EFFECT OF BAMBOO CHARCOAL ADDITIVE ON WEAR PROPERTIES OF NANO-CARBON/CARBON COMPOSITES WITH BACTERIAL CELLULOSE

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Abstract

Bacterial Cellulose (BC) is one of the eco-friendly materials, and is synthesized by the acetic bacterium "Acetobacter xylinum". The fabrication method of Si-C/Carbon/Carbon composites (SiC/C/C composites) with BC and Bamboo Charcoal Powder (BCP) additive and their wear properties are investigated. Wear tests for SiC/C/C composites were conducted by using the pin-on-drum type tribology tester. From the experimental results, the coefficient of wear took the low values of 0.03-0.05 during the tests, and the specific factor of wear element loss is 4.09 - 6.52×10^{-10} mm^2/N. It is revealed that the SiC/C/C composites have excellent wear property in comparison with silicon nitride ceramics and/or DLC coating, and the carbonized BC microfibrils network and SiC additive from BCP could be contributed for low coefficient of wear properties.

1. Introduction

Bacterial Cellulose (BC) is a natural cellulose which is synthesized by the acetic bacterium "*Acetobacter xylinum*", known as "Nata de Coco" for diet foods. The fibrous structure of BC consists of three-dimensional non-woven network of microfibrils, which is held together by glucan chains and hydrogen bonding [1]. BC fibril is about 100 times thinner than that of plant cellulose, and Young's modulus of single BC fibre with diameters ranging from 35 to 90nm at a value of 78±17GPa. Therefore, BC composite materials could be effectively used as the high performance and/or functional components for various applications [2, 3].

The authors have already investigated the mechanical behavior of BC composites with sheet type and that with BC wad [4]. The BC composites of sheet type had a maximum value of Young's modulus at an optimum contents value of calcium carbonate ($CaCO_3$) and clay as reinforcement. Furthermore, the new method is developed by two of the authors, and it is called as "the Direct Impregnation Method (DIM)" [5]. Using the DIM, BC microfibrils network remains in the BC polymer composites. After burning the composites at high temperature, we had the carbonized BC fiber/polymer composites (nano-C/C composites) with nano-scale structure.

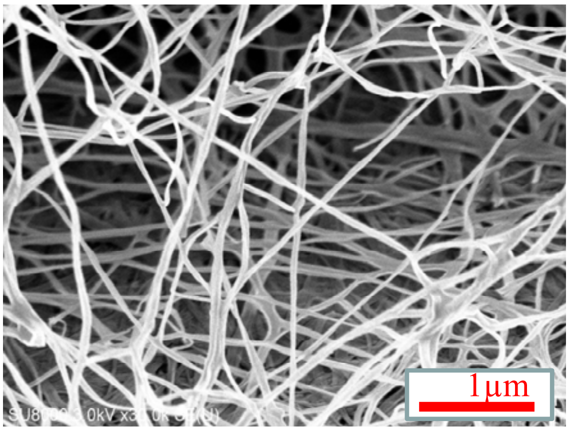


Figure 1. SEM photograph of BC microfibrils.

In this paper, the fabrication method of Si-C/Carbon/Carbon composites (SiC/C/C composites) with Bacterial Cellulose (BC) and Bamboo Charcoal Powder (BCP) additive and their wear properties are investigated. In order to examine the wear properties of nano-C/C composites and nano-SiC/C/C composites, wear tests were conducted by using the pin-on-drum type tribology tester under room condition and dry sliding condition. The effects of temperature condition of fabrication on the properties of nano-C/C composites are clarified, and three dimensional structure of nano-SiC/C/C composites with BCP are observed by using Scanning Electron Microscope (SEM) to examine the effect of BCP additive on the wear property.

