JOURNAL OF MATERIALS SCIENCE **37** (2002) 3693 – 3703

Mechanical and tribological properties of 2-D carbon/carbon composites densified through pulse chemical vapor infiltration

N. H. TAI
Department of Materials Science and Engineering, National Tsing-Hua University, Hsin-Chu, Taiwan, ROC
H. H. KUO, J. H. CHERN LIN, C. P. JU
Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, Taiwan, ROC

This paper presents the mechanical and tribological properties of 2-D carbon/carbon composites (C/C) fabricated by the Pulse Chemical Vapor Infiltration (PCVI) process. In the PCVI process, various fabrication temperatures and different reactant pressures were adopted to investigate the influence of processing condition on physical properties, microstructure and mechanical properties. In the densification process by PCVI, holding time and pulse number are two parameters which significantly affect physical properties (such as density, porosity, and weight gain) and mechanical properties (such as interlaminar strength and wear properties). It is found that the wear properties of carbon/carbon composites can be improved obviously after the densification by 1000 pulses. Effects of initial open porosity on density of the fabricated composites are also studied. In this work, tribological performance of the specimens fabricated through the Isothermal Chemical Vapor Infiltration (ICVI) process and the PCVI process under different pulse cycles are compared. Scanning Electronic Microscopy (SEM) was used to examine the morphology of worn surface. The relationship between the tribological performance and surface morphology was studied.

1. Introduction

Light weight, high specific strength and specific modulus at elevated temperature in inert atmosphere result in the applications of carbon/carbon (C/C) composites as structure materials in re-entry parts of space vehicle, aircraft brakes, rocket nozzles, and other military use. In the industry, the applications involve glass handling tools, high temperature mechanical fasteners, hot gas ducts, heat exchanger, piston, and hot press dies [1]. Further application may extend to the electronic industry due to the requirement of high thermal conductivity for the intensive heat dissipation [2]. Besides, due to the biocompatibility of C/C composites with bones, blood, and soft tissue, second operation can be avoided when the C/C composites were adopted in the repair of fractures of human bones. Moreover, one of the most important applications of C/C composite is in brake discs for transport aircraft and land transportation vehicles.

Applications of C/C composites in braking system were broadly adopted due to the aforementioned advantages as well as self-lubricating capability. In military and civil subsonic aircraft, such as F-18, Mirage 2000, Concorde, Airbus, MD-11, Boeing 747-400, Boeing 737- 500, and Space Shuttle Orbiter, are equipped with C/C composite brakes. Recently, C/C composite has been used in trucks, high-speed train and racing cars [3]. During braking, heat generation due to friction causes the discs heated up. As a result, materials with the property of good thermal shock resistance, high thermal conductivity, and low coefficient of thermal expansion are the primary considerations for braking system; C/C composite is one of the materials having that advantages.

Tribological behavior can be affected by many factors. Chen *et al.* investigated the effect of humidity on the wear performance [4]. Chen and Ju compared the tribological behavior of C/C composites with different structure and starting materials for carbon matrix [5]. Lee *et al.* found that local asperity temperature can induce matrix graphitization during the wear process [6]. Lhymn and Lhymn investigated the wear performance of C/C composite reinforced by short PAN-based carbon fibers [7]. Frye studied the ablation performance of C/C composite which treated under different temperatures and fabricated with different filament orientation and matrix composition [8].

It is no doubt that microstructure, which is influenced by the fabrication process, affects the wear performance of C/C composites. There are two primary routes for the fabrication of C/C composite; one is the resin impregnation, the other is Chemical Vapor Infiltration (CVI). In the resin impregnation process, thermosetting resins are adopted as matrix precursors of C/C composites. All the fabrication methods used in the polymeric composites can be adopted to densify the preform for subsequent C/C composite fabrication. The primary advantage of the liquid impregnation process is that large structure with complex geometry and thick thickness can be manufactured. However, this method is less effective to densify the composites having fine open pores.

Compared to the resin impregnation route, the CVI process is more efficient to fill the fine pores with carbon matrix in C/C composites. In the CVI process, the vapors penetrate into the fibrous preform and deposit the solid product onto the pore surface to densify the composite. Various CVI processes were developed, the most well known method is isothermal CVI process (ICVI) [9, 10], in which where reactants penetrate into the preform by diffusion. In order to prevent the premature closure during processing, a forced-flow, temperature-gradient process CVI (FCVI) was developed for the fabrication of Ceramic Matrix Composites (CMC) [11]. More recently, the pulse CVI (PCVI) process was proposed, in this process, the reaction chamber was vacuumed and refilled periodically [12, 13]. As a result, the concentration gradient within preform can be alleviated. This process combines advantages of both the ICVI and the FCVI processes. Thus, a uniform deposition with rapid processing rate can be expected when the fabrication parameters are properly controlled.

Based on our knowledge, the discussion on the correlation between friction mechanisms and wear behavior and processing parameters of C/C composite are very limited, especially when C/C composites were fabricated under the PCVI process. The PCVI process has more fabrication parameters than the ICVI process. In this work, four primary factors (reaction temperature, reactant pressure, holding time, and pulse number) were investigated to study their effects on mechanical and tribological properties of C/C composites.

2. Experimental

2.1. Sample preparation

The 2-D plain weave carbon fabrics with the size of 20.0 cm × 20.0 cm were placed in a bath filled with phenolic resin. Table I shows the relative information of raw materials. The resin was impregnated into the fabric under ultrasonic environment for 30 minutes. The excess resin was squeezed out under rolling. The fabrics with proper resin content were placed in an air circular oven at 70°C for 2 hours to remove the solvent.

Twenty-four layers of resin-impregnated fabrics were placed in a picture frame mold and compression molded under 9.0 MPa at 160°C for 2 hours. Stabilization process of the specimens with the dimension of 3.0 cm × 3.0 cm was performed in an air circular oven at 230°C for 8 hours.

Carbonization process was performed in a tube furnace (Lindberg, England) under N_2 atmosphere at 1200°C for 1 hour. Graphitization process was achieved in a graphitization furnace (Thermal Technology Inc, USA) under He atmosphere for 0.5 hour at 2200°C.

2.2. Densification

The PCVI process was applied in this work to densify the porous carbonized and graphitized C/C composites. Fig. 1 shows the schematic figure of the set-up. Variation of the reactant pressure within the horizontal tube furnace during the PCVI process was depicted in Fig. 2.

2.3. Measurements

2.3.1. Density and open porosity

The density of C/C composite was measured on a Precica 180A microbalance using the water immersion method. Open porosity was obtained from the density and the weight increase rate of the specimen when open pores inside the specimen were occupied by water.

2.3.2. Interlaminar shear strength

According to ASTM D-2344, three-point bending test with the span-to-depth ratio of 4 and cross-head speed of 1.3 mm/min was adopted. The interlaminar shear strength (ILSS) of C/C composites is measured according to the equation listed in the following:

$$F_{\mathrm{ILSS}} = 3P/(4bd) \qquad (1)$$

where P is the maximum load, b and d are the width and the thickness of the specimen, respectively. All the physical and mechanical data shown in this paper are the average of at least three specimens.

