The Effect of Amorphous Polysilazane and Infiltration Method on The Densification of SiC\textsubscript{f}/SiC Composites

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Abstract. In this study, we investigated the ability of polysilazane as starting materials to fabricate SiC\textsubscript{f}/SiC composite prepared by slurry infiltration method, i.e., vacuum infiltration (VI) and electrophoretic infiltration (EPI). After infiltration, sintering was performed using hot pressing vacuum furnace at 1750 °C for 1 h in Ar atmosphere and applied pressure of 20 MPa. Phase analysis revealed the formation of \(\alpha\)-SiC for EPI, while \(\alpha\)-SiC and \(\beta\)-SiC were detected for VI. It seems the transformation of \(\beta\)- to \(\alpha\)-SiC enhances significantly in the EPI, resulting in single-phase \(\alpha\)-SiC. Moreover, the presence of excess carbon after sintering indicated that the amount of Si and C was not stoichiometry. The density of SiC\textsubscript{f}/SiC composite infiltrated by VI and EPI was 2.68 and 2.92 g/cm\(^3\), respectively, corresponding to 81.6 and 90.9% of theoretical density. Although the density is quite different, the average flexural strength for VI and EPI was 174 ± 5 and 200 ± 7 MPa, respectively, which does not differ significantly. However, the tail extension was observed for both samples, indicates the toughness increase compared to monolithic ceramic. This study indicates that polysilazane can be used as an alternative precursor for the fabrication of SiC\textsubscript{f}/SiC composites using a slurry infiltration method.

Keywords: Polysilazane, SiC\textsubscript{f}/SiC composite, Electrophoretic infiltration, Vacuum infiltration

1. Introduction

Ceramic matrix composites (CMC), such as SiC\textsubscript{f}/SiC composites, have been developed to overcome the catastrophic fracture behavior of monolithic SiC due to a weak interface between fiber and the matrix that improves the toughness of the composites. Moreover, SiC\textsubscript{f}/SiC composites have recently considered as a structural component for fusion and advanced fission reactors due to their low induced radioactivity and excellent resistance under neutron irradiation [1]. However, the fabrication of SiC\textsubscript{f}/SiC composites is very challenging due to the difficulty of sintering or infiltration methods.

Many technologies used to fabricate SiC\textsubscript{f}/SiC composites, including chemical vapor infiltration (CVI) [2], polymer impregnation and pyrolysis (PIP) [3], reaction sintering (RS) [4], slurry infiltration
[5], and the combination of these technologies [6]. In terms of purity and highly crystalline of SiC/SiC composites, CVI is the best method that shows no degradation of strength under neutron irradiation. However, this process requires quite a long time and produced high porosity [1]. In terms of simplicity, PIP and RS are an alternative method in addition to the former process. However, the free Si existed in the composites might deteriorate the properties for high-temperature applications. Moreover, non-stoichiometry of SiC/SiC composites fabricated by PIP and RS can causes radiation instability under neutron irradiation [7]. In terms of density, the slurry infiltration method is possible to obtain SiC/SiC composites with close-to-zero porosity. Therefore, the mechanical properties of this composite, in general, higher compared to other methods. The key factor of this method is the dispersion of SiC powder in the suspension, which infiltrates the SiC/SiC composites due to capillary force. Several slurry infiltrations were developed, such as nano-infiltrated transient eutectoid (NITE) [8], vacuum infiltration (VI) [9], and electrophoretic infiltration (EPI) [10].

Recently, monolithic SiC can be fabricated using a polymer precursor such as polycarbosilane and polysilazane [11]. High density monolithic SiC is possible to fabricate without the sintering additives when the polymer precursor is used as starting material [12]. These polymer precursors are also used for the fabrication of SiC/SiC composite using the PIP method. To the best of author knowledge, there is no report about the fabrication of SiC/SiC composites prepared by slurry infiltration especially using EPI and VI methods which have low cost and easy to produce with the polysilazane as starting materials.

In this research, we investigated the ability of polysilazane as starting materials to fabricate the densification of SiC/SiC composite prepared by slurry infiltration method. Two infiltration methods were used in this study; VI and EPI. The density, phase, microstructural, and mechanical properties were evaluated and presented in this study.

