

# Fabrication and Characterization of 3D Carbon-fiber/SiC Composites by Slurry - Pulse CVI Joint Process

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**SUMMARY :** For the sake of constructing a process for fabrication of small and medium scale CMCs parts, slurry-pulse CVI joint process has been trying to apply for making 3D carbon-fiber/SiC composites. The pulse CVI process was finally applied for a composite body made by a process consisting of slurry and polycarbosilane infiltrations and pyrolysis. The pulse CVI was carried out by using a source gas system of SiCl<sub>4</sub>-CH<sub>4</sub>-H<sub>2</sub>. Crystalline phases deposited by the pulse CVI varied with temperature, gas concentration and reaction time. At 1373K, a large amount of SiC deposition into matrix was observed, and the deposition rate was at least twice higher than that for CH<sub>3</sub>SiCl<sub>3</sub>-H<sub>2</sub> system in the previous work. Model structure of composite after each process were proposed. Flexural strength of composite remarkably increased after the pulse CVI application.

**KEYWORDS :** 3D carbon fiber, SiC matrix composite, slurry infiltration, Pulse CVI, Joint fabrication process

## INTRODUCTION

Ceramics has 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, it is brittle as monolithic state. The major concern in utilizing ceramics as a structural materials is improving its fracture toughness. Fiber reinforcement, especially continuous fiber reinforcement is one of the most effective method for toughening ceramic. 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 are seem to appear now. These methods have their own strong and weak points. For instance, CVI can easily fabricate a part having complicated shape and highly stiff (high modulus) one with relatively low processing temperature, whereas 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 simple shape one (plate, bar, etc). Consequently, suitable fabrication process of CMCs should be chosen either single method(mentioned above) or combined one according to the scale, quality, cost, number etc. of intended parts. In view of cost-effectiveness consideration or process-easiness, 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.

## EXPERIMENTAL PROCEDURE

### i - Composites fabrication

#### 1)Fiber preform

Three kinds of 3D carbon-fiber fabrics were used for preforms of composites : they are orthogonal weave(OW), 4 step with axial braid(4SAB)and 2 step braid(2SB)[Table1]. Properties of fibers used for weaving of the fabric are listed in Table2.

Table 1 Structure of fabric preforms

Fabric type	Fiber volume fraction, Vf	Fiber orientation			Pitch
		Direction	Rati	Type of fiber	
<u>OW</u> <sup>#</sup> Orthogonal weave	41.3%	X, Y Z Selvage	45.1 8.6 1.2	XN50-20N × 2 T900-6Kf T900-2Kf	Px=Py=3mm  Pz=0.52
<u>4SAB</u> <sup>*</sup> 4 step w/axial braid	39.5%	braider axial	70 30	YS-50-60N YS-50-60N × 2	( 8 × 3 base array)
<u>2SB</u> <sup>*</sup> 2 step braid	43.7%	braider axial	30 70	YS-50-60N YS-50-60N	( 9 × 3 axial)

# from Toyota Automatic Loom Works, Ltd.

\* from University of Delaware, USA

Table 2 Properties of fibers used for weaving of fabric preforms

Fiber type	Filament		Density	Tensile		
	diameter	number		strength	modulus	strain
XN50-20N	10 μ m	2,000	2.09 Mgm <sup>-3</sup>	3.73GPa	490 GPa	0.8%
T900-6Kf	5.3	6,000	1.82	5.6	294	1.9
YS50-60N	7	6,000	2.09	3.73	490	0.8

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

## 2) Fabrication of composites

Fabrication process of SiC matrix composites consists of 3 steps. First step is pressure infiltration of slurry (SI), which is consisted of a  $\alpha$ -SiC powder (Lonza VF-15:  $0.6 \mu\text{m}$ ), dispersant and solvent (water), into a fiber preform (S-body). Second one is a cyclic process in which solution of a preceramic polymer (polycarbosilane) dissolved in xylene is infiltrated into the fiber preform filled with the  $\alpha$ -SiC powder, followed by pyrolysis (PIP process). Third step is a finishing process where SiC is deposited into open pores of a body (PIP body) made by successive process of SI and PIP. The SiC deposition process is carried out by PCVI where  $\text{SiCl}_4$ ,  $\text{CH}_4$  and  $\text{H}_2$  reactant gases are introduced into a reaction chamber where PIP body is placed. The reactant and exhaust gases before and after reactions are intermittently introduced and excreted. The reaction temperature range was 1273-1423 K. Composite fabrication process and schematic drawing of reaction chamber in PCVI are shown in Figs 1 and 2, respectively.