2.3.3. Tribological test

Tribological performance of C/C composites was tested using a disc-on-disc sliding wear tester, as schematically shown in Fig. 3. In order to assure all specimens having the same surface roughness, mechanical polishing to a level of # 1200 grit following ultrasonic treatment to remove the debris was used before wear test.

The simulated-stop (braking) testing was conducted by first accelerating the rotor with a specimen on the end. The power of driving motor was switched off when

TABLE I Relative information of the raw materials

Material	Specification	Company
PAN carbon cloth # 3085	2-D plain weave Yarn size: 3K Tensile strength:400 kg/mm^2 Density: 1.79 g/cm^3	Fiber: Mitsubishi Rayon, Japan Weave: Porcher Industries, France
Phenolic resin PF-650	Resole-type Molecular weight: under 1000	Chung-Chun Plastics Co. Ltd.,
Reactant	Methane	Air Products and Chemicals, Inc.

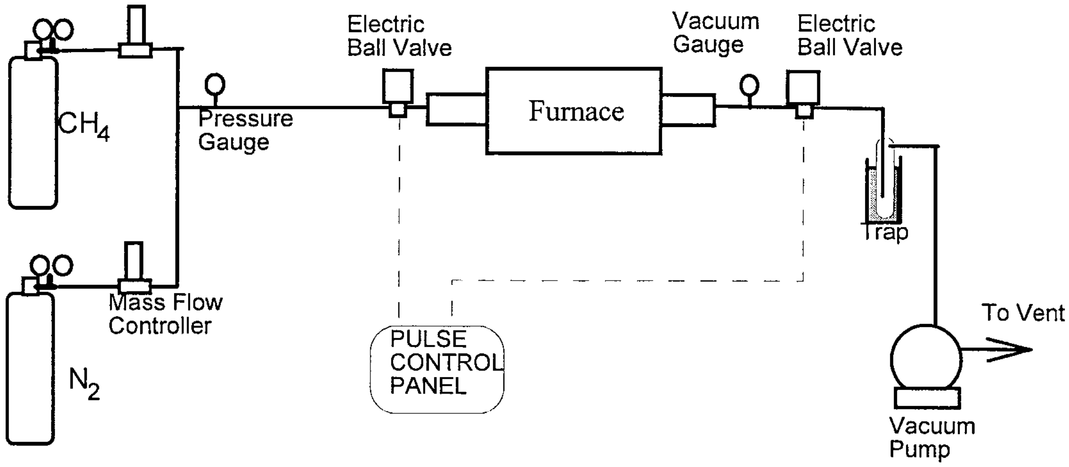


Figure 1 Schematic figure of the set-up for the PCVI process.

	A	B	B’	C
Inlet valve	open	close (start)	close (complete)	close
Outlet valve	close	close	close	open

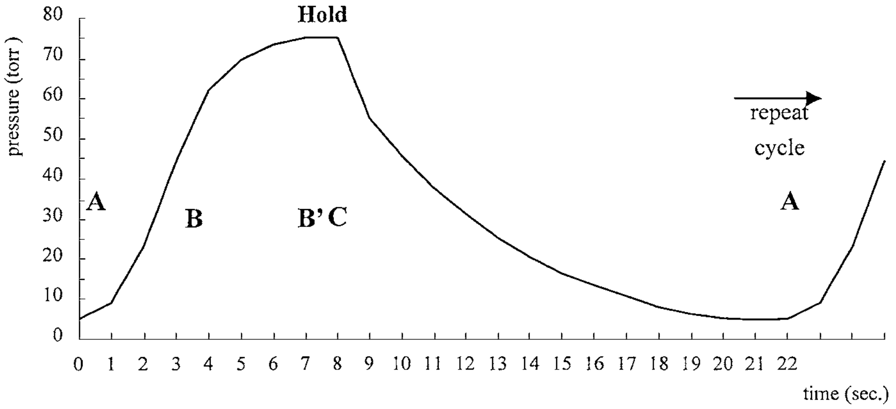


Figure 2 Variation of the reactant pressure within furnace during the PCVI process.

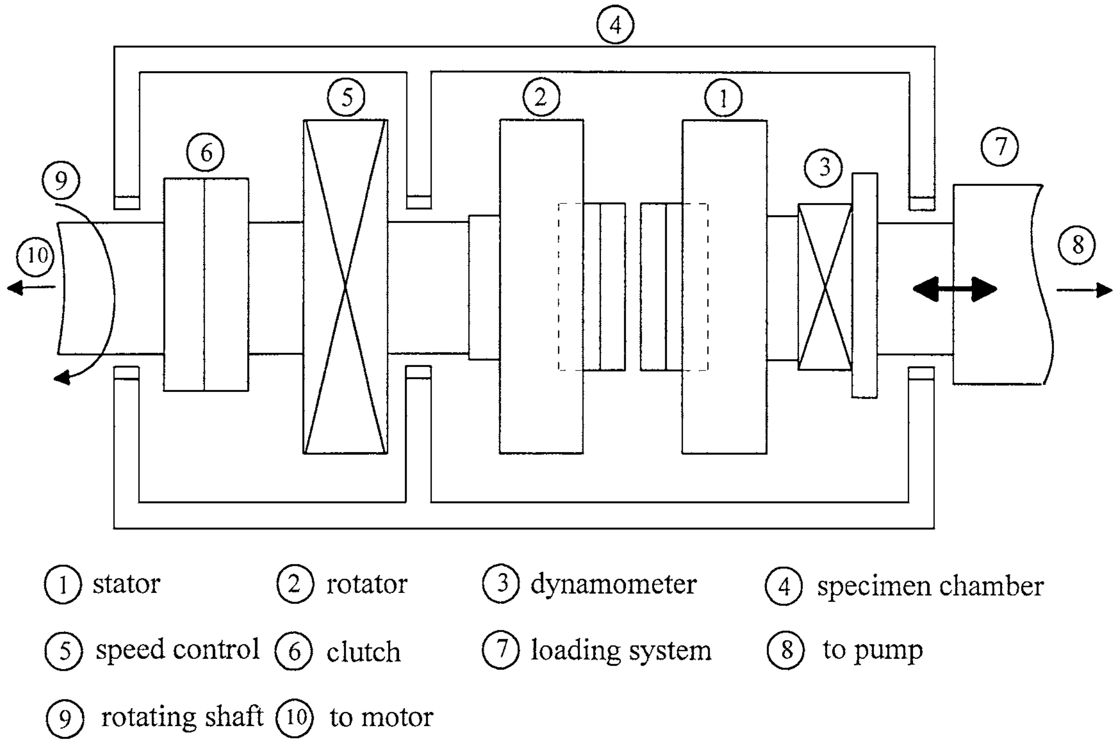


Figure 3 Schematically depict the disc-on-disc sliding wear tester.

the rotor speed of 1200 rpm was achieved. The stator specimen having the same composite and roughness as the rotor specimen was loaded with a pressure of 0.8 MPa to slide against the rotor to a complete stop.

Friction coefficient can be derived from the sliding torque which was *in situ* measured using an AST-BH dynamometer (Sato, Japan). The equation for calculating friction coefficient was listed as follows:

$$M = \mu(2r/3)F_n \tag{2}$$

Where M is the sliding torque, μ the friction coefficient, r the specimen radius, F_n the load.

