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Highly efficient densification of carbon fiber-reinforced SiC-matrix composites by melting infiltration and pyrolysis using polycarbosilane

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Abstract

Carbon fiber-reinforced SiC-matrix composites (C_f/SiC) were fabricated via a precursor infiltration and pyrolysis (PIP) process. A polycarbosilane (PCS) precursor was used, with a halogen element (iodine) for curing. The effects of high-temperature polycarbosilane infiltrate melting and iodine-based curing on the efficiency of the PIP process, as well as the physical characteristics of the fabricated C_f/SiC composites, were investigated. Highly dense C_f/SiC composites with strong fiber/matrix interfacial bonding were fabricated. By melting the infiltrate and using iodine-based preform curing, the ceramic yield of polycarbosilane increased drastically from 38 wt% to 82 wt%. This increase, which is due to pyrolysis, resulted in a low degree of shrinkage in the polycarbosilane-derived matrix. This shrinkage, in turn, increased the density of the C_f/SiC composites and improved the interfacial bonding between the matrix and fibers. As a result, the fabricated C_f/SiC composites exhibited a density of 1.75 g/cm^3. This was much higher than the 0.38 g/cm^3 density of bare carbon fiber preforms after 6 iterations of the PIP process.
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Keywords: Carbon fiber-reinforced SiC-matrix composites; Precursor infiltration and pyrolysis; Halogen-based curing

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1. Introduction

Carbon fiber-reinforced SiC-matrix composites (C_f/SiC) have been developed for use as high-temperature structural materials such as in heat exchangers, advanced airplane engines, racing cars, etc. C_f/SiC composites are attractive due to their light weight and high specific strength and modulus at high temperatures [1–4].

There are a number of methods for preparing C_f/SiC composites. These include polymer infiltration and pyrolysis (PIP), chemical vapor infiltration (CVI), reaction bonding (RB), and hot pressing (HP) [5–9]. Among these processes, PIP combines low cost with the ability to easily fabricate C_f/SiC composites in complex shapes [10].

In the PIP process, a solution of polycarbosilane (PCS), which is the precursor for the SiC matrix in C_f/SiC composites, and either xylene, toluene, or divinylbenzene (DVB), which serves as the solvent, is generally made to infiltrate carbon fiber preforms. The infiltrated preforms are then dried, cured, and pyrolyzed. This process, however, results in a porous matrix with weak fiber/matrix interfacial bonding. Volatilization, low ceramic yield, and shrinkage of the polycarbosilane as a result of the pyrolysis process, during which temperatures can reach up to 1100 °C, are all reasons for this weakness [11].

Because ceramic yield is proportional to the molecular weight of the polycarbosilane precursor, precursors with very high molecular weights (in the range of 2000 Da–300 Da) are preferred. However, the solubility of such polycarbosilanes is limited, and their viscosity is high, and these factors can inhibit the infiltration process [12].

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In this study, C_f/SiC composites were fabricated by a PIP process in which the polycarbosilane infiltrate was melted at a high temperature and halogen (iodine)-based curing was used to increase the ceramic yield. The effects of high-temperature melting of the polycarbosilane infiltrate and iodine-based curing on the PIP process efficiency and the physical characteristics of fabricated C_f/SiC composites were investigated.

2. Materials and methods

2.1. Sample preparation

Carbon fiber preforms were obtained by needle punching 2D 0°/90° fabrics. The volume fraction of fiber in the carbon-fiber preforms was approximately 30 wt%. Characteristics of the polycarbosilane precursor used are listed in Table 1. The molecular weight of the polycarbosilane used was very low, and its melting point was approximately 150 °C, which is lower than those of the polycarbosilane precursors that are normally used in PIP processes, resulting in very low ceramic yields for composites formed from as-received-state polycarbosilane.

The first step of the process was to place the polycarbosilane powder in a vessel. To enhance the infiltration efficiency, the vessel containing the carbon-fiber preforms was evacuated to a pressure within the range of 0.08 MPa to 0.03 MPa and then placed on top of the polycarbosilane powder. The vessel was heated to up to 250 °C at a rate of 2 °C/min and kept at this temperature for 3 h. The polycarbosilane precursor was thus thermally melted, and once melted, it soaked and infiltrated the carbon fiber preforms. The furnace temperature was then increased to 300 °C at a rate of 1 °C/min and maintained at this level for 24 h. Finally, the furnace temperature was again increased at a rate of 1 °C/min to 350 °C, and this final temperature was maintained for another 24 h at a pressure of 0.08 MPa. Fig. 1 shows the heat-treatment regimen used for the polymer-melting-and-infiltration processes in this study.