2. Fabrication of nano-SiC/C/C composites with BC and BCP

2.1. Bacterial Cellulose as reinforcement

The BC is processed as an industrial waste in Japanese traditional vinegar maker. BC is a gel containing about 95% of water by weight, mainly due to its amorphous structure degree of polymerization of about 2000 - 6000 and the contents of nitrogen is about 0.2 - 0.4%. BC possesses an array of unique properties, including high crystallinity, high tensile strength, lightweight, high water absorption, good permeability, porosity, adjustable aperture and good biocompatibility. The fibrous structure of BC is characterized by a three-dimensional structure consisting of nano-scale microfibrils network. The dimensions of the microfibrils are in range of 2-4nm in thickness, 10-50nm in width and 1-9μm in length (Fig. 1).

2.2. Fabrication method of the nano-C/C composites

In order to fabricate composite materials with BC, the effective processing method is required for keeping three-dimensionally oriented BC microfibril networks of nano-scale. In using the BC as reinforcement, the processing is badly affected by the water in BC gel due to the uptake of water, especially in the case that the polymer resin is used as a matrix of composites. Therefore, we have developed a new method of phenol resin directly immersing into BC gel, called as the Direct Impregnation Method (DIM) [5].

By adding the alcohol of 50%V_f into the BC slurry with water, and mixing the resol type of phenolic resin, the water in BC slurry is replaced by the resin in the drying process. When the water is evaporated, the phenolic resin could penetrate into three dimensional BC microfibrils network of nano-scale at the same time. After taking this procedure, the mixture

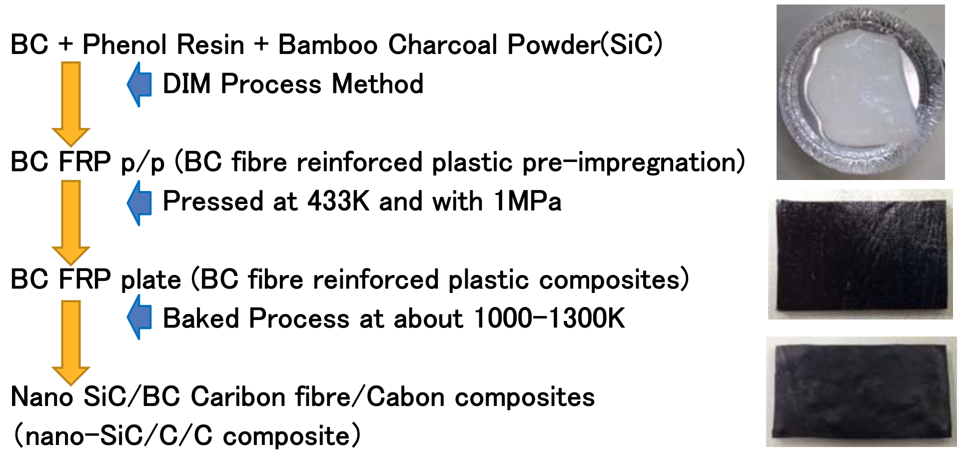


Figure 2. Fabrication method of nano-C/C composites and nano-SiC/C/C composites.

was air dried at room temperature for several days and hardened in order to get the BC FRP pre-impregnation (BC FRP p/p) of desired shape. BC FRP p/p was processed into the B stage, pressed at 433K (160˚C) and with 1MPa, and then we had transparent BC FRP plates of brown color.

The BC FRP plates were burned out in the inactive gas environment at various temperature; 973K (700˚C), 1073K (800˚C), 1173K (900˚C), 1273K (1000˚C), and 1373K (1100˚C) and the heating rate; 5K/hr, 10K/hr and 15K/hr. Finally we obtained a carbonized BC fibre /Phenol resin composite materials. BC microfibrils were changed into the carbon fibres of nano-scale, and the phenol resin of the matrix became the glassy carbon. It means that the composite is a kind of carbon/carbon composites with SiC, that is, “nano-C/C composites”.

2.3. Fabrication method of the nano-SiC/C/C composites with BCP

In order to fabricate nano-SiC/C/C composites, Bamboo Charcoal Powder (BCP) was used because the bamboo consist of a rich content of Si. The improved method must be required to have the mixture of BC and BCP in better condition. BC slurry was smoothed well by using the mixer. The Ball mixer mill could grind and homogenize small volume of BCP into efficiently fine powder down to the nano range by impact and friction in dry condition. In this case, the ratio of resin, BC and BCP is set at 1: 0.1: 0.05 by weight.