The weight loss of the specimen without further treatment was measured in a precise balance (Shimadzu, AEL-40SM, Japan). No obvious difference in weight loss was observed between the rotor and stator specimens since these two specimens are identical material.

2.3.4. Morphological inspection

Optical microscope (Nikon FM2, Japan) and Scanning Electron Microscope (SEM, Hitachi S-2500, Tokyo, Japan) were used to study the surface morphology before and after the braking tests.

3. Results and discussion

3.1. Effects of processing parameters on physical and mechanical properties

3.1.1. Temperature

Three temperatures, 900°C, 1000°C, and 1100°C, were used for the densification of C/C composite. Fig. 4a shows the density variation of the specimens densified under different temperatures. Density reduction at 900°C may be due to the escape of the trapped vapor during the densification process and the low deposition rate at this temperature. Open porosity, as depicted in Fig. 4b, was significantly reduced at 1100°C although the density increase is not obvious, it implies that the high reaction rate at high temperature block the inlet of the open pore, which results in the pore close of the specimen. ILSS as shown in Fig. 4c, increasing with the reaction temperature can be detected. Similar trend of the density indicates that ILSS is significantly affected by the density of the fabricated specimens.

3.1.2. Reactant pressure

Reactant pressure reflects the concentration of reaction species, which affects the reaction rate, and consequentially, the deposition rate. Fig. 5a and b depict the density increase rate and open porosity decrease rate, respectively, under various reactant pressures. Density variation is not obvious, whereas the reduction of open porosity has a significant improvement when a higher reactant pressure at 100 torr is used. However, the ILSS of the composite shows monotonous decrease with reactant concentration, as shown in Fig. 5c. It infers that premature pore close occurs at the composite fabricating under higher reactant pressure, and density and porosity are not the only parameters to affect the mechanical property. Other factors such as microstructure, matrix distribution, and porosity distribution may also play a crucial role in determining the ILSS.

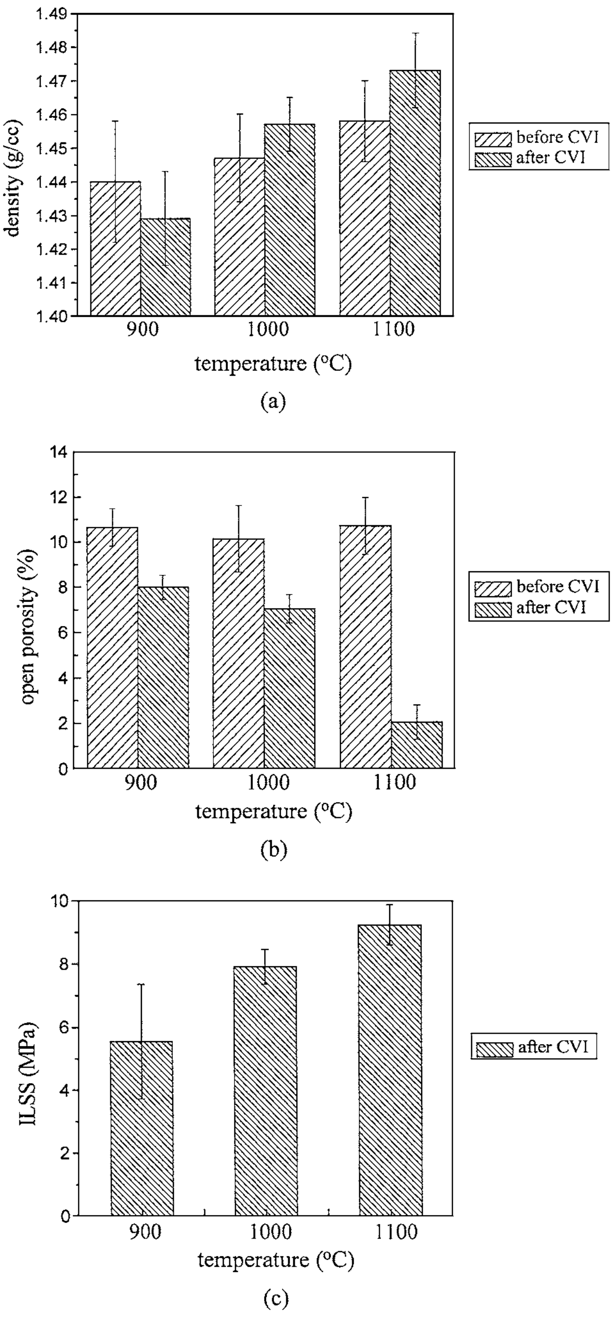


Figure 4 Variations of (a) density, (b) open porosity, (c) interlaminar shear strength (ILSS) of the specimens densified under different temperatures.

3.1.3. Holding time

Holding time reflects the period that the reactants stay in a specific condition. Fig. 6 depicts the variation of density increase rate (6a) and open porosity decrease rate (6b) with holding time. Both density increase rate and open porosity decrease rate increase with holding period. It indicates that longer holding period improves the matrix deposition. However, ILSS (6c) reduces with holding time. The results give further evidence of the mentioned viewpoint.

3.1.4. Pulse number

As mentioned, higher carbon deposition can be obtained under higher temperature, higher reaction pressure, and longer holding period. However, higher deposition rate results in premature pore close in the entrance of the open pores, which generates the improper

