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EFFECTS OF PROCESSING PARAMETERS ON THE GROWTH OF SiC NANOFIBERS IN THE FABRICATION OF CARBON/SiC NANOCOMPOSITES

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SUMMARY: Carbon fibers reinforced silicon carbide ceramic nanocomposites were fabricated through the slurry impregnation process and the pulse chemical vapor infiltration (PCVI) process. The resin impregnation was applied to filling the large voids within the composites and the PCVI process was used to deposit SiC matrix onto the pore surface within the composites for further densification. Slurry was made by adding Si powder and SiC nanopowder into the phenolic resin. Heat treatment at 1450℃ converts carbon and Si powder into silicon carbide matrix. In the PCVI process, TMS (tetramethylsilane) vapor mixed with carrier gas was channeled into the reactor, after staying a short period, the unreacted vapor and gas phase products were evacuated from the chamber. The processes were proceeded periodically. The solid phase produced in the reaction was deposited onto the pore surface within the composites during thermal decomposition process. The objectives of this work are to investigate the influences of nanosize SiC powder and to study the effects of PCVI parameters on the physical and mechanical properties, and microstructure of the nanocomposites.

KEYWORDS: Nanofibers, PCVI, nanocomposites, carbon/SiC

INTRODUCTION

Ceramic material provides several desirable features such as high temperature capability, low density, high strength and hardness, chemical inertness, and refractory properties. However, they are sensitive to flaw and defect, and catastrophic failure may occur during loading. In order to enhance the toughness of ceramic material, second phases such as particles, fibers, or whiskers were introduced into the material system to form ceramic matrix composites. Depending on the form of reinforcement adopted, the fracture mechanisms involving fiber pull-out, fiber bridging, phase transformation toughening, crack deflection, crack branching, crack impeding, and microcracking have been proposed during the past

two decades[1].

A straightforward method to produce CMCs is adding the reinforcements into the monolithic ceramic powder and then followed hot press and sintering. In the process, heat treatment at elevated temperature degraded the reinforcement and the interface, which weakened the strength of the ceramic composites. To alleviate the high temperature effect, the chemical vapor infiltration (CVI) process, a relative low temperature and near-net-shape processing, to produce CMCs can effectively improve the drawbacks of the aforementioned powder route.[2,3]

In the isothermal chemical vapor infiltration (ICVI) process for ceramic composites, the vapors penetrate into fibrous preform and deposit the solid phase onto the surface for forming the matrix of composites[4,5]. In order to improve the long processing period of the ICVI process, the forced-flow, temperature-gradient chemical vapor infiltration (FCVI) process was proposed[6]. The primary advantage of the FCVI process is that the processing period can be reduced. However, only one specimen can be fabricated in a process.

Pulsed chemical vapor infiltration (PCVI) is the process that can improve the drawbacks of the ICVI and the FCVI processes. In the PCVI process, the reactant vapors were channeled into the chamber, after staying a short period, the vapor products mixed with unreacted reactant were evacuated from the reactor. Due to periodic filling and vacuum, forced flow generated by the pressure gradient refresh the reactants within the preform. Thus, a ceramic composite with low gradient of matrix distribution can be fabricated[7,8]. In this study, SiC nanopowder was added to the matrix for investigating the influence of processing parameters on physical and mechanical properties of the fabricated composites.

EXPERIMENTAL

Silicon powder (99.0%, Aldrich) and SiC nanopowders (20nm, MTI) were added into the mixture of PEI (Polyethyleneimine, Alfa Aesar, 99%) and IPA(Isopropyl Alcohol, TEDIA, 99%) which was performed as dispersant. Eight layers of carbon fiber cloths (W3121, 8 harness satin, Toho rayon Co., Ltd, Japan) impregnated with slurry were stacked in a mold. Hot press was performed at 170^0C and 230^0C for the pyrolysis of polymer resin. Carbonization at 1100^0C in a tube furnace (55342-4, LINBERG) was used to evolve the non-carbon species. Reaction sintering process was performed for forming SiC matrix at 1450^0C in a graphitization furnace (ASTRO, Thermal Technology, Inc., USA) for 3 hours.

