC fabrics were then dual coated with boron nitride (BN) and SiC layers through thermal reaction/decomposition of BCl₃, NH₃, SiH₄, and C₃H₈ gases at 920–950°C using a CVI chamber (Thermal CVD system, VTS Corporation, Korea). In the next step, a SiC and carbon black matrix slurry (30 wt.% solid content, 70:30 ratios of SiC and C) was infiltrated into the voids of the SiC fabrics through EPD. A stable slurry composed of β-SiC (∼80 nm, US Research Nanomaterials, Inc., USA) and carbon black (∼75 nm, CABOT, Monarch, USA) was prepared by ball milling after adding appropriate amounts of dispersant (5% with respect to powder, Hypermer KD1, ICI, UK) and phenolic resin (10% w.r.t. solvent, KRDMHM2, Kolon Chemical, Korea) in ethanol as the binder phase. EPD was performed for the SiC fabrics using the slurry in a dual-electrode system at 20 V (Tektronix DC power supply, PWS2721 model) for 10 min. A homogenizer (HG-15D, Daihan Scientific, Korea) was used to maintain the stability of the slurry. The distance between the SiC fabrics and the counter electrodes was 15 mm. The schematic diagram of experimental setup used for EPD is shown in Figure 1. Eight SiC fabrics were stacked and vacuum bagged after EPD and dried. Finally, after performing binder burn-out at 600°C for 1 h in argon atmosphere, LSI was performed using silicon powder (∼4–5 μm, grade 2, SICOMILL, Vesta Ceramics, Sweden) in vacuum at 1600°C for 30 min. The overall schematic diagram for the fabrication of the SiC/SiC composites is presented in Figure 2. The fiber volume content in the composite was found to be approximately 48%.

2.1. Characterization

The microstructures of the composites were observed by scanning electron microscopy (SEM; Model: S-4800, Hitachi Co.) after CVI and LSI. The experimental density and open porosity of the composites after LSI were determined using the Archimedes principle. The viscosity of the slurry was measured using a digital viscometer (DV-I, Brookfield, USA) at room temperature. The flexural strengths of the composites after LSI were measured using a three-point bending test with a universal testing machine (UTM: H5KT, Tinius Olsen, USA) according to the ASTM C1161-13 standard by using polished specimens with dimensions of 25 × 1.5 × 1.5 mm³. Flexural tests were conducted with a cross-head speed of 0.5 mm/min. at room temperature.

**Figure 1.** Schematic diagram of dual-electrode system of EPD used for the infiltration of SiC fabrics.
temperature, and the bending strengths were calculated based on the maximum load after fracture. Averages based on five measurements were used for flexural strength.

3. Results and discussion

CVI relies on the infiltration of the desired source gases into the fiber preforms, and eventually deposition of the interphase layers occurs at the fiber surfaces owing to surface reactions of the adsorbed gases. The thickness of the coating layers depends on the infiltration time. After pre-coating with the BN layer, a SiC coating was deposited. These dual coatings were considered to protect the fibers at high temperatures. The microstructure of a typical CVI dual-coated SiC fabric is shown in Figure 3(a); a higher-magnification view is presented in Figure 3(b). Dual coatings of BN and SiC are clearly observed, with thicknesses of approximately 650 and 300 nm, respectively. The formation of BN and SiC coatings can be understood from the reactions between the constituent gases based on thermodynamic reactions (1) and (2):

\[
\begin{align*}
\text{BCl}_3(g) + \text{NH}_3(g) & \rightarrow \text{BN}(s) + 3\text{HCl}(g) \quad (1) \\
3\text{SiH}_4(g) + \text{C}_2\text{H}_6(g) & \rightarrow 3\text{SiC}(s) + 10\text{H}_2(g) \quad (2)
\end{align*}
\]

Energy dispersive X-ray analysis data confirmed the presence of stoichiometric constituent elements of BN and SiC phases. It is believed that the presence of BN will facilitate high fracture toughness and protect the fibers during high-temperature treatments, whereas the presence of the SiC coating layer will enhance the infiltration of the matrix phase. A previous study explored the advantages of dual coating over a single coating [28–30]. After CVI for an appropriate time, large pores between the fiber bundles remain, and longer times and expensive source gases are required to completely densify the composites. These pores and voids can be effectively filled with ceramic particles using the EPD technique. Because the complete infiltration of the matrix phase through CVI is very time consuming and expensive, EPD was performed as the next step.

![Figure 2](image_url)

Figure 2. Schematic diagram for the fabrication of SiC/SiC composites.

