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Pulse CVI–slurry joint process for manufacturing of small and medium size parts

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Abstract—In order to construct a suitable process for fabricating small and medium size CMC parts, attempts have been made to try to apply a pulse CVI–slurry joint process for making 3D carbon–fiber/SiC composites. The joint process consisted of slurry infiltration, polymer infiltration and pyrolysis, and pulse CVI. In the polymer infiltration and pyrolysis process, polycarbosilane was used as a preceramic polymer. The pulse CVI was carried out in a reaction temperature between 1323 K and 1423 K, using a source gas system of $SiCl_4$–CH_4–H_2. The deposited phase varied with reaction temperature, gas concentration and reacting time. At 1373 K, a large amount of mass filling into a porous-matrix was observed. The flexural strength of the composite remarkably increased after the pulse CVI application. The joint process is effective for fabrication of thin and relatively simple shape parts.

Keywords: 3D carbon fiber; SiC matrix composite; slurry infiltration; pulse CVI; joint fabrication process.

1. INTRODUCTION

Ceramics have excellent characteristics for use in high temperature structural materials and mechanical parts because of their heat-stability, superior strength at high temperature and relatively low density. However, they are brittle in the monolithic state. The major concern in utilizing ceramic as a structural material is improving its fracture toughness.

Fiber reinforcement, especially continuous fiber reinforcement is one of the most effective methods for toughening ceramics. Several processes have been developed for fabricating continuous fiber reinforced ceramic matrix composites (CMCs). Chemical vapour infiltration (CVI) [1–4], preceramic polymer infiltration and pyrolysis (PIP) [3, 5–8] and reaction sintering (RS) [3, 9–11] have been employed as major fabrication methods for CMCs. Main processes for CMCs-fabrication already seem to appear now. These methods have their own strong and weak points. For instance, CVI can easily fabricate a part having complicated shape that is very stiff (high moduli) and with relatively low processing temperature, but it is costly in practice. PIP has a potential for low-cost processing; however, it is not so easy to get a part having compact and stiff structures except a simple shaped one (plate, bar, etc.). Consequently, a suitable fabrication process of CMCs should be chosen, either as a single method (mentioned above) or a combined one according to the scale, quality, cost, number, etc. of the intended parts. In view of cost-effectiveness considerations or ease of processing, the PIP [3, 5–8] route and a slurry–pulse CVI (PCVI) joint process [12, 13] are interesting. Moreover the slurry–PCVI joint process, in which PCVI is applied as a finishing process after a slurry infiltration into a fiber-preform followed by PIP, is very effective for increase of composite strength [12, 13].

In the present work, the slurry–PCVI joint process, which is considered to be suitable for manufacturing of small or medium size CMC parts, was applied for making 3D carbon–fiber/SiC composites and their characterizations were carried out. Validity of this joint process for fabricating small and medium size CMCs parts is also discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Composites fabrication

2.1.1. Fiber preform. Four kinds of 3D carbon–fiber fabrics were used for preforms of composites: they are orthogonal weave (OW), 4 step braid (4SB), 4 step with axial braid (4SAB) and 2 step braid (2SB) (Table 1). Properties of fibers are listed in Table 2.

2.1.2. Fabrication of composites. The fabrication process of SiC matrix composites consists of three steps. The first step is pressure infiltration of slurry (SI), which consisted of a α-SiC powder (Lonza VF-15: 0.6 μm), dispersant and solvent (water), into a fiber preform (S-body). The second step is a cyclic process in which solution of a preceramic polymer (polycarbosilane) dissolved in xylene is infiltrated into the fiber preform filled with the α-SiC powder, followed by pyrolysis (PIP process). The third step is a finishing process where SiC is deposited into the open pores of a body (PIP body) made by the successive processes of SI and PIP. The SiC deposition process is carried out by PCVI where $SiCl_4$, CH_4 and H_2 reactant gases are introduced into a reaction chamber where the PIP body is placed. The reactant and exhaust gases before and after reactions are intermittently introduced and expelled. The reaction temperature range was 1273–1423 K. The composite fabrication process and schematic drawing of the reaction chamber in PCVI are shown in Figs 1 and 2, respectively.