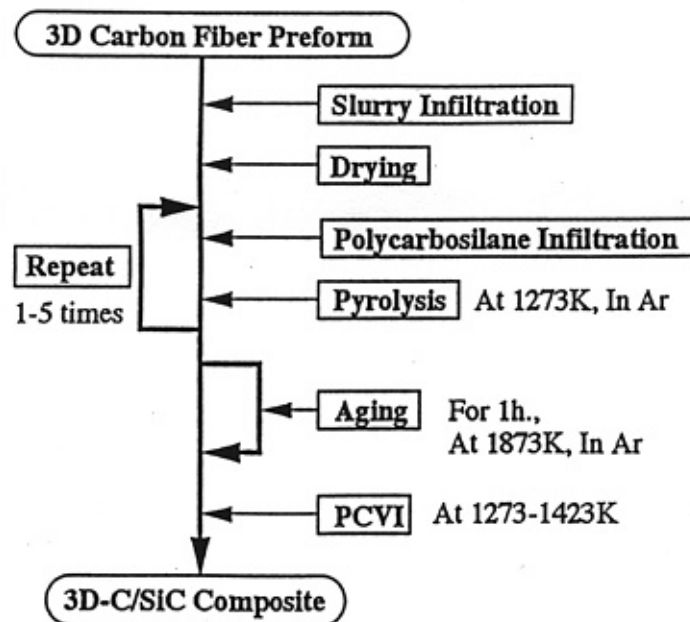


Fig.1. Composite fabrication process

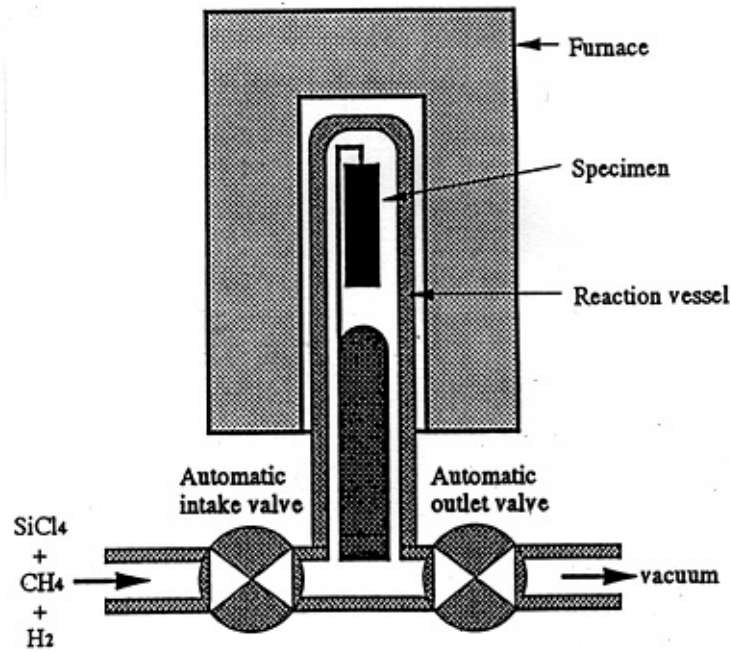


Fig.2. Schematic drawing of PCVI reaction chamber

## ii - Characterization

Porosity and density of composites were measured by Archimedes method with water as a 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(1473K and 1773K)under argon gas.

## RESULTS AND DISCUSSION

### i - Densifying for matrix

Table 3 shows porosity for specimens in several infiltration process.