After infiltration by the melted precursor, two different curing processes were carried out on the infiltrated carbon fiber preforms: exposure to I_2 gas for 3 h and thermal oxidation in air at temperatures ranging from 80 to150 °C. The cured samples were then pyrolyzed at 1200 °C in an argon atmosphere during 3 h (heating rate of 2 °C/min). These pyrolyzed C_f/SiC composites were then subjected to the PIP process five more times, making a total of six process iterations.

2.2. Sample characterization

Changes in the viscosity of polycarbosilane with respect to temperature and time were measured using a viscometer at temperatures ranging from 250 °C to 300 °C. During these measurements, Ar gas was made to flow continuously over the crucible to maintain an inert atmosphere. For comparison, the viscosity of melted polycarbosilane and that of polycarbosilane in a solution (xylene:polycarbosilane = 1:1) was also measured during the infiltration process.

Changes in the functional groups present in polycarbosilane were observed using Fourier transform-infrared (FT-IR) spectroscopy. These observations were made after both the infiltration and the curing process.

The open porosities and densities of the samples were measured by the Archimedes' method. The microstructures of the C_f/SiC composites were investigated by making scanning electron microscopy (SEM)-based observations of polished cross-sections and fracture surfaces of the composite samples.

3. Results

Fig. 2(a), (b), and (c) show the crucible containing polycarbosilane powder, the carbon preform placed over a predetermined amount of polycarbosilane powder, and the crucible containing infiltrated preforms that have been heated to 350 °C for 24 h, respectively. As expected, upon heating, the white polycarbosilane powder melted and infiltrated the carbon fiber preforms. Any excess polycarbosilane precursor that remained enveloped the preforms, causing their surfaces to shine when irradiated with natural light. This clearly indicated that infiltration was completed successfully and bubbles were not formed on the preform surfaces.

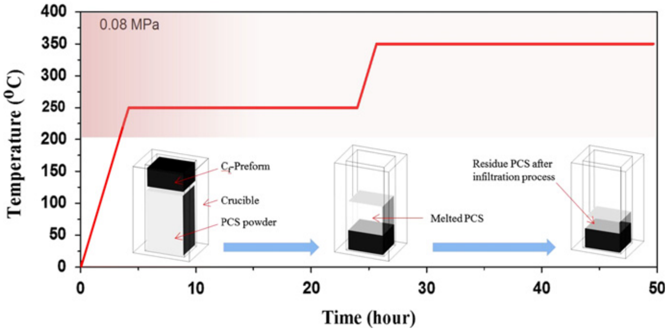

Fig. 1. The heat-treatment regimen used in this study for melting the polymer infiltrate.

Table 1
Characteristics of the polycarbosilane (PCS) used for the PIP process.

Materials	Mw (Daltons)	Melting point (°C)	Ceramic yield (%)	Company
PCS	1439	140	33	ToBeMtech.

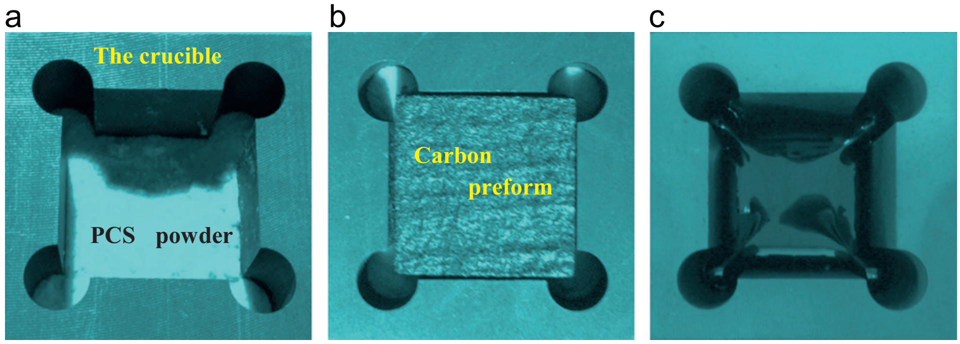

Fig. 2. (a) The crucible containing the polycarbosilane powder, (b) the carbon preforms placed over a predetermined amount of the polycarbosilane powder, and (c) the crucible containing the carbon preforms infiltrated at 350 °C over a period of 24 h.