Table 1.
Structure of preforms

Fabric type	Fiber volume fraction, V_f	Fiber orientation			Pitch
		Direction	Ratio (%)	Type of fiber	
OW[a]		X, Y	45.1	XN50-20N × 2	$P_x = P_y = 3$ mm
Orthogonal weave	41.3%	Z	8.6	T900-6Kf	
		Selvage	1.2	T900-2Kf	$P_z = 0.52$
4SB[b]					
4 step braid	30.4%	braider	100	YS-50-60N	(12 × 4 base array)
4SAB[b]		braider	70	YS-50-60N	
4 step with axial braid	39.5%	axial	30	YS-50-60N × 2	(8 × 3 base array)
2SB[b]		braider	30	YS-50-60N	
2 step braid	43.7%	axial	70	YS-50-60N	(9 × 3 axial)

[a] From Toyota Automatic Loom Works, Ltd.
[b] From University of Delaware, USA.

Table 2.
Properties of fibers

Fiber type	Filament		Density	Tensile		
	diameter μm	number	Mg m^{-3}	strength GPa	modulus GPa	strain %
XN50-20N	10	2000	2.09	3.73	490	0.8
T900-6Kf	5.3	6000	1.82	5.6	294	1.9
YS50-60N	7	6000	2.09	3.73	490	0.8

XN50: GRANOC XN50; T900: TORAYCA T900; YS50: GRANOC YS50.

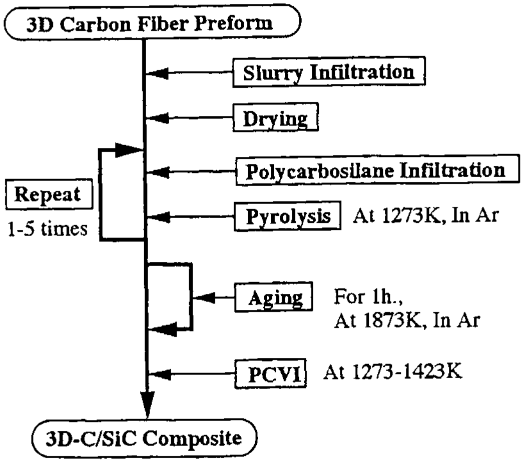

Figure 1. Composite fabrication process.

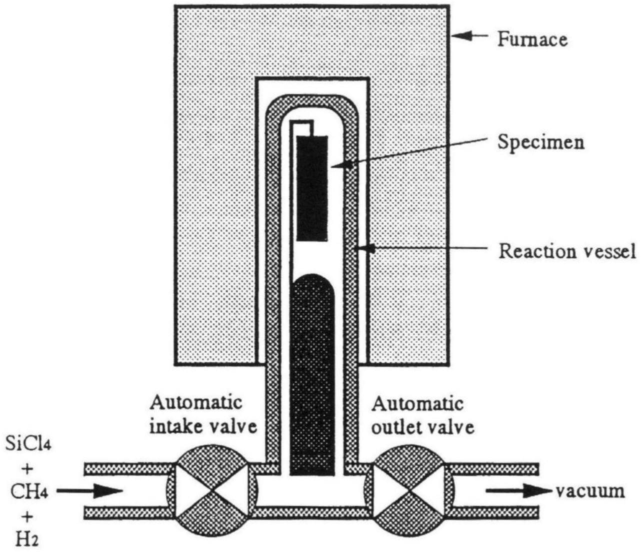

Figure 2. Schematic drawing of PCVI reaction chamber.

2.2. Characterization

Porosity and density of composites were measured by Archimedes' method with water as medium liquid. Structures of composites were observed by SEM or optical microscope. Flexural strengths (3-point bending) of composites were measured at room temperature (RT) and high temperatures (1473 K and 1773 K) under argon gas.

