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# Pressure-pulsed chemical vapour infiltration of pyrolytic carbon into porous carbon or two-dimensional-carbon/SiC particulate preforms from $C_6H_6$–$H_2$–$N_2$

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Pyrolytic carbon was infiltrated into porous carbon or two-dimensionally woven carbon fibre (2D-C)/SiC particulate preforms using pressure-pulsed chemical vapour infiltration from $C_6H_6$ (3–16%)–$H_2$–$N_2$ at 1273–1373 K. Residual porosity of porous carbon decreased from 29 to 10% after $1 \times 10^4$ pulses at 1323 K, and that of 2D-C/SiC particulate preform decreased from 30 to 7.5% after $4 \times 10^4$ pulses at 1273 K. Flexural strength of 2D-C/SiC preform reached about 150 MPa.

## 1. Introduction

Carbon/carbon composites are usually prepared by resin impregnation method followed by carbonization and/or graphitization. In this process, several impregnation/cabonization sequences are repeated usually to obtain dense composites: therefore, this process needs long operation time (several weeks). Another process referred to as chemical vapour infiltration (CVI) has been developed for matrix infiltration into fibre preforms of composites. Among the CVI processes, three main processes have been developed: isothermal and isobaric CVI (ICVI), forced CVI (FCVI), and pressure-pulsed CVI (PCVI). ICVI yields a near-net-shape product; however, it needs long operation time because of slow diffusion [1–5]. FCVI uses steep gradients of pressure and temperature, and operation time was shortened to 20–40 h, but this method lost the advantage of obtaining a near-net-shape product from a restriction of preform shape [6–8]. PCVI process consists of sequential steps of evacuation of reaction vessel, instantaneous introduction of source gases to desired pressure, and holding to allow deposition (holding time) [9–12]. This process also leads to a near-net-shape product with operation time comparable to that in FCVI. Dupel and co-workers have investigated the PCVI deposition to pyrolytic carbon (pyrocarbon) in model straight pores with rectangular cross-section (from 60 to 320 μm in size) from $CH_4$–$H_2$ or $C_3H_8$–$H_2$, and the best infiltration was achieved under conditions of short holding time, low pressure, and low temperature [13–15]. The microstructure of deposited pyrocarbon depends on hydrocarbon species in the gas phase. It has been reported that deposition from $C_6H_6$ results in laminar deposits in which the graphitic planes have an orientation parallel to the substrate surface [16]. In the present study, we investigated PCVI of pyrocarbon from $C_6H_6$–$H_2$–$N_2$ into porous carbon with 0.2–0.5 μm pores or two-dimensional carbon fibre (2D-C)/SiC particulate preforms.

## 2. Experimental procedure

Porous carbon and 2D-C/SiC particulate preforms were used for PCVI of pyrocarbon. Porous carbon samples were prepared by cutting a commercial carbon block, CZR-1 (Poco Graphite Co.), to $20 \times 10 \times 1\ mm^3$. The porosity of CZR-1 is 29% with full open pores, and the pore size distribution is from 0.2 to 0.5 μm. 2D-C/SiC particulate preforms were prepared as follows: two-dimensionally woven carbon cloths (M-40, Toray Industries, Inc.) were painted with SiC fine particles (Showa Denko Co.; average particle size of 5 μm) on both sides using phenolic resin (Phenolite #3000, Dai-Nihon Ink Co.) as a tentative binder. Two sheets of cloth were stacked, pressed, and dried at room temperature for 24 h. The stacked cloths were baked in Ar at 1273 K for 4 h, and were cut to $35 \times 10 \times 1.2\ mm^3$. The porosity of 2D-C/SiC particulate preforms is about 30%.

The PCVI apparatus is shown in Fig. 1. $H_2$ stream saturated with $C_6H_6$ was held in a reservoir together with $N_2$ stream. The gas mixture in the reservoir was introduced instantaneously into a reaction vessel up to 0.1 MPa, and held here for 0.5–10 s to allow pyrocarbon deposition, and then evacuated to below 0.7 KPa. The normal duration of holding time and evacuation time were 0.5 and 1 s, respectively; therefore, one pulse requires 1.5 s, and $10^4$ pulses require about 4.2 h. The concentrations of $C_6H_6$ and $N_2$ were varied between 3 and 16%, and between 0 and 44%, respectively. Three porous carbon samples or 2D-C/SiC particulate preforms were hung in a run at the top of the reaction vessel.