To increase the density of composites, the specimens were subjected to slurry impregnation and heat treatment at 1450^0C for three times; further densification through the PCVI process was performed by placing the specimens into an isothermal reaction chamber. In the PCVI

process, the vapor phase precursor (Tetramethylsilane, TMS, 99.9%, Acros) mixed with carrier gas (hydrogen) was channeled into the reactor. Products of the pyrolysis reaction at elevated temperature were deposited onto the pore surface for forming the matrix of nanocomposites. In the PCVI process, the chamber was filled with reactants and was vacuumed from the chamber after a short stay, the processes were proceed periodically. As a result, forced flow instead of diffusion dominated the supply of the reactant during the deposition process. In this work, a reaction temperature at 1100^0C and a working pressure of 2.5 torrs (holding pressure) were used. Figure 1 schematically depicts the set-up of the PCVI process.

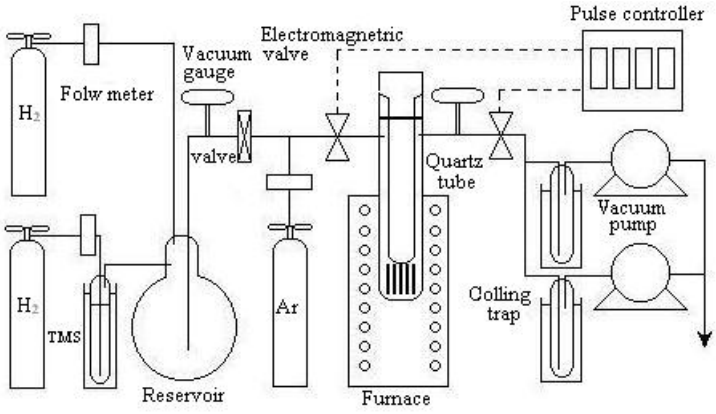


Figure 1 Schematic figure of set-up for the PCVI process

Density and porosity measurements following ASTM D792 and ASTM C20 codes, respectively, were performed. Flexural strength (specimen dimension of 70.0 mm x 10.0 mm x 3.0 mm) was measured by a three-point bending method with a span-to-depth ratio of 20.0 and a crosshead rate of 1.0 mm/min (ASTM ASTM D790). Interlaminar shear strength (ILSS) (specimen dimension of 21.0 mm x 5.0 mm x 3.0 mm) was tested under the same procedure as flexural strength measurement except that the span-to-depth ratio of 5.0 (ASTM D2344) was used. Field Emission Gun Scanning Electron Microscopy (FEGSEM, JEOL, JSM-6330F, Japan) was used for the examination of microstructure on both the surface and interior of the composites.

RESULTS AND DISCUSSIONS

Figure 2 depicts the variations of density and open porosity after carbonization at 1100^oC and reaction sintering at 1450^oC. As shown in the figure, open porosity increases significantly when first time sintering process was applied; the evolution of non-carbon elements and the rearrangement of graphene layers in carbonized matrix at elevated temperature contribute the porosity. The open porosity is further reduced after subsequent resin impregnation. Generally, the density increased with the number of impregnation.

It is known that the density affects significantly the mechanical properties of the composites. The higher the density, the better the mechanical properties. In the process of slurry impregnation, multiple impregnation was required to achieve a highly densified composites. In this study, ILSS and flexural strength of the composites fabricated after each densification step were measured. The results are shown in Figure 3. Unfortunately, both ILSS and flexural strength reduced with the number of impregnation.