2. Experimental method

Polysilazane (KiON Ceraset Polysilazane 20, USA) is used as a matrix phase for SiC/SiC composites. The as-received polysilazane, which is in liquid form, was heated at 200 °C for 90 min to obtain a cross-link polysilazane. The cross-linked polysilazane was ground by mortar and pestle to get the powder. The powder was pyrolyzed at 1000 °C for 2 h in Ar atmosphere to achieve the amorphous powder. The pyrolyzed powder added with 10% of sintering additives (Al₂O₃, D_m = 150 nm, >99.9% purity, Baikowski, Japan and Y₂O₃, D_m = 200 nm, >99.9% purity, Acros Organics, USA with mass ratio of 60:40) and mixed with ball milling for 24 h in wet condition using ethanol as medium. Before mixing, 3 wt% of Hypermer (KD1, ICI, UK) as a dispersant and 10 wt% of polyvinyl butyral-98 (Butvar B-98, Solutia, USA) as a binder was added to the suspension to improve the properties of the suspension. The suspension used to infiltrate Tyranno SA3 fabrics (Ube Industries LTD., Japan) that have a woven structure and coated with pyrolytic carbon (PyC) with a thickness of 400 nm. This experiment used two infiltration methods i.e., vacuum infiltration (VI) and electrophoretic infiltration (EPI). For VI, five layers of SiC fabrics were stacked and infiltrated in the special VI apparatus. Details about VI method were further explained by Yonathan et al [13]. The dual system electrode was used in EPI, whereas the distance between fabrics and the electrode was 20 mm, with 10 V as an applied voltage for 30 min. The surface sealing effect during EPI was minimized by using ultrasonicator (HD 2070, Bandelin, Germany) for the first 20 min. After drying the infiltrate fabrics both for VI and EPI, lamination of 15 layers of fabrics was performed under an applied pressure of 10 MPa at 80°C. Binder burn-out was carried out at 350°C for 2 h in air with the heating rate was 0.5°C/min to remove volatile materials in the infiltrate fabrics. SiC/SiC composites were sintered in the hot-pressing furnace at 1750°C for 1 h in Ar atmosphere.

The density of SiC/SiC composites measured with the Archimedes principle using distilled water as a medium. The scanning electron microscopy (SEM, S-4800, Hitachi, Japan) used to observe and analyze the microstructure of the sintered SiC/SiC composites. A three-point bending test was performed using the ultimate testing machine (UTM AG-50E, Shimadzu, Japan). The composites cut
into 4 × 2 × 20 mm and polished using 1 µm diamond paste to remove the scratch from the samples for bending test purposes.

3. Results and discussion

Figure 1 (a) shows the amorphous polysilazane after pyrolysis, showing the coarse particle size. Milling was performed in order to decrease the particle size of the pyrolyzed powder; hence it could be comparable with the size of sintering additives. Beads mill was performed at 3000 rpm for 1 h, resulting in excellent particle size of amorphous polysilazane powder (Figure 1 (b)). The initial particle size of pyrolyzed powder before and after milling was > 10 µm and < 1 µm, respectively.

![SEM images of (a) pyrolyzed polysilazane and (b) milled pyrolyzed polysilazane. Different magnifications were used for clarity.](image)

Zeta potential of each constituent in the suspension is imperative for the infiltration of SiC fabrics using EPI due to its stabilization and the direction of the particle. Figure 2 shows the zeta potential of the suspension that contains amorphous polysilazane and sintering additives. According to the manufacturer, the polysilazane comprises Si, C, N, and O. Therefore, the zeta potential of Si, C, Al₂O₃, and Y₂O₃ was determined for the electrophoretic infiltration. As shown in Figure 2, positive zeta potential for each powder was obtained at pH < 10, while the isoelectric point for all fine particles was at pH 9.5-9.7. The highest zeta potential was Y₂O₃, i.e., 35 mV, and the lowest was ~ 15 mV. Thus, pH 1 was chosen for the electrophoretic infiltration.

![Zeta potential of the suspension containing amorphous polysilazane and sintering additives.](image)
Figure 3 displays the XRD patterns of SiC/\(\text{SiC}\) composites prepared by vacuum infiltration and electrophoretic infiltration. The results showed the formation of \(\alpha\)-SiC in the SiC/\(\text{SiC}\) composite infiltrated by EPI, while the structure of \(\alpha\)-SiC along with \(\beta\)-SiC observed for VI samples. Moreover, the presence of excess C was observed both in EPI and VI, indicates that the amount of Si and C in the amorphous polysilazane was not stoichiometry to form SiC. The effect of the infiltration technic influences the crystal structure of SiC. Single-phase \(\alpha\)-SiC formed in the SiC/\(\text{SiC}\) composites infiltrated by electrophoretic infiltration, while the presence of \(\beta\)-SiC detected in the vacuum infiltration. Compared to \(\alpha\)-SiC, \(\beta\)-SiC is metastable at 1600-1900°C and might transform to \(\alpha\)-SiC, then, the phase transformation from \(\beta\)- to \(\alpha\)-SiC during sintering at high temperature is universal phenomena. Several factors enhance the change of \(\beta\)- to \(\alpha\)-SiC, such as temperature, pressure, sintering additive, and sintering atmosphere [14]. Sintering atmosphere plays a vital role in the transformation of \(\beta\)- to \(\alpha\)-SiC. For instance, the \(\text{N}_2\) atmosphere inhibits the conversion from \(\beta\)- to \(\alpha\)-SiC [15], while the Ar atmosphere increases the transformation. Since the Argon atmosphere used in this study, the \(\beta\)- to \(\alpha\)-SiC transformation is inevitable, which is in agreement with the other report [16].