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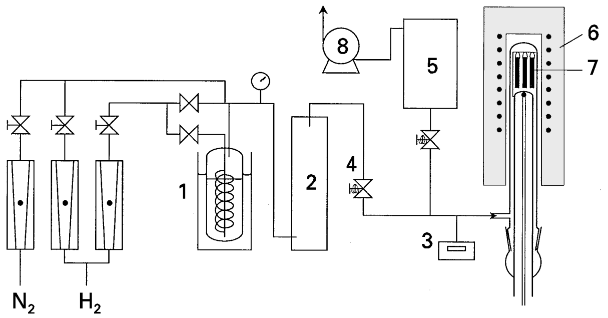

*Figure 1* Apparatus for pressure-pulsed CVI of pyrolytic carbon. 1, $C_6H_6$ saturator; 2, reservoir; 3, pressure gauge; 4, electromagnetic valve; 5, vacuum tank; 6, furnace; 7, preform; 8, vacuum pump.

The filling ratio of pyrocarbon infiltrated into preform is defined as follows

$$\text{(Filling ratio, \%)} = 100 \times \text{(Volume of infiltrated pyrocarbon)}/\text{(Volume of initial pore in preform)}$$

The volume of infiltrated pyrocarbon was roughly estimated from the weight increase subtracted from that of the macrostructure film, the thickness of which was measured by scanning electron microscopy, and assuming the density of pyrocarbon to be 1.8 $g\,cm^{-3}$ [17]. Flexural strength was measured by three-point bending at room temperature.

## 3. Results and discussion

### 3.1. PCVI of pyrocarbon into porous carbon

Fig. 2 shows the dependence of weight increase at 1323 K after 3000 pulses on the $C_6H_6$ concentration. The deposit weight increases with increasing of $C_6H_6$ concentration. However, under high $C_6H_6$ concentration (i.e. above 8%), films were formed on macrosurface of CZR-1 even after 3000 pulses. Films on macrosurface prevent the in-depth source gas penetration in the preform, therefore, $C_6H_6$ concentration has to be lowered below 8% to attain high infiltration at 1323 K. Tar formation from $C_6H_6$–$H_2$–$N_2$ was low under the conditions used in the present study compared with the case from $CH_4$ or $C_3H_8$. The equilibrium $C_6H_6$ concentration from the source gas system 8% $C_6H_6$–$H_2$, which was calculated from the following reactions $C_6H_6 \leftrightharpoons 6C(s) + 3H_2$, $CH_4 \leftrightharpoons C(s) + 2H_2$, and $C_2H_2 \leftrightharpoons 2C(s) + H_2$, is considerably low (below $10^{-12}$). This result indicates that carbon formation from $C_6H_6$ is very easy thermodynamically, and it is suggested that high molecular weight compounds such as tar are rather hard to form.

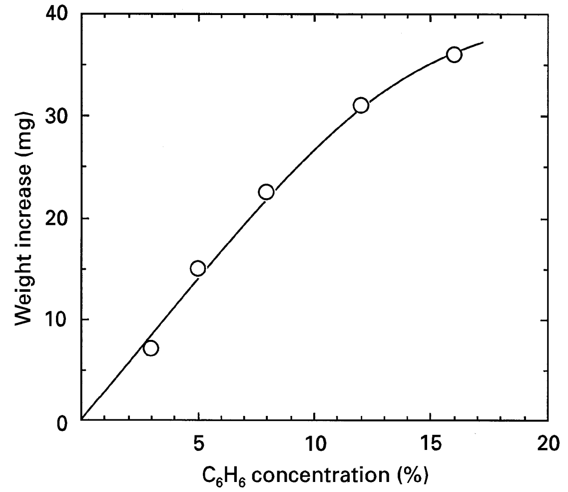

*Figure 2* Dependence of weight increase on $C_6H_6$ concentration. Porous carbon; gas system, $C_6H_6$–$H_2$; CVI temperature, 1323 K; holding time, 1 s; number of pulses, 3000.