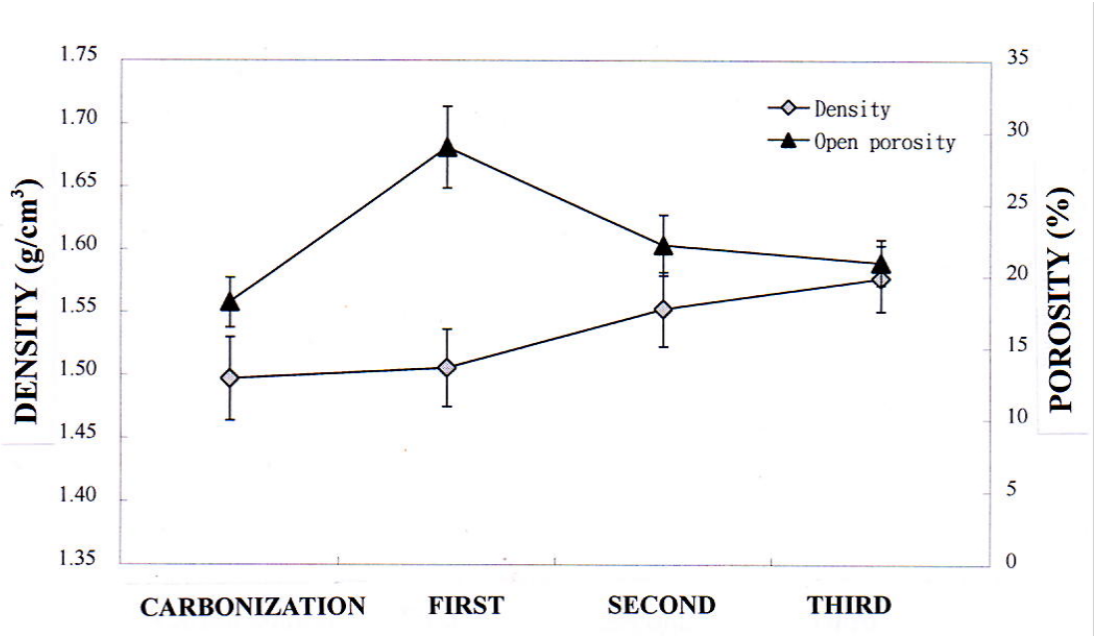


Figure 2 Variations of density and open porosity after carbonization and multiple impregnation