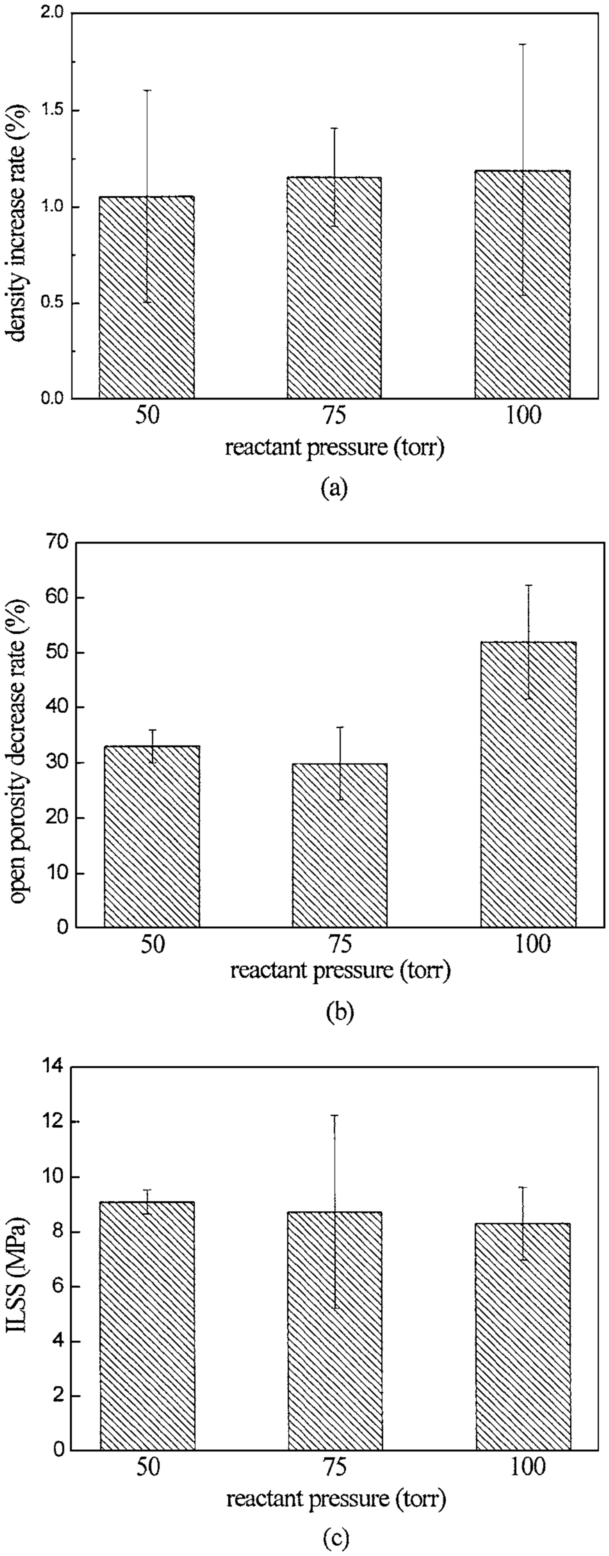


Figure 5 Variation of (a) density increase rate, (b) open porosity decrease rate, (c) ILSS under various reactant pressures.

condition for further densification. In this study, according to the obtained results, reaction temperature of 1000°C, reaction pressure of 75 torr, and holding period of 4.5 sec were selected for long period densification.

Fig. 7 shows the variation of weight gain (7a), open porosity (7b), density increase rate (7c) and ILSS (7d) with pulse number. Significant weight gain and obvious reduction in open porosity with pulse number up to 8000 cycles can be detected. After 8000 pulse cycles, the increase in weight and the decrease in open

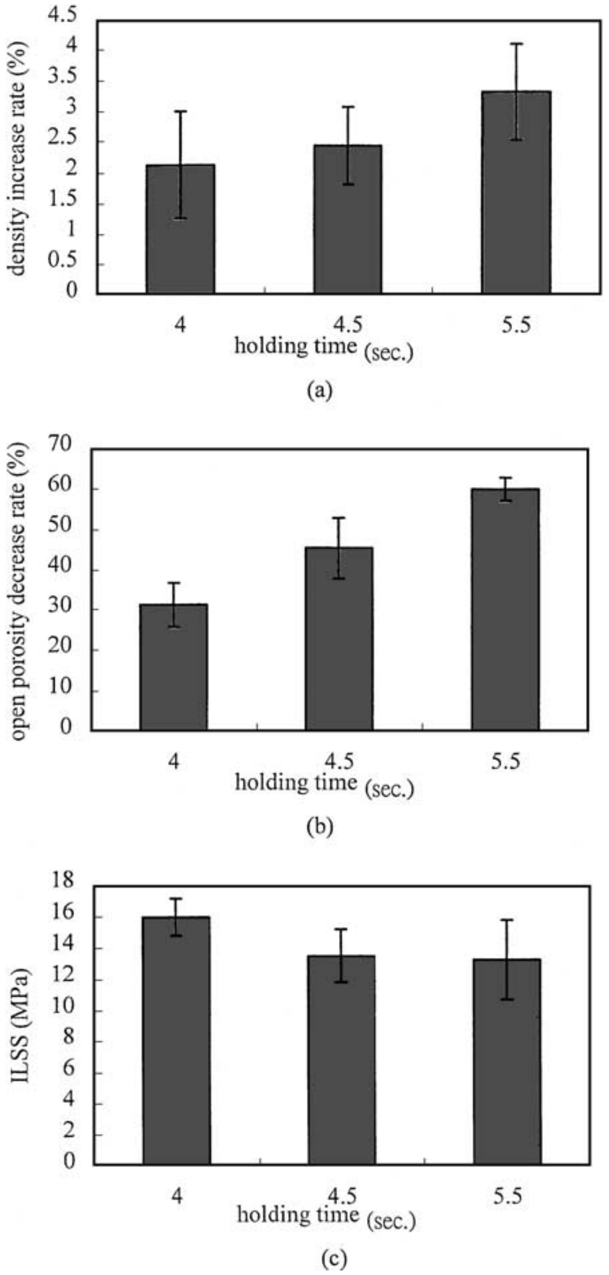
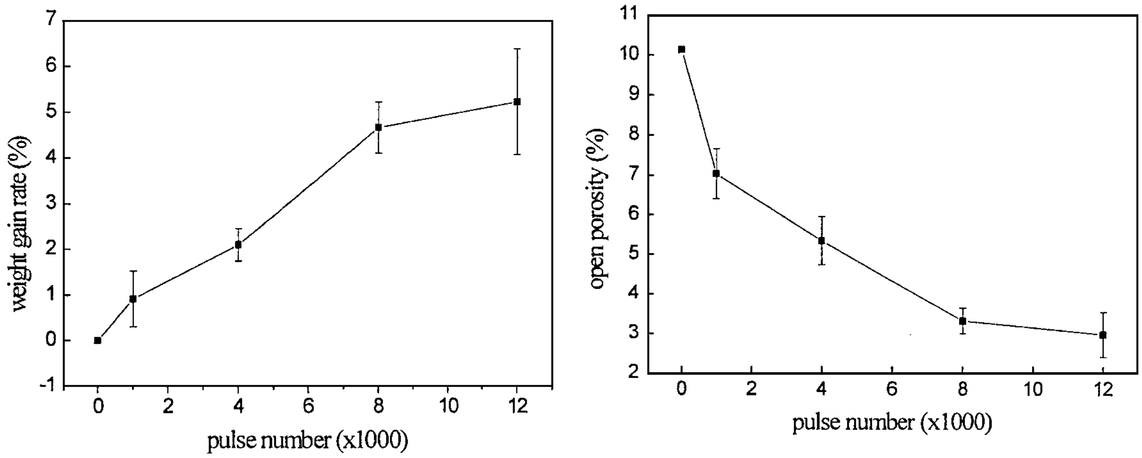


Figure 6 Variation of (a) density increase rate, (b) porosity reduced rate, (c) ILSS with holding time.

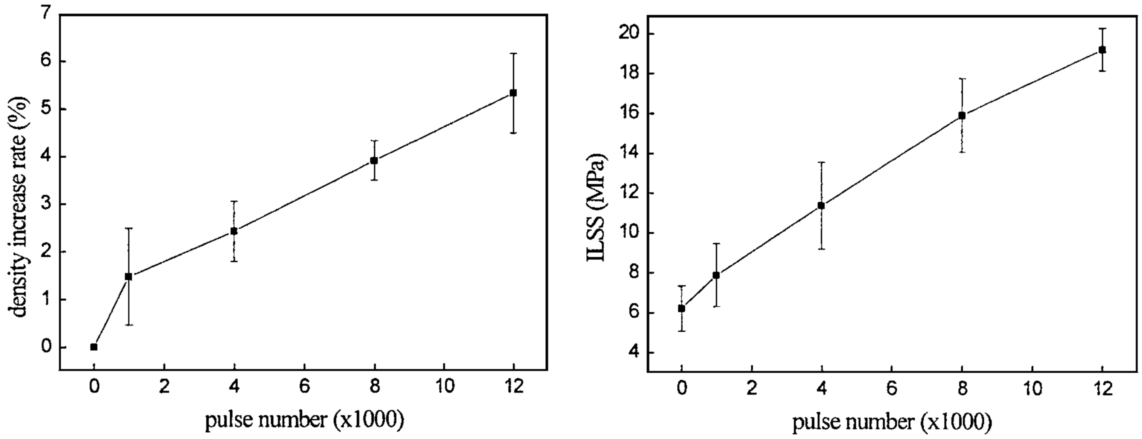
porosity become insignificant. The reason is obvious because the specific deposition surface area was reduced due to void filling and pore close. However, density increased with pulse number up to 12000 cycles. Comparing the results shown in Fig. 7b, c, and d, it is obvious that ILSS increases with density and decreases with residue porosity when proper fabrication condition was conducted.