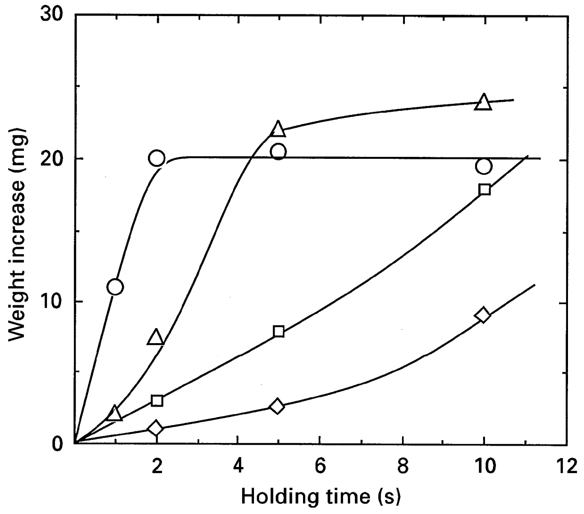

*Figure 3* Relation between weight increase and holding time. Porous carbon; gas concentration, 3% $C_6H_6$–53% $H_2$–44% $N_2$; number of pulses, 1000. (△) 1323 K; (○) 1373 K; (□) 1298 K; (◇) 1273 K.

Fig. 3 shows the relation between holding time and weight increase after 1000 pulses for different deposition temperatures. $C_6H_6$, $H_2$ and $N_2$ concentrations are 3, 53 and 44%, respectively. Below 1298 K, deposits increase with increasing the holding time up to 10 s. At 1323 and 1373 K, weight increase curves almost saturate at holding time beyond 5 and 2 s, respectively. The saturation of weight increase indicates the reactant gas around the preform has been consumed below these holding times. Fig. 4 shows the schematic diagram of the variation in temperature at several positions in preform during one pulse. In PCVI process, the source gas at room temperature is introduced instantaneously into the vessel without sufficient preheating, and the gas cools the macrosurface of the preform. Therefore, the deposition rate near macrosurface becomes lower than that in the deep levels of the preform. However, as holding time becomes longer, the temperature of the cooled macrosurface recovers its normal value, and the deposition on the macrosurface from the dead space gas becomes remarkable, which results in the film formation on macrosurface. On the basis of the above scheme, holding time has to be shortened below that of temperature recovery, and the times were below at least 2 s at 1373 K and 5 s at 1323 K in the present study.

Fig. 5 shows the dependence of filling ratio and flexural strength of the sample obtained at 1323 K on number of pulses. Filling ratio increases with number

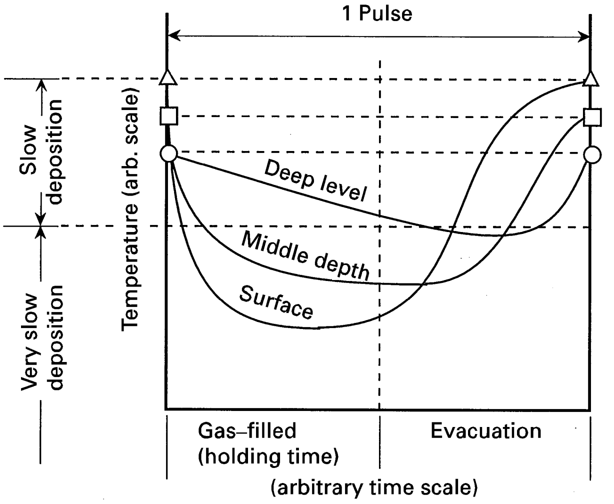

*Figure 4* Schematic diagram showing the variation in temperature at several positions in preform during a pulse.

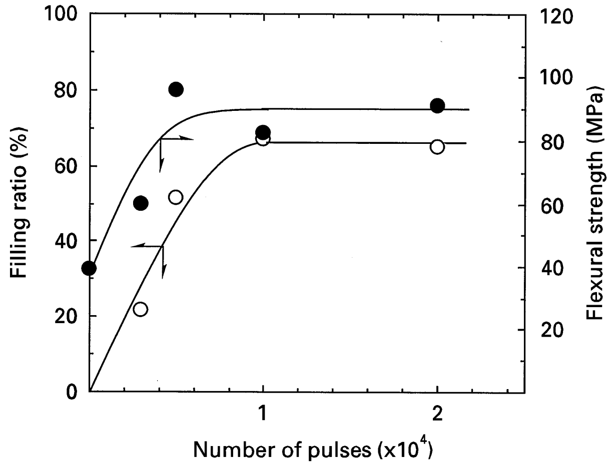

*Figure 5* Dependence of filling ratio and flexural strength on number of pulses. Porous carbon; gas concentration, 3% $C_6H_6$–53% $H_2$–44% $N_2$; CVI temperature, 1273 K; holding time 2 s.

of pulses up to $1 \times 10^4$ pulses, after which it saturates at about 65% by film formation on the macrosurface. Filling ratio of 65% is equivalent to residual porosity of about 10%. Reflecting the saturation of filling ratio, flexural strength also saturates at about 90 MPa, which is about 2.3 times higher than that of original porous carbon.