Preform	Thicknes	$V_f$	$V_{SI}(V_{P0})$	$V_{SI} / V_{P0}$	$V_{PIP}(V_{P1})$	$V_{PCVI}(V_{P2})$	$V_{P3}$	$V_{SI} / V_{P0}$	$V_{PIP} / V_{P1}$
OW	4.0mm	41.9%	27.0%(58.1%)	0.46	17.6%(31.1%)	4.3%(13.5%)	9.2	46.5%	56.6%
4SAB	4.0	40.5	27.8 (59.5)	0.47	18.0 (31.7)	4.4 (13.7)	9.3	46.7	56.8
2SB	3.2	43.9	25.2 (56.1)	0.45	17.0 (30.9)	5.5 (13.9)	8.4	44.9	55.0

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 low- $V_f$  one. This may be attributed that the preform with high- $V_f$  has smaller size of pores between fiber rows compared to those of low- $V_f$  one. Similarly, compact body(S-body)having low porosity before PIP application had low efficiency( $V_{PIP}/V_{P1}$ )in matrix-filling by 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, 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 nearly the same value regardless of preform. Consequently, the lower the  $V_f$  is, the more the filled matrix.

For densifying process by PCVI, two kinds of bodies, which had relative densities of 70.2%(specimen type A) and 81.1%(specimen type B) after SI and PIP process applications, were used for investigating conditions of PCVI application. Deposited phases formed by PCVI are dependent upon both reaction temperature and holding time of reaction in this system( $\text{SiCl}_4 + \text{CH}_4 + \text{H}_2$ ) as shown in Fig 3, whereas in  $\text{CH}_3\text{SiCl}_3 + \text{H}_2$  system, the deposited phases are only dependent upon reaction temperature. In the case that  $\text{SiCl}_4 = \text{CH}_4 = 5$  mole% and the holding time = 1sec, the lowest temperature, in which only SiC phase is deposited, is 1348K(Fig.3).

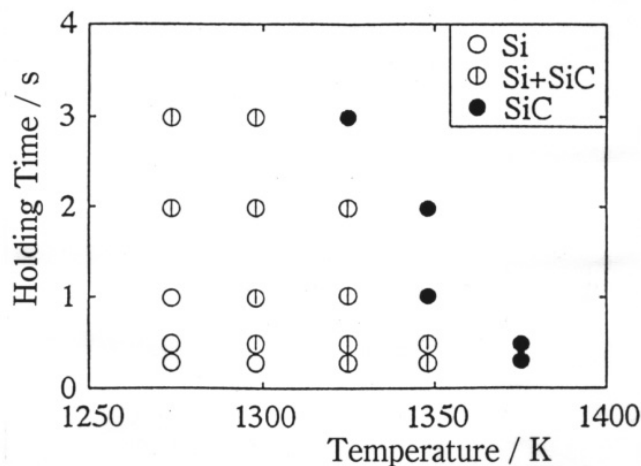


Fig.3. Deposited phase as a function of the reaction temperature and the holding time of reaction( $\text{SiCl}_4 = \text{CH}_4 = 5$  mole%)

Fig.4 shows a relationship between number of pulse and filled-mass in the reaction temperature between 1348K and 1423K. Here the other reaction condition such as the concentration of  $\text{CH}_4$  and  $\text{SiCl}_4$  ( $\text{CH}_4 = \text{SiCl}_4 = 5$  mole%) and the holding time.

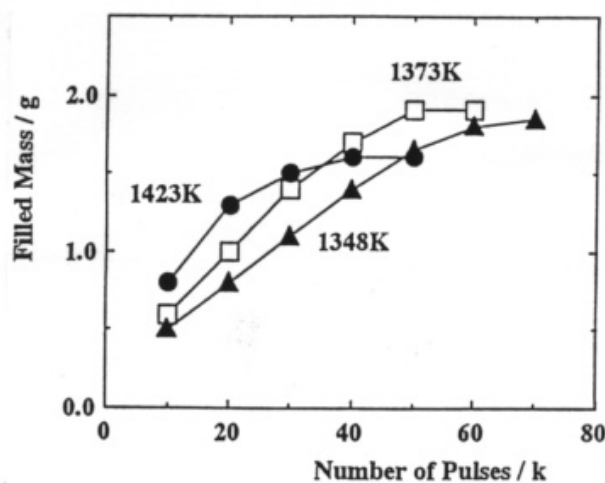


Fig.4. Relationships between number of pulses and filled mass at various temperatures