Fig. 8a and b show the deposition layer onto the fiber surface under different pulse numbers. The thickness increases with pulse number is apparent in these two figures. Even deposition after 8000 cycles, the gap within fiber bundles can't be filled; thus, a longer pulse number is required to fully densify the composites. A further conclusion is also made that the PCVI process is more suitable for the densification of micro pore than that of major void.



(a) weight gain

(b) open porosity



(c) density

(d) ILSS

Figure 7 Variation of (a) weight gain, (b) open porosity, (c) density, and (d) ILSS with pulse number.

3.2. Effects of initial open porosity on density

Initial open porosity of the composites also affects the final densification density. Fig. 9 shows the density increase rate with initial open porosity. Fig. 9a depicts the density increase rate for the specimens subjected PCVI process for 12,000 times, and Fig. 9b shows the density increase rate for the specimens subjected to graphitization after PCVI process. It is observed that the higher the initial porosity, the higher the final density. Higher initial porosity means higher deposition surface area, therefore, a higher density can be expected after a specific deposition pulse cycle. Compare Fig. 9b with 9a, it is detected that graphitization process after PCVI can not improve effectively the density. It is understandable because the deposited carbon during the PCVI process have well graphene layers arrangement, as a results, the graphitization process at high temperature improves the arrangement of graphene layers very limited.

3.3. Effects of graphitization on mechanical properties

Heat treatment affects the microstructure very significant. Carbonization treatment results in obvious matrix shrinkage and subsequent formation of microcracks. During heat treatment at elevated temperature, the random entanglement of carbon ribbons becomes relatively parallel. The existence of fibers enhances the formation of graphene layers along fiber direction. When the heat treatment temperature increases further up to 2200°C or over (graphitization treatment), the turbostratic structure gradually forms a graphite crystal structure. It is believed that the stresses resulting from the mismatch of coefficient of thermal expansion between fibers and matrix drives the formation of parallel graphene layers [1].

Graphitization treatment not only enhances the alignment of graphene layers but also increases the open porosity and alters the pore shape. Fig. 10 depicts the variations of density and open porosity after carbonization and graphitization treatments. It is observed that the graphitization treatment improved the open porosity very insignificant, on the other hand, density increased very obvious after graphitization treatment. Based upon the experimental results, it is concluded that open porosity apparently controls the densification results, however, it is not the only parameter to affect the densification performance. Pore size and shape (pore entrance) determined whether premature pore close occurs or not. Pores with larger entrance size prevent premature pore close, however, it required longer period of matrix deposition to achieve a highly densified composite.

Fig. 11a depicts density variation before and after the PCVI process for the specimens subjected to

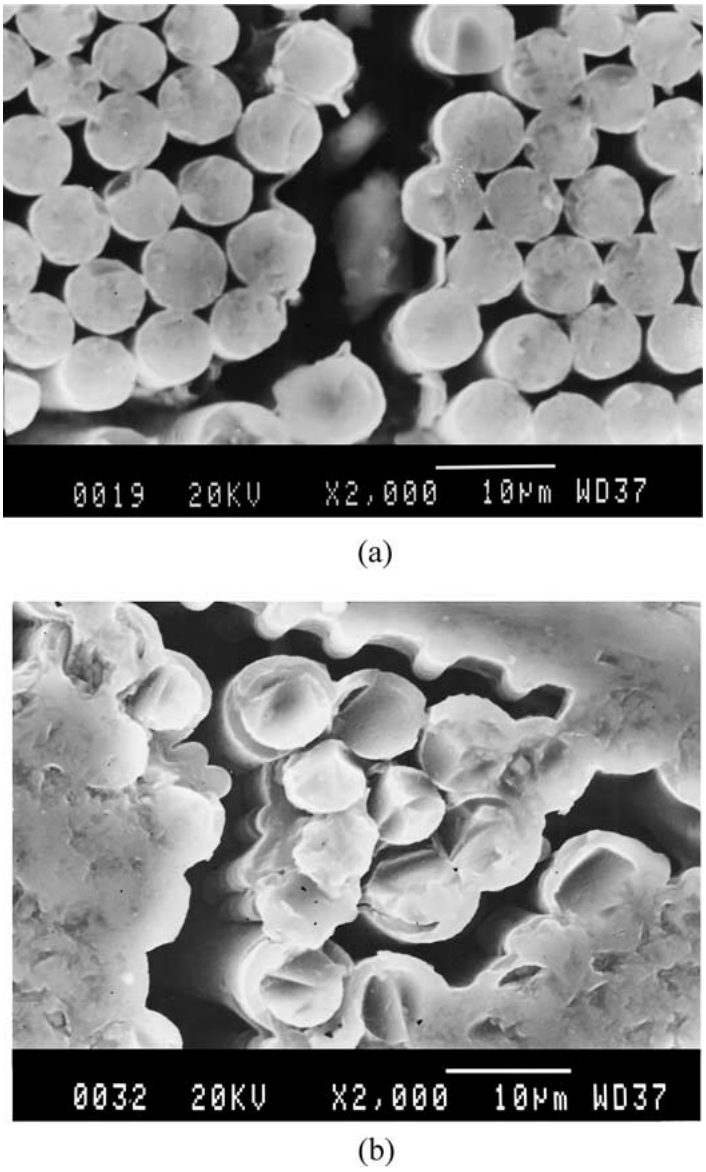


Figure 8 Deposition morphologies of carbon matrix onto the fiber surface (a) after 1000 pulse cycles and (b) after 8000 pulse cycles.

carbonization and graphitization treatments. Compared to carbonized specimen, significant increase in density of the graphitized specimen after the PCVI densification process indicates the graphitized specimen offers a better condition for matrix deposition. This result can be further verified by examining the open porosity after PCVI densification for both the carbonized and the graphitized specimens. Fig. 11b shows that the densification efficiency of graphitized composites (from 16.32% to 3.21%) is better than that of the carbonized composites (from 10.56% to 2.99%). Although the difference of open porosity for these two densified composites is not obvious, however, as shown in Fig. 11a, the density difference (1.53 for carbonized specimen and 1.62 for graphitized specimen) of these two composites is very evident.

Fig. 11c indicates ILSS and fracture toughness of these two PCVI-densified composites, although graphitized composite has a higher density, heat treatment at elevated temperature weakens the interface between carbon fibers and matrix, as a result, it reduces the ILSS. However, graphitization specimen presents higher fracture toughness than carbonization specimen, which indicates that weak interface prevents the penetration of crack front through the reinforcements.