## 3.2. PCVI of pyrocarbon into 2D-C/SiC particulate preforms

Fig. 6 shows the relation between temperature and filling ratio after $2 \times 10^4$ and $5 \times 10^4$ pulses. $C_6H_6$, $H_2$, and $N_2$ concentrations are 3, 53, and 44%, respectively. For $2 \times 10^4$ pulses, filling ratio increases with the temperature elevation. Below 1323 K, filling ratio increases with increasing the number of pulses from $2 \times 10^4$ to $5 \times 10^4$; however, at 1373 K, filling ratio does not change. This result means films have been formed on macrosurface around $2 \times 10^4$ pulses. Therefore, temperature has to be lowered below 1323 K to

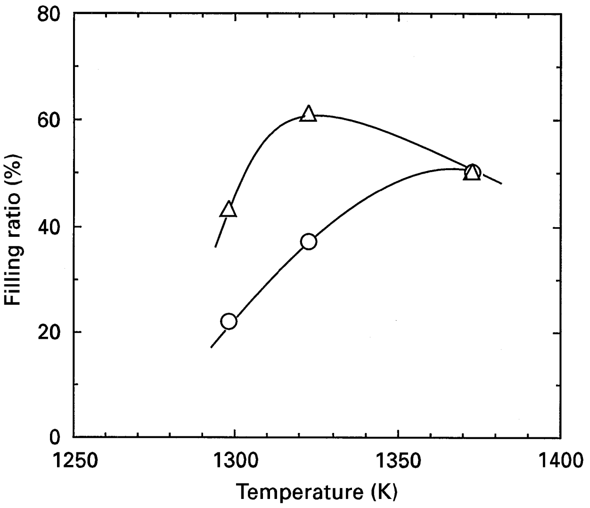

*Figure 6* Relation between temperature and filling ratio of pyrocarbon into 2D-C/SiC particulate preform. Gas concentration, 3% $C_6H_6$–53% $H_2$–44% $N_2$; holding time, 0.5 s. (△) 50 000 pulses; (○) 20 000 pulses.

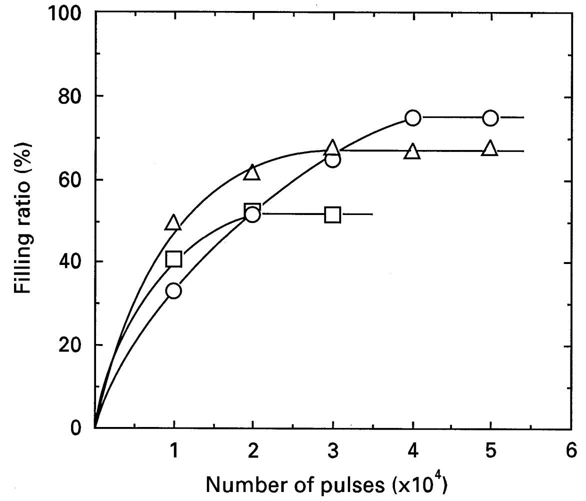

*Figure 7* Relation between number of pulses and filling ratio of pyrocarbon into 2D-C/SiC particulate preform. Gas concentration: (○ 1273 K) and (△ 1323 K) 7% $C_6H_6$–93% $H_2$; (□ 1373 K) 5% $C_6H_6$–93% $H_2$; holding time, 0.5 s.

attain high filling ratio. Fig. 7 shows the relation between number of pulses and filling ratio under various temperatures and $C_6H_6$ concentrations. In the case of $C_6H_6$ concentration of 7% at 1273 K, filling ratio increases up to $4 \times 10^4$ pulses, after which it saturates at the ratio of 75%, which is equivalent to residual porosity of 7.5%. The saturation value decreases with the temperature elevation by the film formation on macrosurface in early stage. At 1373 K, the saturation value is low in spite of low $C_6H_6$ concentration. Below 1273 K and at $C_6H_6$ concentration below 3%, the deposition rate was very slow, whereas under the $C_6H_6$ concentration above 8%, films formed on macrosurface. Suitable PCVI conditions of temperature and $C_6H_6$ concentration are considered to be between 1273–1323 K and 3–7%, respectively.