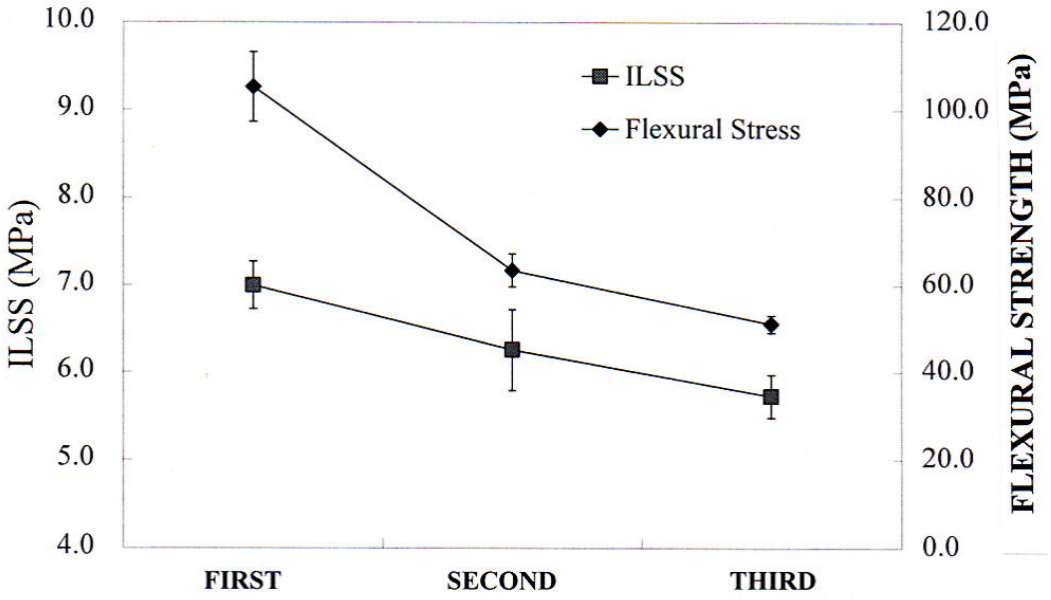
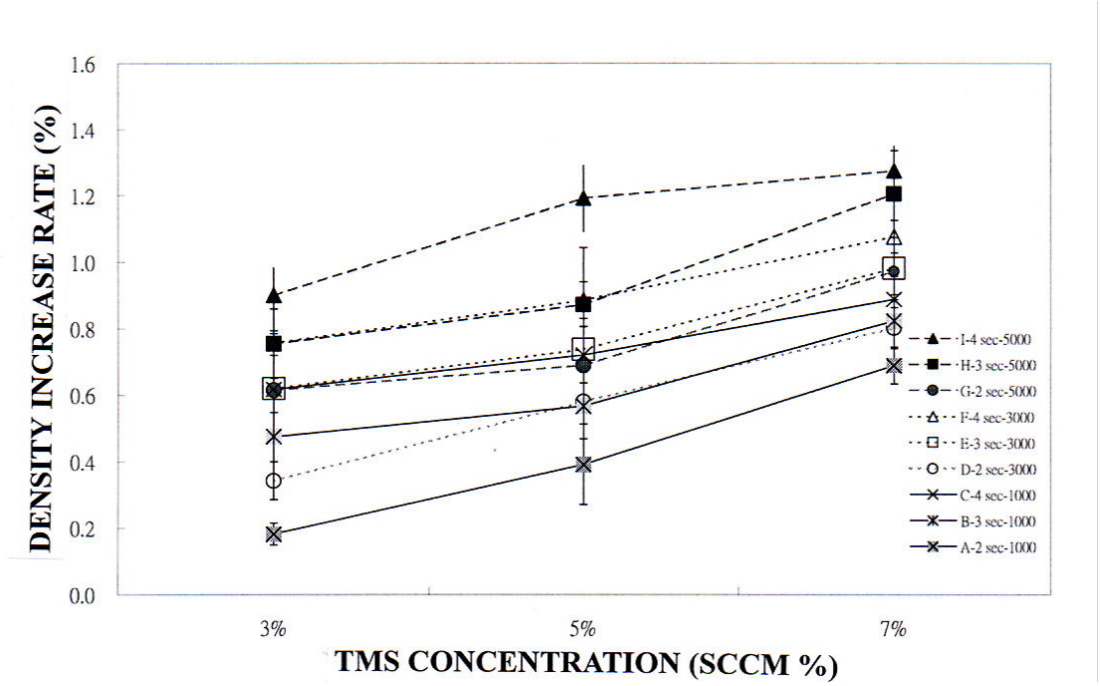


Figure 3 Interlaminar shear strength and flexural strength variations after multiple impregnation

The matrix deposition in the PCVI process was affected primarily by the reactor temperature, reactor pressure, precursor concentration, pulsed number, and holding time. Based on the experimental results, it shows that the density increases with reactant concentration, pulse number, and holding period. Thus only the results of the specimens fabricated under longest holding period were discussed. Figure 4 depicts the density increase rate under different pulse numbers, holding time, and reactant concentrations. It is observed that density increase rate is very low, which results from the low deposition rate of the thermal decomposition reaction. When the surface morphology was examined, no significant deposition layer could be



detected.

Figure 4 Density increase rate under different pulse numbers and reactant concentrations

Deposition rate is affected by reactant concentration and deposition rate constant. According to Arrehious equation, deposition rate constant is a function of temperature and activation energy of the reaction. Therefore, when a constant temperature was kept during the processing, the parameters that influence the deposition rate are reactant concentration and process period, thus it is understood that the density increases with pulse number and reactant concentration. Similar trend can also be detected in the porosity reduction.

Figures 5 and 6 depict the flexural strength and ILSS, respectively, of the specimens fabricated under various pulse numbers and reactant concentration at the holding time of 4 seconds. As expected, flexural strength and ILSS increased with the density which was affected significantly by the pulse number and the concentration of the vapor. Monotonic increase of the measuring results indicated that both these two mechanical properties can be further enhanced by increasing the pulse number and the vapor concentration.