3. RESULTS AND DISCUSSION

The relative densities of the bodies (PIP body) made by the SI and PIP processes were 70.2% (specimen type A) and 81.1% (specimen type B), respectively. These bodies were used for SiC deposition by PCVI as the finishing process. Deposited phases formed by PCVI are dependent upon both reaction temperature and holding time of reaction in this system ($SiCl_4 + CH_4 + H_2$) as shown in Fig. 3, whereas in the $CH_3SiCl_3 + H_2$ system, the deposited phases are only dependent upon reaction temperature. In the case that $SiCl_4 = CH_4 = 5$ mole% and the holding time = 1 s, the lowest temperature, in which only SiC phase is deposited, is 1348 K (Fig. 3).

The orthogonal woven preform was used in the results shown for Figs 3 to 6. Figure 4 shows a relationship between number of pulse and filled-mass in the reaction temperature between 1348 K and 1423 K. Here, the other reaction condition such as the concentration of CH_4 and $SiCl_4$ ($CH_4 = SiCl_4 = 5$ mole%) and the holding time of reaction (= 1 s) were kept the same at all reaction temperatures. In the case of 1423 K, the filled mass was rapidly increased with increase of pulse number until 40 000 pulses; however, it saturated at a lower level of mass

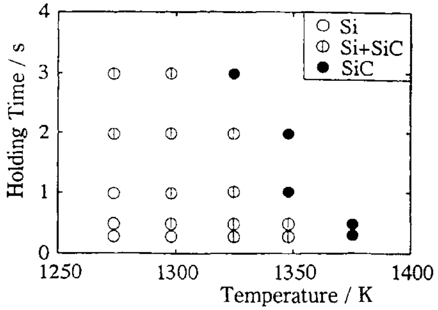

Figure 3. Deposited phase as a function of reaction temperature and holding time of reaction ($SiCl_4 = CH_4 = 5$ mole%).

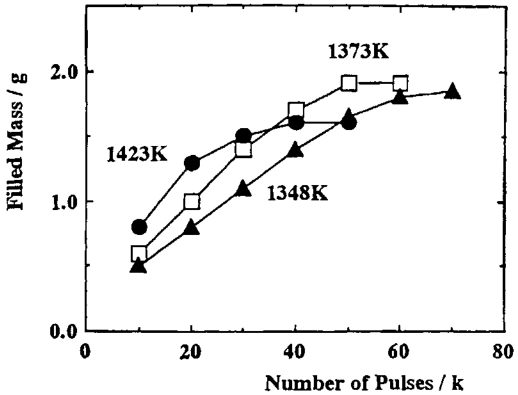

Figure 4. Relationships between number of pulses and filled mass at various temperatures.

quantity compared to the case of 1348 K and 1373 K. This means that the reaction in the early stage mainly takes place around the surface of the PIP body which is used for PCVI application. In the case of the 1348 K run, the deposition rate gradually decreased beyond 50 000 pulses although the mass saturation level was nearly the same as in the case at 1373 K. Various examinations showed that the aforementioned conditions ($CH_4 = SiCl_4 = 5$ mole%, holding time = 1 s, reaction temperature = 1373 K) were most effective for PCVI application as the finishing process. It is clear that in this system the deposition rate of SiC is twice as great as that of the CH_3SiCl_3–H_2 system [12, 13].