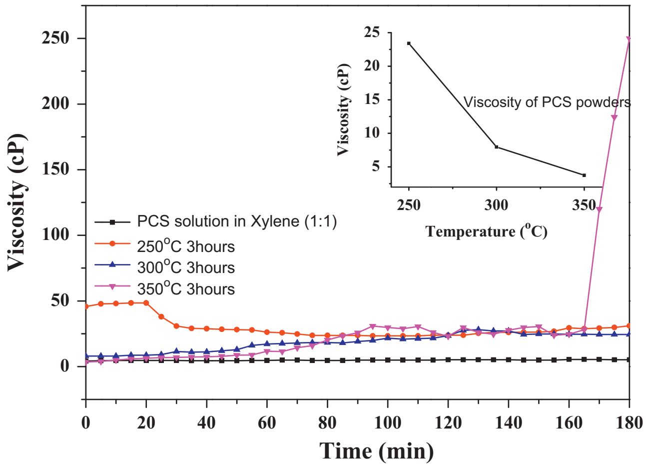

Fig. 3. Changes in the viscosity of polycarbosilane with temperature and time. The temperatures used for the viscosity measurements were 250 °C, 300 °C, and 350 °C.

After the 350 °C heat treatment, it was noticed that the melted polycarbosilane had completely infiltrated the carbon-fiber preforms. To examine the high-temperature-based infiltration process in greater detail, the process was broken into three heat treatment steps: 250 °C for 3 h, 300 °C for 24 h, and 350 °C for 24 h. Polycarbosilane infiltrated the preforms in each step, but the introduction of steps could affect the molecular-weight distribution of polycarbosilane as well as the extent of precursor polymerization. Therefore, to characterize the effect of these steps, we analyzed the polycarbosilane materials both before and after the infiltration process using a viscometer, a thermogravimetric (TG) analyzer, and an FT-IR spectroscope.

Fig. 3 shows the changes in the viscosity of polycarbosilane with temperature and time when the polycarbosilane was heated to 250 °C, 300 °C, and 350 °C. The viscosity of melted polycarbosilane at 250 °C was measured to be approximately 45.7 mPa s; this value decreased slightly during the initial phase of the 3 h-long heat treatment. This initial decrease was not chemical in origin but due to homogeneous melting. Subsequently, the viscosity was constant at 23.4 mPa s for up to 95 min, a value that is still higher than that of the polycarbosilane solution (xylene: polycarbosilane = 1:1) that is generally used as a liquid filler in PIP processes. The viscosity of polycarbosilane at 250 °C increased slightly after a period of 2 h. This increase is attributable to an increase in the average molecular weight (M_n) of the melted polycarbosilane due to the melting-induced removal of volatile low-molecular-weight components from polycarbosilane.

The final viscosity of polycarbosilane melted at 250 °C was approximately 25.8 mPa s. After the polycarbosilane was heated to 300 °C, this value was reduced to 10 mPa s and then further decreased to less than 4 mPa s after the material was heated to 350 °C. The polycarbosilane solution (xylene:polycarbosilane = 1:1) viscosity was measured to be 4.22 mPa s at room temperature, so heating polycarbosilane to temperatures greater than 300 °C lowers the viscosity enough that the polycarbosilane can infiltrate the carbon preforms. Successful infiltration by melted polycarbosilane was also confirmed by the morphologies of infiltrated carbon fiber preforms, shown in Fig. 2(d).