3.4. Wear test

Based on the experimental results, the processing under reaction temperature of 1000°C, reactant pressure of 75 torr, and holding time of 4.5 second was selected for composite densification. Different pulse numbers were adopted to investigate the influence of densification efficient on wear performance. In the following context, C is the carbonized C/C composites without PCVI densification, $\mathrm{C} + n\mathrm{KP}$ represents the carbonized specimen subjected to PCVI densification for n thousand cycles, where K stands for 1000 times and P for PCVI process.

3.4.1. Pulse number

Densification through the PCVI process significantly improves the wear performance. Fig. 12 shows the weight loss during the braking test for the carbonized composites without PCVI densification and densified under different pulse cycles. Apparent reduction in weight loss can be detected even if lower pulse number

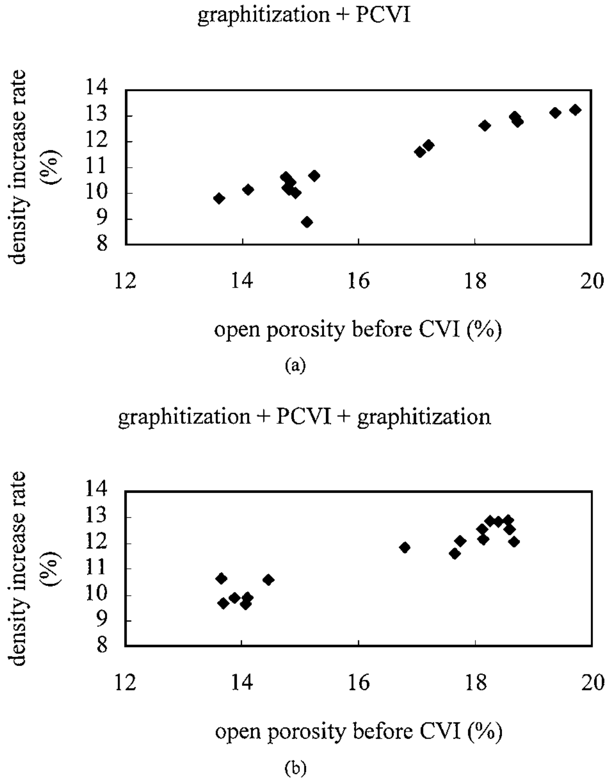


Figure 9 Density increase rate with initial open porosity for different specimens (a) specimens subjected PCVI process for 12,000 times, (b) specimens subjected to graphitization after PCVI process.

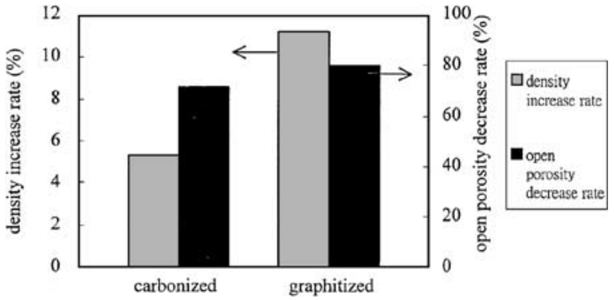


Figure 10 Variations of density and open porosity after carbonization and graphitization treatments.

such as 1000 cycles was adopted. However, the weight loss decreases further with the pulse cycle.

The variations of friction coefficient of the corresponding composites were shown in Fig. 13. The stopping period reduces with pulse number except the specimen densified by 12,000 pulse cycles (specimen C + 12KP). The longer stopping period of the specimen is probably due to the low coefficient (around 0.3) during the braking testing from 6th second to 20th second.

3.4.2. Reaction temperature

Braking tests of two specimens were performed, the specimen denoted as specimen A was PCVI densified at 1000°C for 1000 pulse cycles, the other which denoted as specimen B was fabricated by the same route except the temperature of 1100°C was adopted. Fig. 14 showed the results of the first braking test. The weight loss of specimen B is significantly lower than that of specimen A. Higher processing temperature results in higher reaction rate, which produces relatively dense and thicker deposition layer with fine microstructure on the specimen surface. Fig. 15 depicts the variation of friction coefficient of specimen B during the first time braking test. The specimen takes less than 20 seconds to stop the brake system. Weight loss of specimen B is compatible to that of the specimen C + 8KP although the density and ILSS of specimen B is much lower. Density of specimen C + 8KP and specimen B is 1.473 and 1.502, respectively; ILSS of specimen C + 8KP and specimen B is 15.90 and 9.23, respectively. Based on this result, it deduces that ILSS may not be the key role to affect the wear property of the C/C composites.

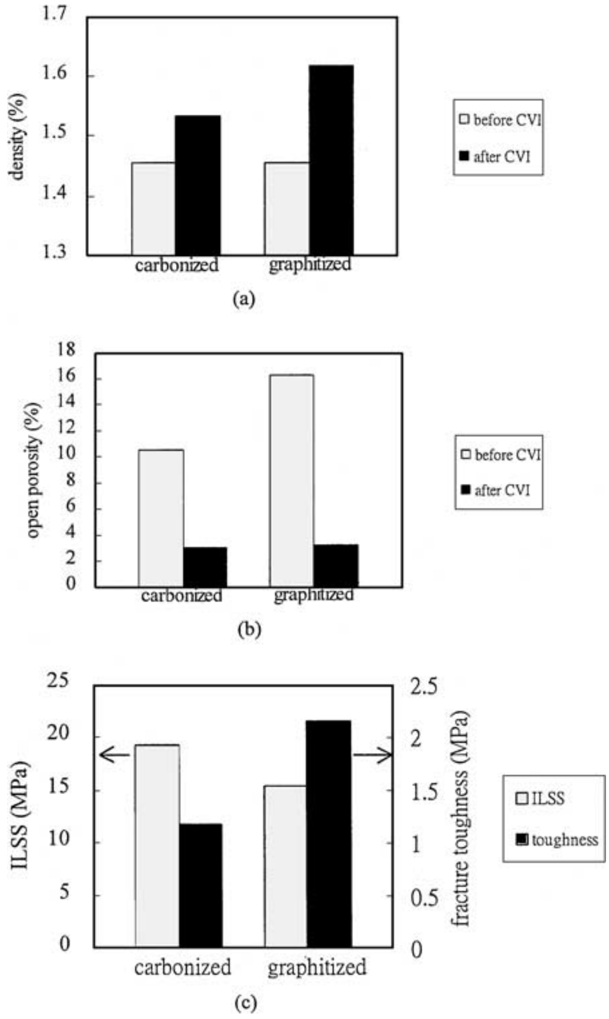


Figure 11 Mechanical properties and densification efficient of PCVI process on carbonized and graphitized composites. (a) density variation, (b) open porosity variation, (c) ILSS and fracture toughness.