Fig. 8 shows scanning electron microscope (SEM) images of the cross-section of the sample obtained at

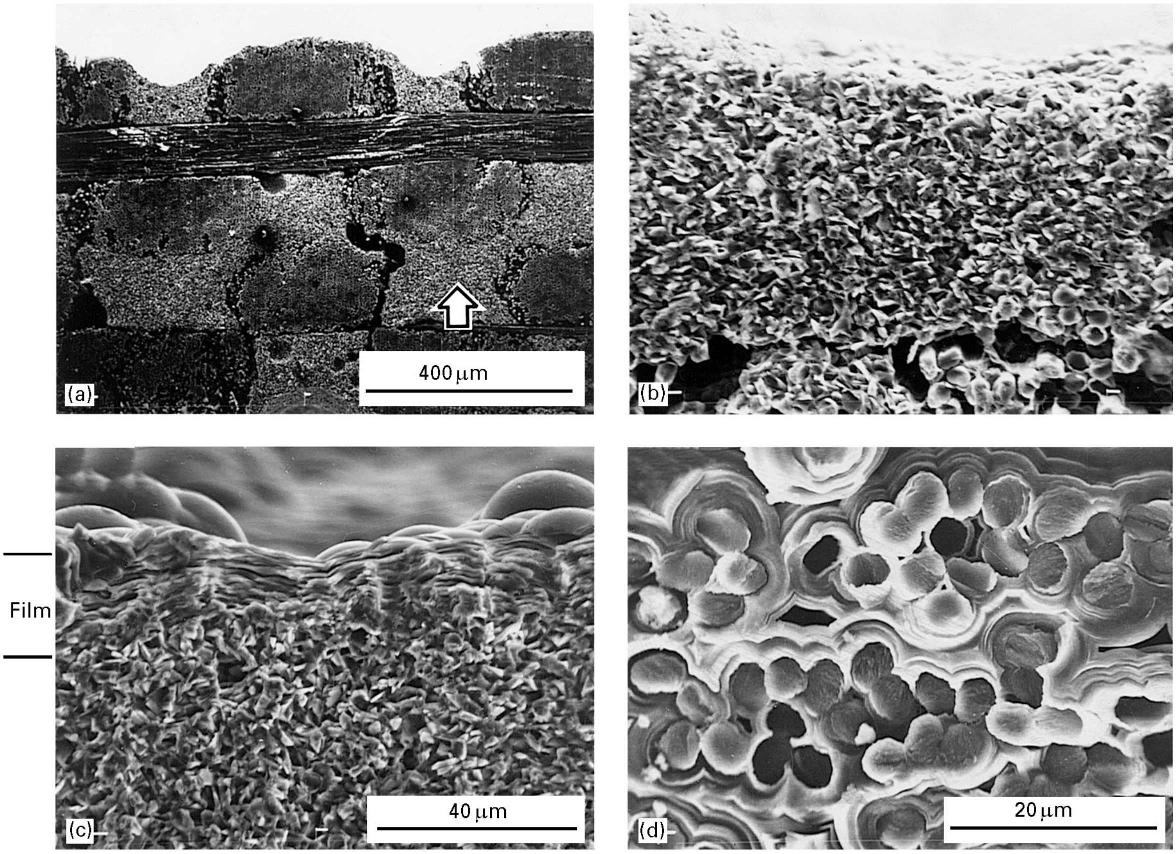

*Figure 8* SEM images of the cross-section of the sample obtained at 1323 K after $1 \times 10^4$ (a, b) and $5 \times 10^4$ (c, d) pulses. 2D-C/SiC particulate preform; gas concentration, 3% $C_6H_6$–53% $H_2$–44% $N_2$; holding time, 0.5 s. Photograph (b) and (c) show the images near surface, and (d) shows that at half thickness. Arrow on photograph (a) shows the filler of SiC particles.