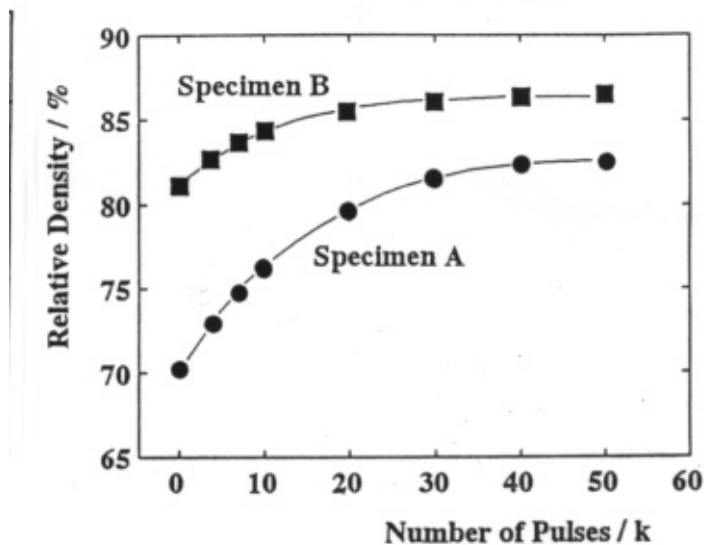


Fig.5. Relations between number of pulses and relative density

reaction (=1 sec) were kept the same in all reaction temperatures. In the case of 1423K, the filled mass was rapidly increased with increase of pulse number until 40,000 pulses, however, it saturated at a lower level of mass quantity compared to the case of 1348K and 1373K. This means that the reaction in the early stage mainly take place around surface of the PIP body which is used for PCVI application. In the case of the 1348K, the deposition rate gradually decreased beyond 50,000 pulses although the mass saturation level was nearly the same as the case of 1373K. Various examinations showed that the aforementioned conditions ( $\text{CH}_4=\text{SiCl}_4=5\text{mole}\%$ , holding time=1 sec, reaction temperature=1373K) were most effective for PCVI application as the finishing process. It is clear that in this system the deposition rate of SiC is twice higher than that of  $\text{CH}_3\text{SiCl}_3\text{-H}_2$  system [12,13]. Relationship between number of pulse and relative density in two kinds of specimens having different residual porosities are shown in Fig.5. The specimen A had RD of 82.5% after 50,000 pulses. Likewise, the specimen B 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 large size of pores made it possible to introduce a large amount of reactant-gases into pores of the specimen A. However, the final relative density of the specimen B was higher than that of the 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 PCVI process.

Fig.6 shows SEM micrograph on fracture surface of a specimen made by this joint process. Part A corresponds to structure made by the slurry process, which has coarse aggregates constructed with many fine grains, whereas structures made by PIP(B) and PCVI(C) are constructed with larger grains. Structures made by PCVI contained about 2 at.% oxygen, whereas structures made by PIP and slurry processes contained about 10 at.% oxygen (by EDS).



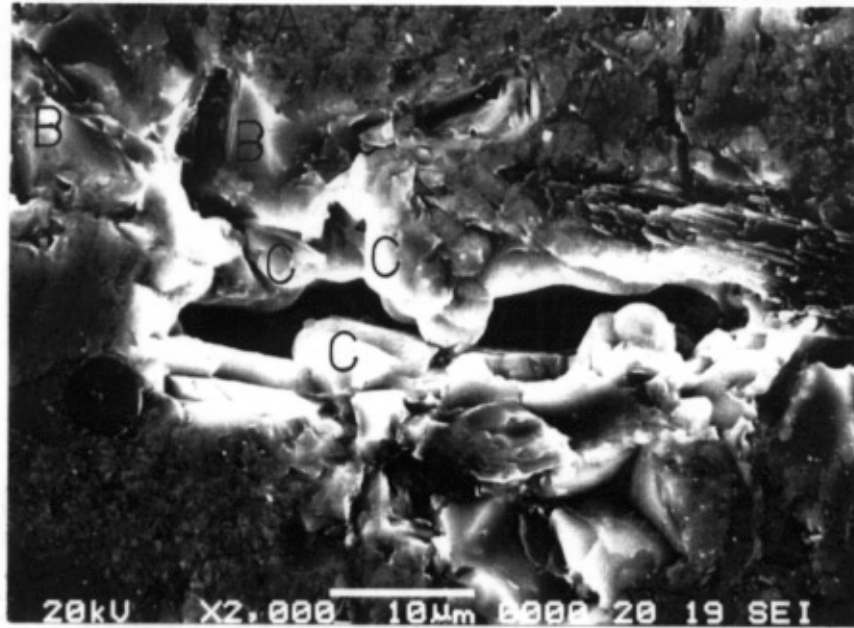


Fig.6 SEM micrograph on fracture surface of a specimen made by this joint process : part A, B and C show structures made by the slurry, PIP and PCVI processes, respectively.