Moreover, the additives may enhance this \(\beta\)- to \(\alpha\)-SiC transformation. Another possibility that enhances the transformation \(\beta\)- to \(\alpha\)-SiC is the infiltration method itself, in particular for the EPI. In this study, amorphous polysilazane used as a precursor for the SiC instead of SiC powder. Since the amorphous polysilazane contain Si and C, the moving speed of these particles during EPI depends on the zeta potential. Although the zeta potential of those particles is similar, the ability to infiltrate SiC fabrics of those particles would be different during EPI. Therefore, the distribution of Si and C on the SiC fabric is not homogeneous, and lead to the formation of \(\alpha\)-SiC without the presence of \(\beta\)-SiC. On the other hand, SiC/\(\text{SiC}\) composite that infiltrated by vacuum infiltration showed the presence of \(\alpha\)-SiC and \(\beta\)-SiC, indicates that incomplete transformation of \(\beta\)- to \(\alpha\)-SiC. Regardless of the formation of SiC, these results imply that amorphous polysilazane is an alternative as a precursor for SiC.

Table 1. Density, relative density and flexural strength of SiC/\(\text{SiC}\) composite using different infiltration method.

| Infiltration Method       | Density (g/cm\(^3\)) | Relative density (%) |
|--------------------------|-----------------------|---------------------|
| Vacuum infiltration      | 2.68 ± 0.04           | 81.6                |
| Electrophoretic infiltration | 2.92 ± 0.05          | 90.9                |

Table 1 shows the density and relative density of SiC/\(\text{SiC}\) composite infiltrated by VI and EPI was 2.68 and 2.92 g/cm\(^3\), respectively. The EPI process imparts a higher density compared to VI. However, it still lowers if compared with EPI using SiC powder instead of amorphous polysilazane.
Figure 4 presents the SEM images of SiC\textsubscript{f}/SiC composite infiltrated by VI and EPI. Both of the infiltration methods revealed dense microstructure in the matrix area (Figure 4(a) and (c)). Nevertheless, the presence of pores was still observed in the fiber area. It shows that EPI results in smaller pores rather than VI so that it can produce a higher density. This is because the suspension of VI did not go through deep into the fiber area, resulting in many pores (Figure 4 (b)). Since the VI process depends on the properties of suspension, it seems the improvement of suspension is needed to infiltrate the SiC fabric deeply into the fiber area. Although the presence of pores observed in the SiC\textsubscript{f}/SiC composite infiltrated by EPI showed the capability of infiltrating the SiC\textsubscript{f} deeply (Figure 4 (d)) and showing better relative density than VI. However, the improvement is needed to achieve SiC\textsubscript{f}/SiC composite near the theoretical density by EPI [17].

![Figure 4](image_url)

**Figure 4.** SEM images of sintered SiC\textsubscript{f}/SiC composites at low magnification for (a) VI and (c) EPI, and at high magnification in fiber area for (b) VI and (d) EPI.
Figure 5. Flexural strength of SiC\textsubscript{f}/SiC composites prepared by different infiltration methods.

Figure 6. Fractured surface of SiC\textsubscript{f}/SiC composites after bending test prepared by (a) vacuum infiltration and (b) electrophoretic infiltration.

Figure 5 shows the flexural strength of SiC\textsubscript{f}/SiC composite prepared by different infiltration method. Although the density of SiC\textsubscript{f}/SiC composite infiltrated by VI and EPI quite different, the flexural strength of these composites is almost similar. The average flexural strength for VI and EPI was 174 ± 5 and 200 ± 7 MPa, respectively. It should be noted that abrupt load after maximum flexural strength, i.e., typical ceramic, was not occurred in both samples, as shown in Figure 5. Some tail extension, which generally occurs in metal, observed in both methods. This tail extension indicates pseudo-ductility fracture behavior, i.e., nonlinear regions appear clearly after proportional limits and the load will go down gradually after the maximum load [18]. The elongation at VI is more significant than EPI, where it is related to the morphology of the two infiltration methods, as shown in Figure 6. Indeed, the primary mechanism of tail extension of both samples was delamination, however, the degree of delamination in VI (Figure 6 (a)) higher compared to EPI (Figure 6 (b)). Thus, we observed prolonged displacement in the VI compared to EPI, as shown in Figure 5. This can be explained due to the density of VI is lower than EPI, thus the delamination of woven fabric occurs easily. Contrary, dense matrix observed in SiC\textsubscript{f}/SiC composites infiltrated by EPI, as shown in Figure 6 (b), with a little delamination. Based on the load-displacement graphics analyzed by a non-brittle fracture activity in the SiC fabric increases the toughness of SiC\textsubscript{f}/SiC composites compared to other methods at the other reports [19].
4. Conclusion
SiC/SiC composites were successfully fabricated using an amorphous polysilazane as a precursor for SiC, and two infiltration methods were used to infiltrate SiC fibres: vacuum infiltration and electrophoretic infiltration. This study showed the possibility to used polysilazane for fabricating SiC/SiC composite with the slurry infiltration method. The dense structure in the matrix area was observed for VI and EPI samples, even though the pores exist in the fiber area. The average flexural strength for VI and EPI did not differ significantly. However, tail extension observed for both samples, showing in the toughness of this composite increase compared to a general monolithic SiC.

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