Fig. 4 shows the results of the thermogravimetric analysis of as-received polycarbosilane and melted polycarbosilane after the infiltration process. The ceramic yield of as-received polycarbosilane was approximately 33.4 wt%. After completion of the infiltration process, the ceramic yield of the polycarbosilane was approximately 41.9 wt%. Thus, there was an increase of approximately 9 wt% in the ceramic yield. This increase in the ceramic yield was due to the evaporation of all the low-molecular-weight components of polycarbosilane as it was slowly heated to up to 350 °C and then maintained at that temperature for 24 h. Thus, heating the polycarbosilane-infiltrated carbon-fiber preforms to 300 °C, and then to 350 °C, resulted in the removal of all low-molecular-weight components from polycarbosilane. The addition of heating steps within the melting process also ensured that pores and bubbles were not generated within the composites. As seen in Fig. 2(d), this method of slow infiltration via melting and then increasing the melting temperatures to ensure the complete removal of volatile low-molecular-weight components was very effective.

After completion of the iodine-based curing process, it was noticed that the ceramic yield increased to 91.7 wt%. This was due to two factors: (1) the prior removal of all

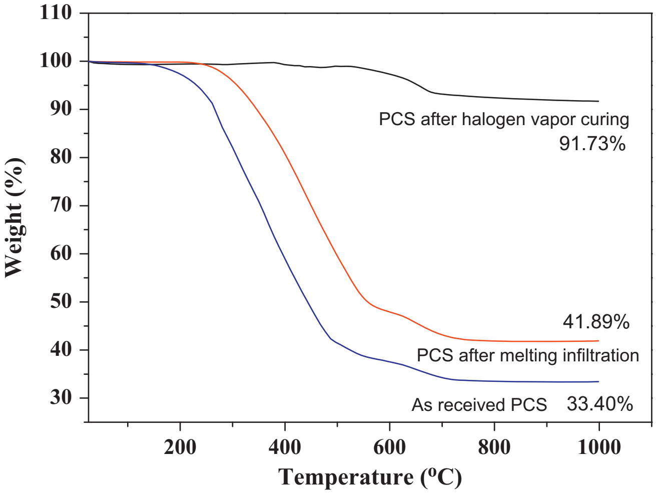

Fig. 4. Results of the thermogravimetric analysis of polycarbosilane.

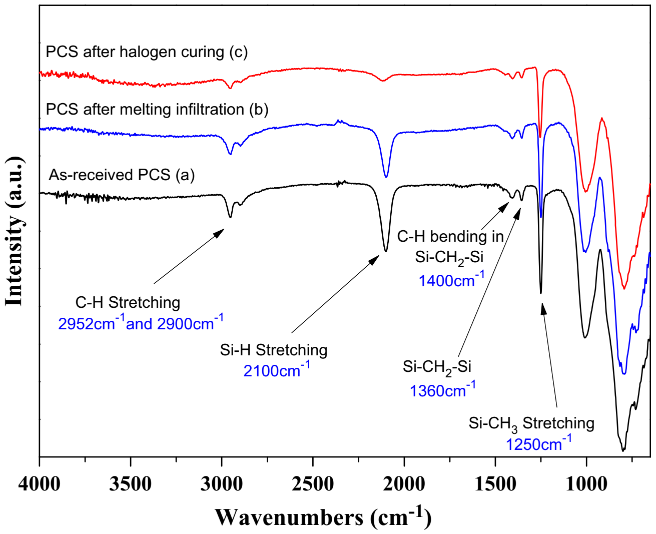

Fig. 5. FT-IR spectra of the as-received polycarbosilane and the melted polycarbosilane infiltrate.

low–molecular-weight components from polycarbosilane during the 350 °C melting step in the infiltration process and (2) the curing of polycarbosilane in the presence of iodine gas. It should be mentioned that only small amounts of the preforms/polycarbosilane powder were used in the ceramic yield measurements.

Owing to the large volume of the preforms, the melted-polycarbosilane preform infiltration was not completely homogeneous, making it difficult to measure the ceramic yields of the sample powders accurately. As a result, the iodine-cured polycarbosilane-infiltrated preforms exhibited the same yield as those cured by pyrolysis. When the yield was calculated based on the change in weight of the infiltrated preforms before and after the pyrolysis process, a value of 77 wt% was obtained. When hot isotactic pressing (HIP) was employed during the infiltration process, a yield of 90 wt% was obtained.