1323 K after $1 \times 10^4$ (a and b) and $5 \times 10^4$ (c and d) pulses. Photograph (b) and (c) show the images near surface and (d) shows that at half thickness. In the low-magnification photograph (a), it is observed that SiC particles fill the large pores (above 20 μm in size) between yarn to yarn of the carbon fibres. The usual PCVI process is unsuitable to close such a large pore, because the thickness of the deposits per pulse is estimated as below 0.1 nm. The filler such as SiC particles is effective to close the large pores in original preforms. After $1 \times 10^4$ pulses, infiltration is insufficient; however, films have not been formed on macrosurface at this stage (Fig. 8b). After $5 \times 10^4$ pulses, infiltration becomes high (Fig. 8d); however, macrosurface films are observed (Fig. 8c). Photograph (d) also shows that the pyrocarbon has laminar microstructure orientated parallel to the surface of carbon fibre.

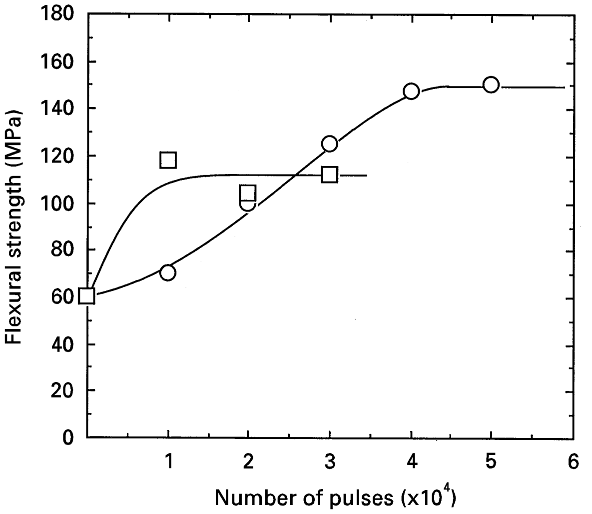

*Figure 9* Relation between flexural strength and number of pulses. 2D-C/SiC particulate preform; gas concentration: (○ 1273 K) 7% $C_6H_6$–93% $H_2$; (□ 1373 K) 5% $C_6H_6$–95% $H_2$; holding time, 0.5 s.

Fig. 9 shows the relation between number of pulses and flexural strength of the sample obtained under the conditions shown in Fig. 7. At 1273 K, flexural strength increases with number of pulses up to $4 \times 10^4$ pulses, after which saturates at about 150 MPa, reflecting the saturation of the filling ratio (Fig. 7). The strength of 150 MPa is 2.5 times higher than that of original preform. On the other hand, at 1373 K, the strength saturates at about 110 MPa beyond $1 \times 10^4$ pulses. The low strength of the sample obtained at 1373 K resulted from the low filling ratio as shown in Fig. 7. From photograph (d) in Fig. 8, the pull-out of carbon fibres can scarcely be observed. This result indicates the adhesion between carbon fibre and carbon matrix is tight. To improve the strength, a method of weakening the adhesion such as the use of interlayer has to be developed. Furthermore, Kimura and coworkers have reported the strength of the C/C composites was increased by heat treatment at high temperature above 2673 K, because the graphite layers grown from the amorphous-like matrix surrounded the carbon fibre, and reflected the crack path [18]. It is supposed that heat treatment is also necessary to improve the strength of the present sample.

## 4. Conclusion

Pressure-pulsed chemical vapour infiltration (PCVI) process of pyrocarbon from a gas system $C_6H_6$–$H_2$–$N_2$ was investigated using porous carbon or 2D-C/SiC particulate preforms. The following results were obtained.

1. When holding time was long, films were formed on macrosurface of the preform at the early stage of PCVI. Therefore, holding time must be shortened to at least 5 s at 1323 K and 2 s at 1373 K.
2. Under $C_6H_6$ concentration above 8% at 1373 K, films on macrosurface grew dominantly, whereas, under $C_6H_6$ concentration below 3% below 1273 K, the deposition rate was very slow. Suitable PCVI temperature and $C_6H_6$ concentration are considered to be between 1273–1323 K and 3–7%, respectively.
3. After PCVI of $1 \times 10^4$ pulses at 1323 K, filling ratio of pyrocarbon into porous carbon reached 65% (i.e. residual porosity of 10%), and flexural strength increased from 39 MPa to 90 MPa.
4. After $4 \times 10^4$ pulses at 1273 K, filling ratio into 2D-C/SiC preform reached 75% (i.e. residual porosity of 7.5%), and flexural strength increased from 60 MPa to 150 MPa.

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