The relationship between the number of pulses and relative density in two kinds of specimens having different residual porosities are shown in Fig. 5. The specimen A (relative density (RD) = 70.2%, before PCVI application) had RD of 82.5% after 50 000 pulses. Likewise, the specimen B (RD = 81.1%, before PCVI application) had RD of 86.5% after same pulse number application. In both specimens, the relative density monotonously increased with increase of the pulse number. Cumulative filled-mass of specimen A was larger than that of specimen B, because the large size of pores made it possible to introduce a large amount of reactant-gases

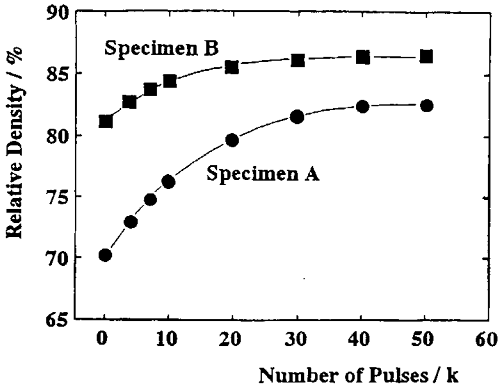

Figure 5. Relationship between number of pulses and relative density.

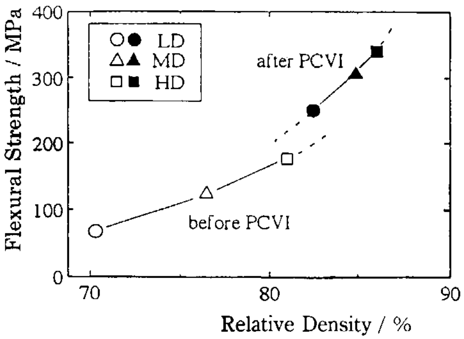

Figure 6. Relationship between relative density and flexural strength.

into the pores of specimen A. However, the final relative density of the specimen B was higher than that of specimen A. This result suggests that there may exist a suitable pore size distribution and a thickness of specimen for effective densification of specimen by using the PCVI process. Flexural strength of the specimen A at room temperature (RT) monotonously increased with increase of pulse number up to 50 000 pulses. This behavior coincided with that of specimen density variation with the pulse number. In specimen B, open porosity decreased from 13.5%, before PCVI application, to 9.2% after 50 000 pulses, which corresponded to increase of flexural strength from 172 MPa to 341 MPa (~ 100% increase). Figure 6 shows the relationship between relative density and flexural strength at RT. It is understood that flexural strength increases with increase of relative density; moreover, PCVI application is remarkably effective for increase of the flexural strength.

Figure 7 shows SEM micrographs on fracture surfaces of specimens made by SI + PIP (Fig. 7a) and SI + PIP + PCVI (Fig. 7b) processes, respectively. In the micrograph (Fig. 7a), many SiC grains were embedded in the matrix made by the PIP process. Some cracks, which may have originated during these processes, were observed; however, such cracks were rarely seen on the fracture surface of the sample made by SI + PIP + PCVI processes (Fig. 7b). Some indications of fiber