Fig. 5 shows the FT-IR spectra of as-received polycarbosilane and the melted polycarbosilane infiltrate. Significant changes were observed in the Si–H and Si–CH_2 bending vibrations over the course of the PIP process. Fig. 5(a), (b), and (c) show the FI-IR spectra of as-received polycarbosilane, polycarbosilane infiltrate after melting, and polycarbosilane/carbon fiber preforms after the curing process, respectively. In the case of the as-received polycarbosilane FT-IR spectra, the peaks observed at approximately 1400 cm^{-1} and 1360 cm^{-1} can be assigned to Si–CH_3–Si stretching in the SiC polycarbosilane backbone. Additional peaks appearing at approximately 2952 cm^{-1} and 2100 cm^{-1} can be associated with C–H stretching and Si–H stretching, respectively. As seen in Fig. 5(c), the intensities of the C–H and Si–H stretching peaks decreased dramatically after the curing process.

The intensities of the Si–CH_3–Si stretching peaks, however, did not decrease. This implies that only volatile functional groups were removed from the polycarbosilane by halogen (iodine)-vapor curing.

These results suggest that the swelling of polycarbosilane can be restricted by using an element that exhibits sublimation, such as iodine, and that the ceramic yield can be increased by dehydrogenation via pyrolysis. Changes in the stretching peaks recorded in the melted-polycarbosilane infiltrate FT-IR spectra, as shown in Fig. 5(b), were slightly similar to those in the spectra for as-received polycarbosilane. This could be because halogen-vapor-based curing eliminated more of the volatile functional groups and low-molecular-weight components of polycarbosilane than the polycarbosilane heat treatments were able to remove.

Fig. 6 shows the microstructures of C_f/SiC created by the first iteration of a polycarbosilane xylene solution infiltration before curing and pyrolysis, as well as those of the C_f/SiC composites formed after melted polycarbosilane infiltration, iodine curing and pyrolysis. The microstructures of the polycarbosilane xylene solution/carbon fiber perform constructs after the first iteration of the PIP process were not continuous. The matrix, consisting of SiC derived from polycarbosilane, was divided into a number of small pieces. Interfacial bonding between the matrix and the fibers was negligible. This result was attributed to shrinkage of the matrix and volatilization of low-molecular-weight material from polycarbosilane during pyrolysis. On the other hand, the microstructures of the C_f/SiC composites after the first iteration of the PIP process, i.e., after melting-induced infiltration and halide curing, were denser, and interfacial bonding between the matrix and fibers was improved. This result was attributed to the high ceramic yield of polycarbosilane because of the removal of its low-molecular-weight components and to a cross-linking reaction.

Fig. 7 shows the densities and porosities of C_f/SiC composites as a function of PIP process times. The density of the C_f/SiC composites increased from 0.38 g/cm^3, the density of the untreated carbon-fiber preforms, to up to

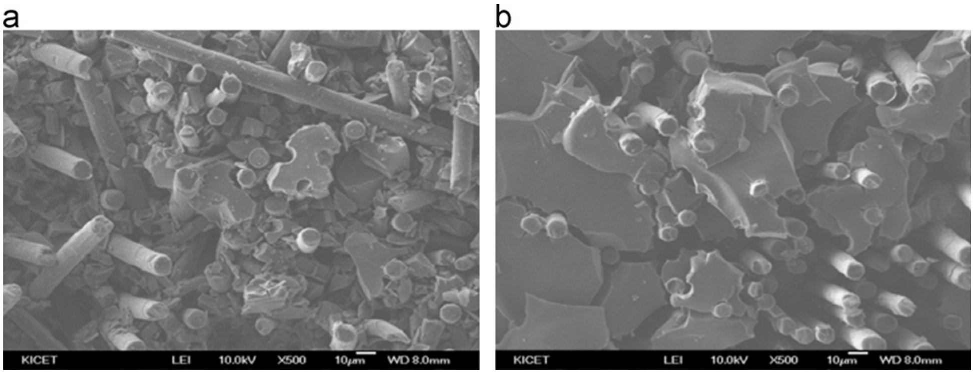

Fig. 6. (a) Microstructures of the uncured and infiltrated polycarbosilane xylene solution, (b) the carbon fiber perform constructs and the C_f/SiC composites formed after the infiltration and curing processes.