Structures of a composite after application of each infiltration process can be drawn as follows. For a structure made by the slurry infiltration, matrix is consisted of compact SiC powder aggregates, which occupy more than 50 vol % of interstitial space in fiber preform(Fig.7-(a)). The matrix made by PIP infiltration is constructed with the SiC powders bonded by a substance(Si-C-O)derived from pyrolyzation of precursor-polymer(polycarbosilane)and some cracks caused by shrinkage from the pyrolyzed polymer(Fig.7-(b)). In the PCVI process, SiC formed by gas reaction are filled in the interstitial spaces of matrix made by the slurry and the PIP processes and in the cracks(Fig.7-(c)). Some SiC are deposited on the surface of the composite(Fig.7-(c)). The composite after the PCVI application has a porosity less than 8 vol %.

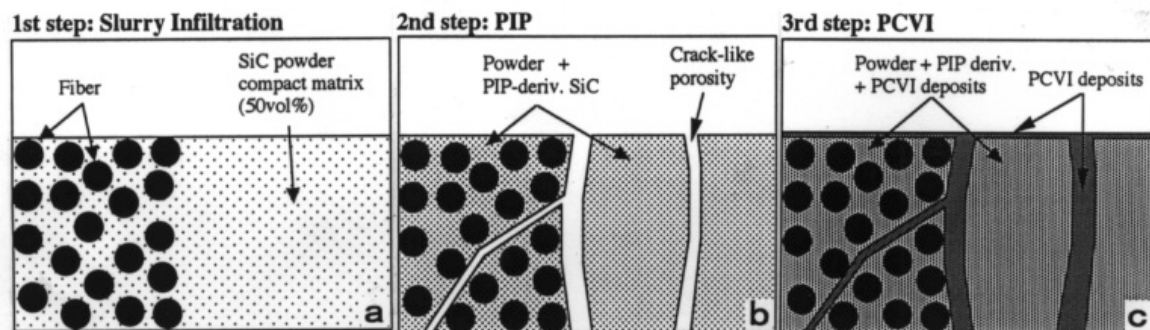


Fig.7 Schematic illustration of structures in a composite made by several processes : a)slurry process, b)PIP process, c)PCVI process.

## Strength of Composites

Flexural strength of composites monotonously increased with increase of relative density which corresponded to increase of pulse number in PCVI process(Fig.5). Table 4 shows flexural strengths of composites fabricated by using 3 kinds of preforms, which were measured at room temperature to 1773K. The composite fabricated by using 2SB showed the highest strength and the composite by using OW showed the lowest one in all measured temperatures. The highest strength of the composite (2SB) may be affected by both the  $V_f$  and the lowest final open-porosity(Table 3). The lowest strength of the composite(OW) was little affected by both the factors, may be affected by another one such as structure defects.

Table 4. Flexural strength at R.T.-1773K

Preform	Flexural strength (MPa)		
	R.T.	1473K	1773K
OW	341	468	422
4SAB	383	543	461
2SB	410	582	474

## CONCLUSION

The pulse CVI-slurry joint process has been trying to apply for making 3D carbon-fiber/SiC composites. The joint process was consisted of SI, PIP and PCVI processes. In the PCVI process,  $\text{SiCl}_4$ ,  $\text{CH}_4$  and  $\text{H}_2$  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  $\text{SiCl}_4$  and  $\text{CH}_4$  were 1 sec., 1373 K and 5 mol % in each, respectively.
- 2)In the case of  $\text{SiCl}_4$  -  $\text{CH}_4$  -  $\text{H}_2$  system, the deposition rate was over twice as rapid as that of MTS -  $\text{H}_2$  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 relative density which corresponded to increase of pulse number in PCVI.
- 4)The texture of fiber preform had little influence on final residual porosity.
- 5)The composites fabricated by using the two step braided preforms had the highest flexural strength and the composite fabricated from orthogonal weave showed the lowest one in all measured temperatures.

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