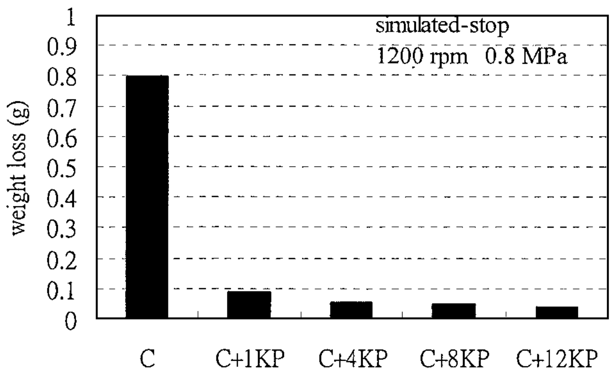
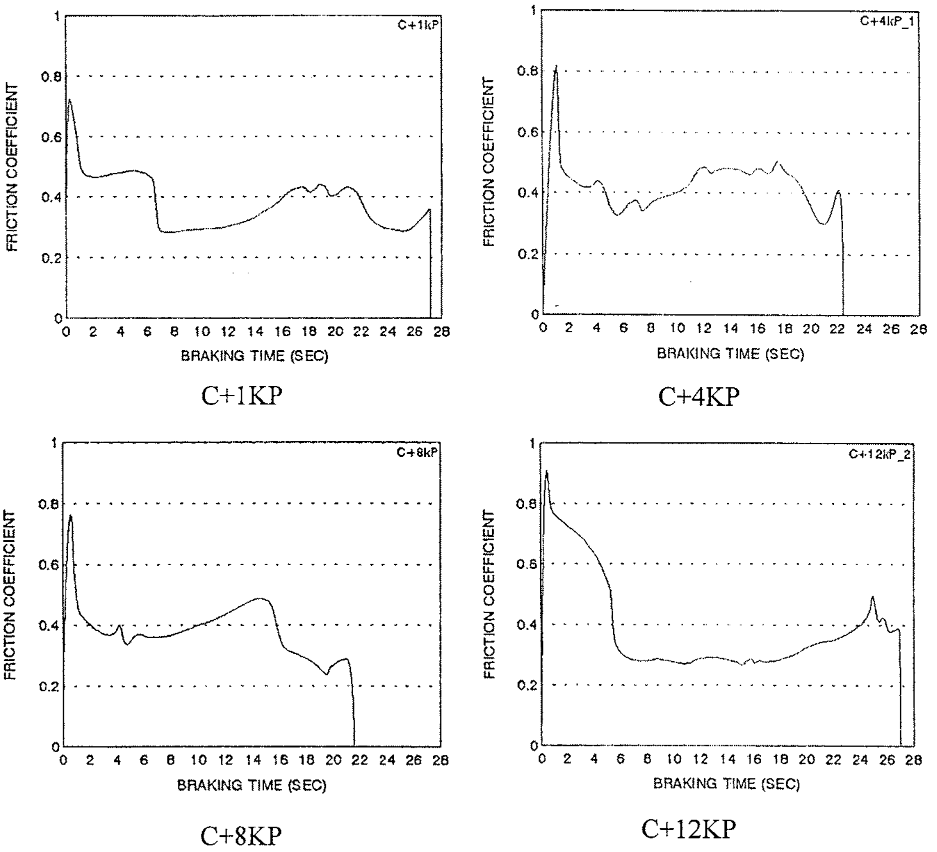


Figure 12 Weight loss of the first cycle braking test for the carbonized composites without PCVI densification and densified under different pulse cycles.



C+1KP C+4KP

C+8KP C+12KP

Figure 13 Variations of friction coefficient during first braking test for the composites densified under different pulse cycles.

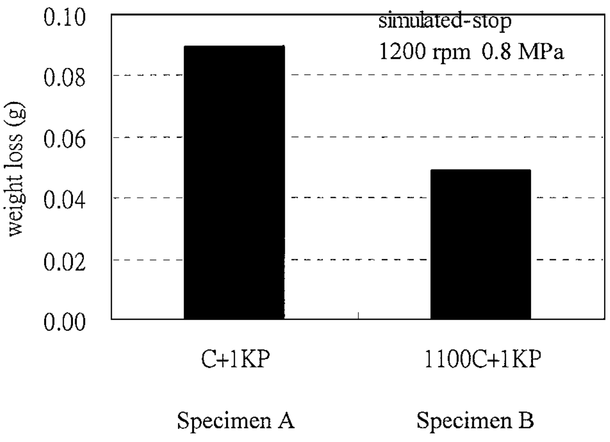


Figure 14 Weight loss during wear test of the composite densified under different temperature.

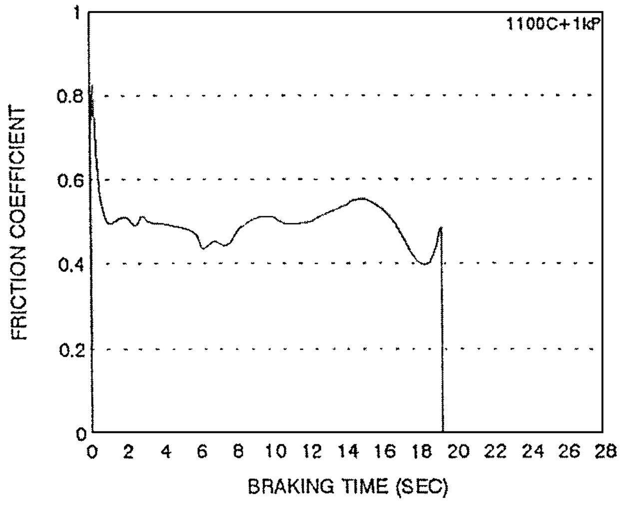


Figure 15 Variation of friction coefficient of specimen B during the first time braking test.

3.4.3. Comparison between PCVI and ICVI

For comparison, specimens densified through the ICVI process were also fabricated (specimen denoted as C + I). In the ICVI process, methane was thermal decomposed at 1000°C under the pressure of 75 torr for 24 hours. The average density of specimen C + I is 1.505 g/cm^3, which is compatible to the specimen C + 12KP (average density of 1.510 g/cm^3). However, the specimen C + 12KP has lower weight loss during braking test than specimen C + I, as shown in Fig. 16. When examining the worn surface, the woven structure on the surface of the specimen C + 12KP is not detectable, as shown in Fig. 17a; whereas the woven structure on the worn surface of specimen C + I, as depicted in Fig. 17c, can be clearly recognized. A more

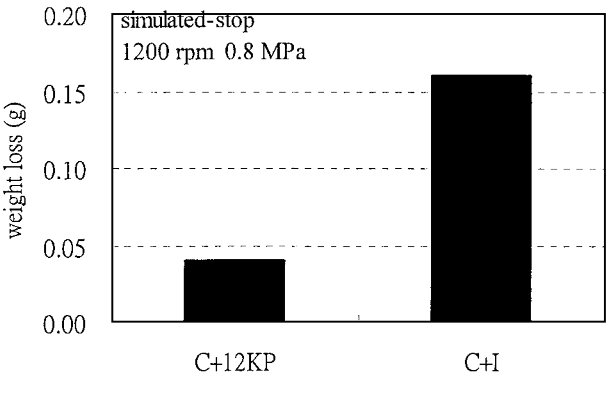


Figure 16 Comparison of weight loss during wear test for the C + 12KP and the isothermal specimens.