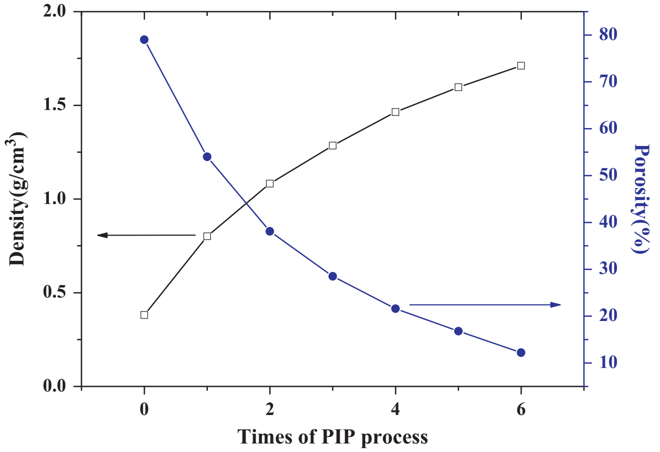

Fig. 7. Density and porosity of the C_f/SiC composites as a function of the PIP process duration.

1.75 g/cm^3 after the 6th iteration of the PIP process. After the first iteration, the density of the C_f/SiC composites increased to 0.42 g/cm^3. This density is higher than the density of these composites before being subjected to a PIP process [4]. The density of the C_f/SiC composites continued to increase between the 4th and 6th PIP process iterations in an almost linear fashion. These results suggest that introducing open pores in the C_f/SiC composite matrix through additional iterations of the PIP process is advantageous because it results in increased composite density. The porosity of C_f/SiC composites is inversely proportional to their density and was found to be 13.2% after the 6th iteration of the PIP process.

Fig. 8 shows cross-sectional micrographs of the fabricated C_f/SiC composites. As seen in Fig. 8(a), no pores were observed in the intrabundle after the 6th iteration, suggesting that the PIP processes were effective. Generally, pores present in the intrabundle of the C_f/SiC composite matrix disappear after 10 or more cycles of conventional PIP processes [13]. Pores and cracks are formed as intrinsic volatile components escape from the polycarbosilane in gaseous form, inducing swelling in the matrix. In Fig. 8(b), a high-magnification SEM image of the microstructure of a fiber boundary can be seen. Circular cracks were not observed around the fiber's surface, as is commonly the case for C_f/SiC composites. The increase in ceramic yield of polycarbosilane, which is due to repeated pyrolysis during the many PIP process iterations, helps to reduce shrinkage of the matrix around the fiber.

The in situ pyrolysis of melted polycarbosilane infiltrate at high temperatures did not affect the carbon fibers or damage the fiber bundles. However, it is possible that excessive shrinkage of the polymer matrix could have stressed the fiber bundle.

4. Discussion

Using melted polycarbosilanes as infiltrates is a process that has its limits. Because of the thermosetting behavior of the polycarbosilane precursor, there are upper limits to the temperatures that can be used to melt the infiltrates. As shown in Fig. 3, when the melting is performed in a nitrogen gas atmosphere, there is always a loss of low-molecular-weight polycarbosilane components, resulting in highly viscous melted polycarbosilane at temperatures greater than 350 °C.

A new strategy is required to further increase the ceramic yield. To this end, we have used an iodine-based curing technique with polycarbosilane-infiltrated composite systems. Our process resulted in the ceramic yield of the composites increasing significantly. It should also be noted that the final infiltrated and cured composite did not exhibit any bubble-like formations. Bubbles are generally generated by the evaporation of volatile low-molecular–weight components in polycarbosilane, though gases generated by dehydrogenation as a result of the cross-linking process can also cause these bubbles. As shown in Fig. 2, when the infiltrated composites were thermally cured in air, the curing process could not suppress the generation of these bubbles, resulting in the composites exhibiting sponge-like topologies after pyrolysis.