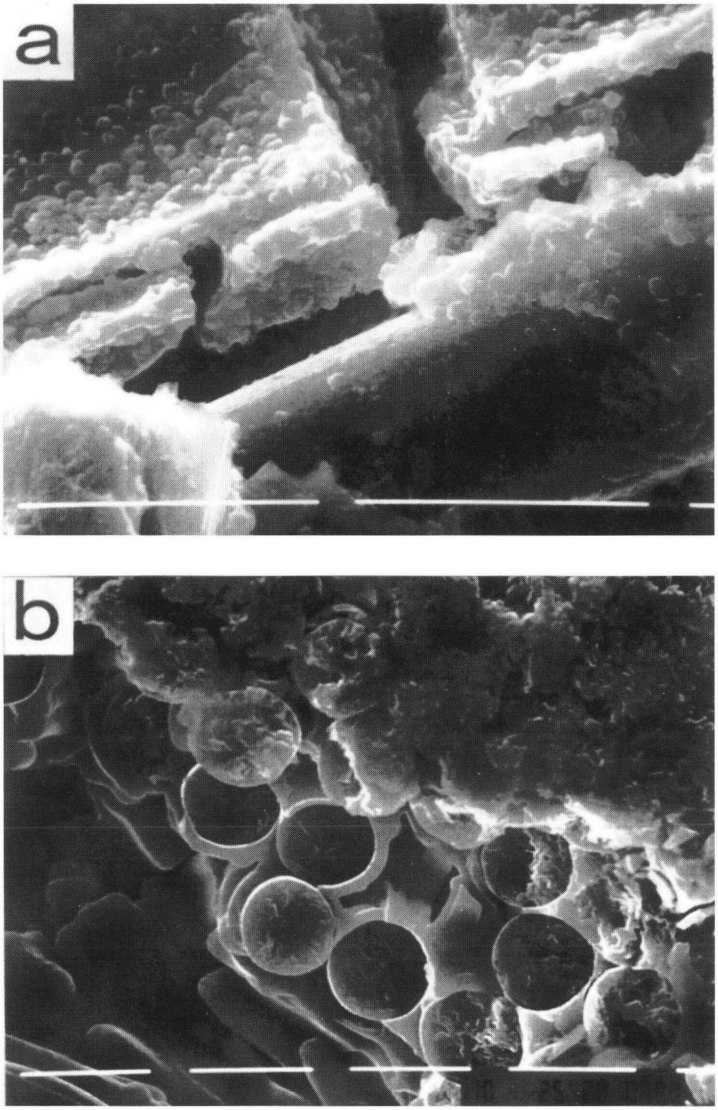

Figure 7. SEM micrographs on fracture surfaces of specimens (white bar = 10 μm): (a) made by SI + PIP processes; (b) made by SI + PIP + PCVI processes.

pull-out were observed on the fracture surface of the specimen made by a similar process (Fig. 7b).

Porosity and flexural strength for specimens fabricated by using four kinds of preforms are listed in Tables 3 and 4, respectively. With regard to slurry infiltration process (SI), the matrix filling efficiency (V_{SI}/V_{P0}) in high-V_f preform was lower than that of the low-V_f specimen. This may be attributed to the fact that the preform with high-V_f has smaller size of pores between fiber rows compared to those of the low-V_f specimen. Similarly, a compact body (S-body) having low porosity before

Table 3.
Porosity and volume fraction of filled matrix in specimen by several infiltration process

Preform	Thickness (mm)	V_f (%)	$V_{SI}(V_{P0})$ (%)	$V_{PIP}(V_{P1})$ (%)	$V_{PCVI}(V_{P2})$ (%)	V_{P3} (%)	V_{SI}/V_{P0} (%)	V_{PIP}/V_{P1} (%)
OW	4.0	41.9	27.0 (58.1)	17.6 (31.1)	4.3 (13.5)	9.2	46.5	56.6
4SB	4.0	31.4	33.7 (68.6)	20.8 (34.9)	4.6 (14.1)	9.5	49.1	59.6
4SAB	4.0	40.5	27.8 (59.5)	18.0 (31.7)	4.4 (13.7)	9.3	46.7	56.8
2SB	3.2	43.9	25.2 (56.1)	17.0 (30.9)	5.5 (13.9)	8.4	44.9	55.0

V_f, volume fraction of fiber; V_{SI}, volume fraction by SI; V_{PIP}, volume fraction by PIP; V_{PCVI}, volume fraction by PCVI; V_{P0}, porosity before SI; V_{P1}, porosity before PIP; V_{P2}, porosity before PCVI; V_{P3}, final open-porosity.

Table 4.
Flexural strength at RT–1773 K

Preform	Flexural strength (MPa)		
	RT	1473 K	1773 K
OW	341	468	422
4SB	366	553	457
4SAB	383	543	461
2SB	410	582	474