Submicrofibers and nanofibers, as depicted in Figures 7 and 8, were observed on the specimen surface and within the pores of the interlaminar layer, respectively. It is obvious that heterogeneous and anisotropic reactions occur during matrix deposition. However, layer deposition is not observed. The anisotropic growth of submicrofibers and nanofibers indicated that the catalytic reaction at the tip of nanofibers.

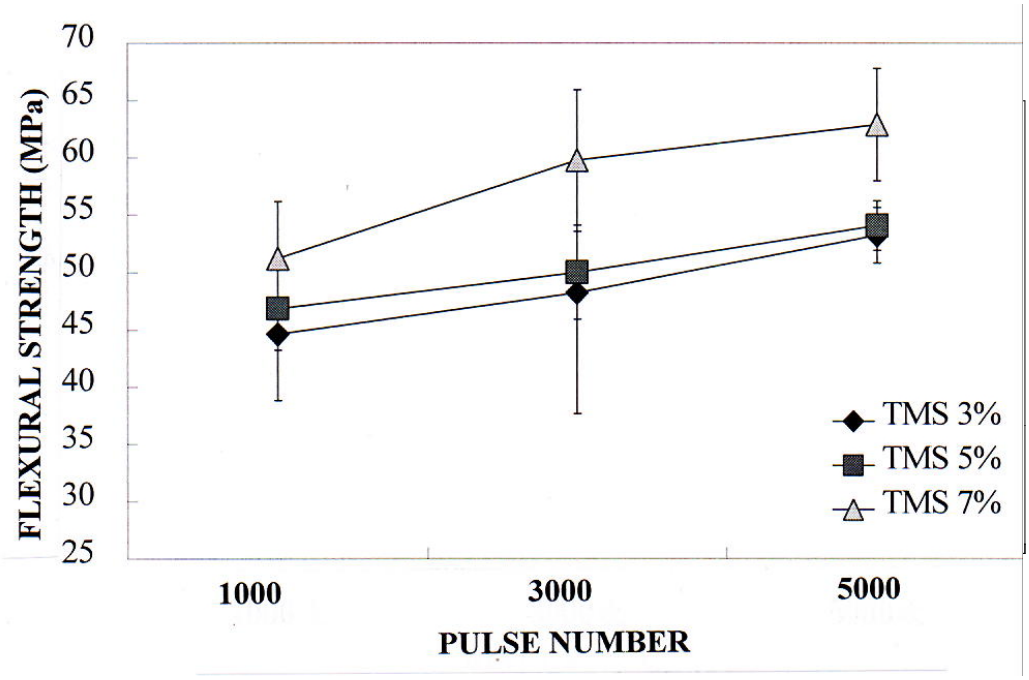


Figure 5 Flexural strength of the specimens fabricated under various pulse numbers and reactant concentration at the holding time of 4 seconds