In our process, in situ polymerization during infiltration effectively increases the molecular weight of the composites, and curing using iodine vapors furthers this increase,

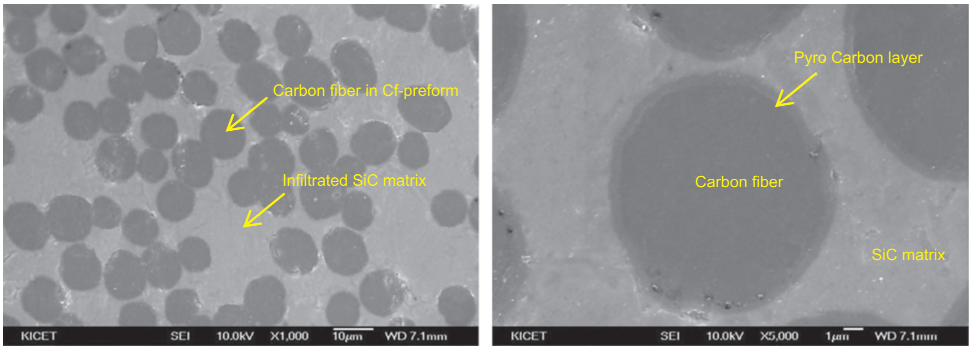

Fig. 8. Cross-sectional micrographs of fabricated C_f/SiC composites.

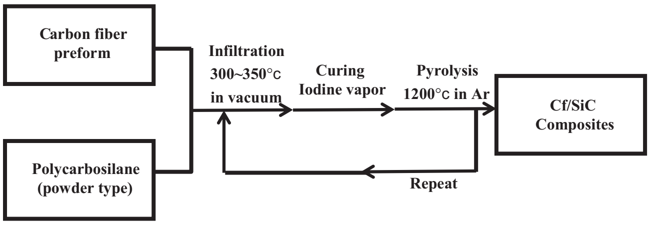

Fig. 9. Schematic of the combined polymer melting-based infiltration and iodine-based curing processes.

resulting in morphologically stable composites that exhibit high ceramic yields. We are now investigating the possibility of enhancing the infiltration effect even further by incorporating high-pressure polymerization techniques in the PIP process. We are also exploring iodine-based curing in greater detail to further shorten the PIP process cycle. It is hoped that the combination of the in situ infiltration-based polymerization process with iodine-based curing will be an effective method for producing C_f/SiC composites for aerospace applications. By using additional high-pressure polymerization techniques, we expect to further shorten the duration of the infiltration process.

Fig. 9 shows the schematics of the combined melting-based infiltration and iodine-based curing processes. The polycarbosilane powder wets the carbon-fiber preforms and slowly infiltrates the preforms as the temperature increases, decreasing the viscosity of polycarbosilane to 3.51 mPa s. After the infiltration process is complete, in situ polymerization, an in situ process to increase the average molecular weight of the polycarbosilane/precursor constructs, is performed in two steps, one at 300 °C and the next at 350 °C. During these steps, the low-molecular-weight components of polycarbosilane are removed from the melted infiltrate without sacrificing infiltration efficiency. Instead, the main causes for a decrease in the infiltration efficiency in this process are increases in the viscosity of polycarbosilane and the thermosetting behavior of the polycarbosilane precursor. Finally, the C_f/SiC composites are cured using iodine vapors, resulting in a dramatic increase in the ceramic yield. Yasuda et al. have shown that iodine-based curing significantly increased the post-pyrolysis ceramic yield of pitch-based carbon materials [14–15]. The effects of iodine vapors on ceramic yields are now being analyzed using other tools such as an electron probe microanalyzer (EPMA) and a secondary ion mass spectrometer (SIMS). More work is needed to reveal the underlying mechanism responsible for the effect that iodine vapors have on the ceramic yields of polycarbosilane-infiltrated carbon composites.

5. Conclusions

An infiltration process that employed melted polycarbosilane as the infiltrate was used to fabricate C_f/SiC composites. To increase the extent of infiltration, the heat-treatment stage was divided into three steps. During this multistep infiltration process, the average molecular weight of polycarbosilane increased, resulting in up to a 9 wt% increase in the ceramic yield of the C_f/SiC composites. When these composites were cured using iodine vapors, their ceramic yield increased further, up to 90 wt%. This increase in the yield was not accompanied by swelling, as is usually the case.

This melting-based PIP process, comprising in situ polymerization and evidenced by an increase in the average molecular weight of the polycarbosilane/precursor constructs, and iodine-vapor curing were found to be extremely effective in fabricating C_f/SiC composites with high ceramic yields. It is hoped that this process will be an effective method for producing C_f/SiC composites for aerospace applications. By incorporating additional high-pressure polymerization techniques, we expect to further decrease the duration of the infiltration process.

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