PIP application had low efficiency (V_{PIP}/V_{P1}) in matrix-filling by the PIP process compared to a body having high porosity. In other words, the matrix filling by both the SI and the PIP processes act as decrease of porosity in the fiber preform. Likewise, the PCVI process contributes to decrease of porosity. In the specimens having the same thickness, cumulative volume fraction of the matrix after the final PCVI application may have the same value regardless of preform. Consequently, the lower the V_f, the more the matrix is filled. For the specimens fabricated by using 4SB and 4SAB, the strength was little affected by either the V_f or the fiber orientation, which was understandable from the aforementioned effects (Table 4). Namely, the strength is predominantly affected by the matrix. In the case of 2SB, the specimen had high volume fraction of matrix in spite of high V_f because of thin thickness of specimen. Therefore, the specimen 2SB had the lowest final porosity (V_{P3}) and the highest strength (410 MPa at RT). The strength of 2SB at 1473 K was high enough (582 MPa), and the strength at 1773 K was over 80% of that at 1473 K.

4. VALIDITY OF THE SLURRY–PCVI JOINT PROCESS FOR FABRICATION OF SMALL OR MEDIUM SIZE PARTS

Processing and characterization of CMCs, by using the slurry–PCVI joint process, have been mentioned so far, with the 3D carbon–fiber/SiC system as a typical example. The validity for application of this process in the fabrication of CMCs must be discussed. 1D CMCs are not considered because of easy fabrication by using the filament winding method.

In this joint process, filling of a ceramic powder into the interstices of fibers in a 3D (2D)-preform by using the pressure infiltration of slurry (SI process) is an effective method as the first step of matrix densification. About 47 (SiC matrix: Table 3) and 55 vol% (Si_3N_4 matrix [14]) of pores in a body can be filled with ceramic powder by one-time pressure infiltration with a low viscosity slurry comprising well dispersed fine powder. These powder fillings can be done for a thick preform (10–15 mm) having complex shape, if isostatic pressure infiltration of the slurry is applicable. Following the SI process, 3-time PIP application made it possible to obtain cumulative matrix-filling of 78 vol%. The PIP process is naturally applicable for a body having thick and complex shape as is the case of SI. After successive processes of SI and PIP, PCVI is applied as a finishing process. For the PCVI process, a smooth stream (not turbulent flow) of reactant gases is necessary in order to enter the gases into the pores deep inside of a body, followed by deposition of a monolithic matrix (for instance SiC only). In order to obtain a smooth stream, a complex shape of body is not desirable.

Actually, matrix filling deep inside the body, by this process, is very difficult. In the case of the matrix filling over 10 vol% by this process, the filling depth may be limited to 1 mm from the surface. The time which is needed for the 10 vol% of matrix-filling by the PCVI (application of 50 000 pulses) is less than 1.8 days. From a practical viewpoint, PCVI densification is applicable for thin (less than 3 mm) and non-complex shape parts. Finally, this joint process is effective for fabrication of thin and relatively simple shape parts.

5. CONCLUSION

In order to construct a suitable process for fabricating small and medium size CMC parts, the pulse CVI–slurry joint process has been tried for making 3D carbon–fiber/SiC composites. The joint process consisted of SI, PIP and PCVI processes. In the PCVI process, $SiCl_4$, CH_4 and H_2 were used as reactant gases. The following results were obtained:

(1) Efficiency of the PCVI on densification of matrix was highest in the condition that the holding time, the reaction temperature and the concentrations of $SiCl_4$ and CH_4 were 1 s, 1373 K and 5 mole% in each, respectively.

(2) In the case of the $SiCl_4$–CH_4–H_2 system, the deposition rate was over twice as rapid as that of the MTS–H_2 system, though there was little difference in the filled-mass at the saturation point between the two.

(3) The strength monotonously increased with increase of pulse-number, which coincided with the relation between density variation and pulse-number.

(4) The texture of the fiber preform had little influence on final residual porosity.

(5) The thinner the specimen, the higher the volume fraction filled by the PCVI.

(6) The composites fabricated by using the two step braided preforms had the highest flexural strength. The strengths at RT and 1473 K in Ar were 410 MPa and 582 MPa, respectively. Moreover, the strength at 1773 K was over 80% of that at 1473 K.

(7) The joint process is effective for fabrication of thin and relatively simple shape parts.

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