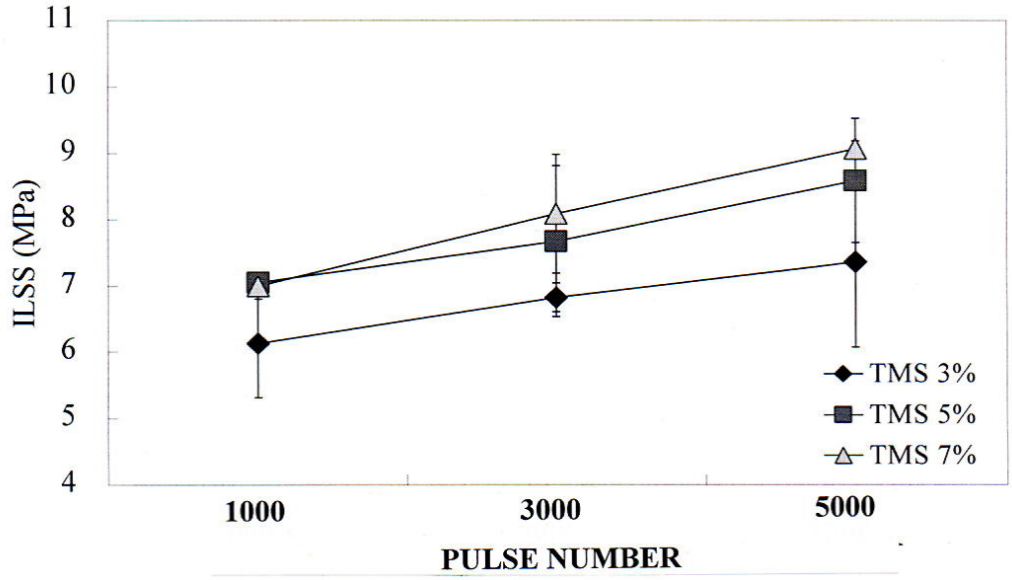


Figure 6 Interlaminar shear strength of the specimens fabricated under various pulse numbers and reactant concentration at the holding time of 4 seconds

Because the growth of nanofiber depends on the concentration of the TMS vapor; the higher the concentration, the higher the growth rate. The diameter of nanofiber reduces with depth was detected. It implies that a concentration gradient is still inevitable in this study. Moreover, nodes were found in the fiber, where a sharp change in growth direction occurred.

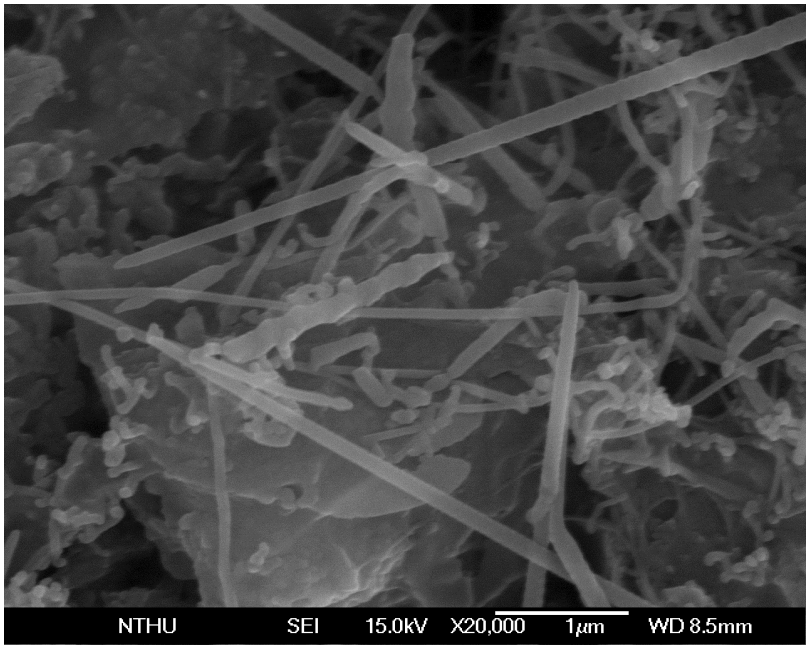


Figure 7 Morphology of the surface within the specimen

Figure 8 Morphology of the surface on the specimen

CONCLUSIONS

This work demonstrated the fabrication of ceramic nanocomposite through the slurry impregnation and pulse chemical vapor infiltration method. Density increases with pulse number and reactant concentration. Similar trend can also be detected in the porosity reduction. ILSS reduces with the number of slurry impregnation. In the pulse chemical vapor infiltration (PCVI) process to densify the nanocomposite, effects of reactant concentration, pulse number, and holding time were studied. Nanofibers and submicrofibers were detected on the specimen surface and within the nanocomposite. Diameters of the nano and the submicrofibers were dependent on the depth of the location; the deeper the depth from surface, the finer the diameter of the fiber. Reactant concentration is the most important factor among the investigated parameters for nanofiber growth, whereas pulse number and holding period play less significant role.

ACKNOWLEDGEMENTS

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