![Figure 3](image_url)

Figure 3. Microstructure of a typical CVI dual coated SiC fabric at two different magnifications.
It is well known that EPD is fundamentally a wet colloidal process in which electrically charged ceramic particles in a suitable suspension are deposited onto the surface of a counter electrode owing to the applied electric voltage. To infiltrate the ceramic particles into the fine voids of fabrics, a dual-electrode system was used in the present work, where the fabrics were placed between two stainless-steel counter electrodes [9]. EPD requires a well-dispersed and stable slurry composed of the required matrix phase for successful infiltration into the voids of the fiber preforms. For this purpose, nano-sized ceramic powders are preferred over micron-sized powders to facilitate infiltration into the fabrics. Therefore, in the present work, SiC and carbon black of almost similar particle sizes were used. The use of an optimized slurry is essential in EPD so that uniform deposition can be achieved. Before performing EPD, the viscosity of the slurry was checked because appropriate viscosity is necessary for successful infiltration. The viscosity of the slurry displayed (Figure 4) suitable shear thinning behavior, with a value of approximately 0.2 Pa.s at a shear rate of 60 s⁻¹. EPD was performed at an operational pH of approximately 3 by considering the zeta potential behaviors of SiC and carbon black from the previous results [23, 29 – 30]. Figure 5 shows a comparison of digital camera images of the SiC fabrics before and after EPD. It can be observed from the images that the matrix phase homogenously infiltrated and deposited onto the SiC fabrics. This demonstrates the effectiveness of EPD with the slurry used and optimized conditions. No major cracks were observed and the matrix did not peel off, even after drying, owing to the use of phenolic resin as a binder in the slurry. Other binders such as Polyvinyl butyral binder resin may experience cracks and peel-off behavior upon de-binding. When used as a binder, thermosetting phenolic resin has more advantages than other binders. It

![Figure 4](image1.png)

**Figure 4.** Viscosity of the slurry used for EPD as a function of the shear rate.

![Figure 5](image2.png)

**Figure 5.** Comparison of digital camera images before and after EPD of SiC fabrics.
acts as both a binder phase and a carbon source during the LSI process after de-binding. Moreover, the handling of fabrics becomes easy.

During LSI, at temperatures higher than the melting temperature of silicon, liquid silicon infiltrated into a porous preform under the driving of capillary force. The liquid silicon expanded to fill the pores and reacted with the carbon in the porous preform, which ultimately resulted in a dense, Si-rich SiC composite matrix. The cross-sectional microstructure of the prepared composite after LSI at two different magnifications is shown in Figure 6. It can be observed from the figure that a completely dense structure was obtained. The SiC fibers retained their original circular shape and were not damaged after heat treatment. Complete pore filling of the Si and SiC matrix is observed, which implies that almost zero porosity was achieved. The experimental density was found to be 2.62 g/cc, with an open porosity of 0.55. Flexural strength was evaluated to be 111 ± 10 MPa after LSI. All these values are presented in Table 1. The observed flexural strength value is relatively lower even though the porosity is very low. Similar lower flexural strengths of about 130 – 170 MPa were reported earlier [17] in the case of cross-ply SiC/SiC composites and these lower values are explained based on the fiber orientation. The SiC fibers aligned in 0° direction would contribute for toughening and strengthening of composites effectively whereas the fibers aligned in 90° direction may not contribute since these fibers exist parallel to the crack propagation during bending test. SEM images of the fractured composites after the flexural test are presented in Figure 7. Si-rich SiC matrix and SiC fibers in both the 0 and 90° orientations are clearly observed to be undamaged. It can also be observed from the magnified images that the coating on the fibers was maintained after LSI. Strong bonding between the ceramic matrix and the SiC fibers is clearly visible, which is accountable for the brittle fracture behavior. Little fiber pull-out with a small fiber length was observed owing to strong bonding, even with the dual coating. These SEM images clearly demonstrate that the ceramic matrix was well infiltrated without damaging the SiC fibers, leading to dense and low-porosity composites.

From the above results and discussion, considering the dense microstructures and low porosities of the SiC/SiC composites, it is evident that by combining the different fabrication techniques, a novel low-cost hybrid processing technique could be developed. Although CVI is a well-established technique for fabricating composites of any size and shape, it is very challenging to achieve compact structures.

Table 1. Experimental bulk density, porosity and flexural strength of SiC/SiC composites.

| Exp. density (g/cc) | Porosity (%) | Flexural strength (MPa) |
|---------------------|--------------|------------------------|
| 2.62 ± 0.04         | 0.55 ± 0.20  | 111 ± 10               |

Figure 6. Cross-sectional microstructure of composites at two different magnifications after LSI.

Figure 7. SEM images of fractured composites after flexural test.
Additionally, it is a time- and energy-consuming process to obtain homogeneous matrix infiltration of composites. Therefore, matrix infiltration was performed in this work by exploiting the advantages of the EPD technique. For this purpose, a stable slurry was prepared and infiltrated into the voids of the SiC fabrics. Finally, LSI was performed to obtain dense structures with low porosities by filling the gaps and reacting Si with C to form SiC. By adjusting the parameters such as the thickness of the coating layers by CVI and the slurry compositions for EPD, further high-density composites could be fabricated.

4. Conclusions

In conclusion, the present work demonstrates the effectiveness of a novel hybrid processing technique comprising CVI, EPD, and LSI techniques for the successful fabrication of high-density and low-porosity SiC/SiC composites by considering the advantages of each fabrication technique. After dual coating with BN and SiC using CVI, the matrix was infiltrated using EPD, and finally LSI was performed. The results indicated a dense microstructure with no damage to the fibers, and the composites exhibited an experimental density of 2.62 g/cc with an open porosity of 0.55. The flexural strength was evaluated to be 111 MPa, and strong bonding between the ceramic matrix and SiC fibers was observed, which accounted for the brittle fracture behavior. Finally, these results are encouraging from an industrial point of view for fabricating low-cost and relatively large-sized SiC/SiC composites.

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Disclosure of potential conflicts of interest

The authors declare that they have no known competing financial interests.

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