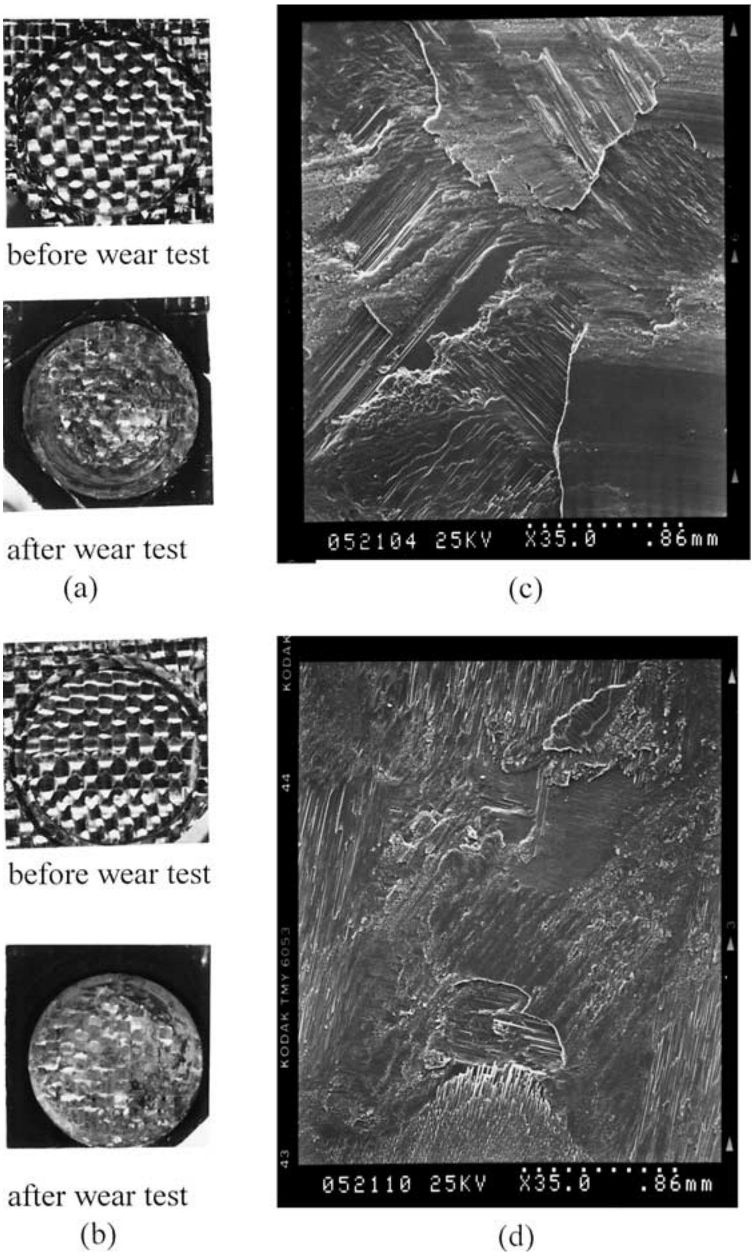


Figure 17 Surface morphology of (a) the C + 12KP specimen and (b) the C + I specimen.

uniform powder-compacted layer on the worn surface of specimen C + 12KP than that of specimen C + I can be observed, as shown in Fig. 17b and d. This is probably the reason why specimen C + 12KP has lower friction coefficient than that of specimen C + I.

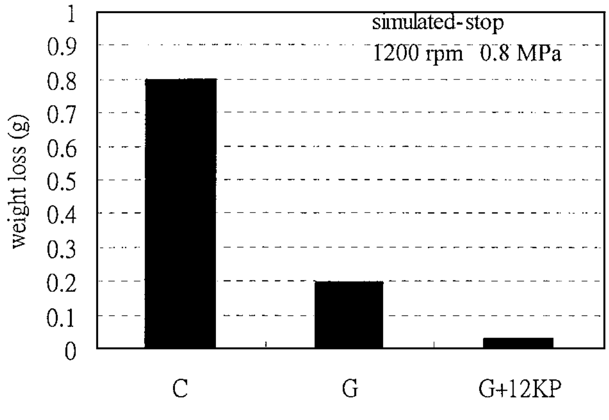


Figure 18 Weight loss of the carbonized (C), graphitized (G), and PCVI-densified graphitized C/C composites (G + 12KP) subjected to braking test.

3.4.4. Effect of graphitization on wear property

Fig. 18 depicts the weight loss of the carbonized, graphitized, and PCVI-densified graphitized C/C composites subjected to braking test. Lower weight loss of the graphitized than that of the carbonized composite is due to the transformation of turbostratic structure in carbonized composite to form preferred oriented carbon of the graphitized composite, which enhances the lubricating effect of the graphitized composites. This effect can be further enhanced the composite densified by PCVI under 12,000 cycles (density 1.624 g/cm3).

4. Conclusions

This paper demonstrated the densification of carbon/carbon composite by the PCVI process. Among the fabrication parameters been studied, the densification process under 1000°C with the pressure of 75 torr and holding period of 4.5 sec is the most proper parameter. Obvious densification efficiency is increased with pulse number up to 8000 cycles. On the other hand, ILSS is increased through the pulse number adopted in this study. This work also found that initial open porosity of the composite affects the densification result; the higher the open porosity, the higher the density of final densified composite. Furthermore, graphitization process has a very significantly obvious influence on fracture toughness and PCVI densification. Wear tests were performed for all the specimen fabricated under different pulse number, and the results showed that C/C composite densified through PCVI even only 1000 pulse cycles can improve the wear property very significant. Moreover, a comparison of wear performances of the composites densified by both the PCVI and ICVI is also made, it shows that composites densified by PCVI has a better performance in wear property than that of densified through ICVI. This study also found that graphitization treatment before PCVI densification process achieves a best wear performance in all specimens fabricated in this work.

Acknowledgements

The authors would like to thank the support of the work by the National Science Council, Taiwan under grant No. NSC-86-2216-E-007-007.

References

1. G. SAVAGE, "Carbon-Carbon Composites" (Chapman and Hall, London, 1993).
2. W. KOWBEL, J. WEBB and J. C. WITHERS, in "Evolving and Revolutionary Technologies for the New Millenium," 44th International SAMPE Symposium, edited by Leslie Jay Cohen, Jerome L. Bauer and William E. Davis, Vol. 44, no. 2 (1999).
3. J. W. HAGER, in Proceeding of the 1993 Conference on Processing, Fabrication and Applications of Advanced Composites, Long Beach, CA, 9–11 August 1993, p. 33.
4. J. D. CHEN, J. H. CHERN LIN, C. P. JU, *Wear* **193** (1996) 38.
5. J. D. CHEN and C. P. JU, *Carbon* **33**(1) (1995) 57.
6. K. J. LEE, J. H. CHERN LIN and C. P. JU, *ibid.* **35**(5) (1997) 613.
7. C. LHYMN and Y. LHYMN, *Advances in Polymer Technology* **9**(1) (1989) 33.
8. E. R. FRYE, *Nuclear Technology* **12** (1971) 93.
9. I. M. K. ISMAIL, M. M. ROSE and M. A. MAHOWALD, *Carbon* **29**(4/5) (1991) 575.
10. S. T. DIMITRIJEVIC, *ibid.* **29**(4/5) (1991) 605.
11. D. P. STINTON, A. J. CAPUTO and R. A. LOWDEN, *American Ceramic Society Bulletin* **65**(2) (1986) 347.
12. P. DUPEL, R. PAILLER and F. LANGLAIS, *J. Mater. Sci.* **29** (1994) 1341.
13. K. SUGIYAMA and T. KISHIDA, *ibid.* **31** (1996) 3661.

Received 11 July 2001
and accepted 29 March 2002