By adding the alcohol of 50%V_f into the smoothed wet BC slurry and fine BCP additive of nano scale, and then these materials were mixed well. Furthermore, mixing the resol type of phenolic resin, the phenolic resin could penetrate into the fine mixture of BC microfibrils and BCP fine powder of nano-scale in the drying process. After taking this treatment, the similar procedure to the nano-C/C composites were taken to get the SiC/BC FRP pre-impregnation (SiC/BC p/p). SiC/BC p/p was processed into the SiC/BC FRP plates which were burned out in the inactive gas environment at various temperature into the SiC/C/C composites.

3. Wear test for nano-C/C composites and nano-SiC/C/C composites

3.1. Wear tests for the composites

In order to examine the properties of the nano-C/C composites the wear tests were conducted by using the pin-on-drum type tribology tester (Fig. 3). The specimen of 3.5mm×3.5mm square was sliding on the surface of SUS304 drum of the surface roughness R_a 0.3 - 0.5. The

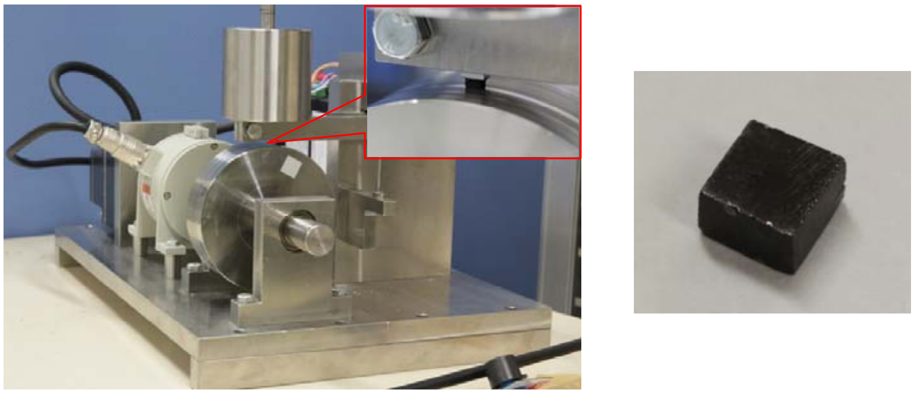


Figure 3. The pin-on-drum type tribology tester and test specimen of nano-SiC/C/C composites.

sliding conditions were as follows: sliding speed 1.5m/sec, sliding distance 130 km, and contact pressure 1MPa.

The factor of specific wear element loss f_w [mm^2/N] is given by the following equation;

$$f_w = W / (P \times L) \quad (1)$$

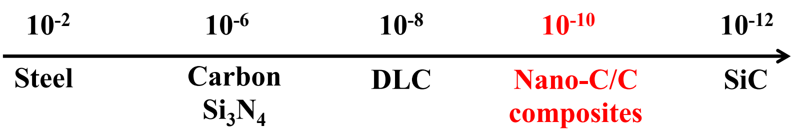
Here, W indicates the volume of wear [mm^3], P is the contact load [N] and the sliding distance L [m]. The coefficient of friction μ_c for the specimen were calculated by the following equation;

$$\mu_c = T / (P \times R) \quad (2)$$

where T is the torque change of drive monitored by torque sensor and R means the radius of the drum rotor.

3.2. Experimental results of Wear tests

According to wear tests, C/C composites have sufficiently low dynamic frictional coefficient μ_c and specific factor of wear element loss f_w, in the comparison with the value of silicon nitride (Si_3N_4) ceramics and Diamond-Like Carbon (DLC) coating etc. The μ_c took the low values of 0.13 - 0.22 during tests. The f_w are the range of 2.21 - 9.65×10^{-10} [mm^2/N]. Table 1 schematically shows the results of wear properties of nano-C/C composites. The results are precisely shown in Fig 4 to 6.



Materials	SiC	C	Nano-C/C composites	DLC
Friction coefficient	0.50	0.15	0.13-0.22	0.10

Table 1. Wear properties of nano-C/C composites in comparison with other engineering materials.

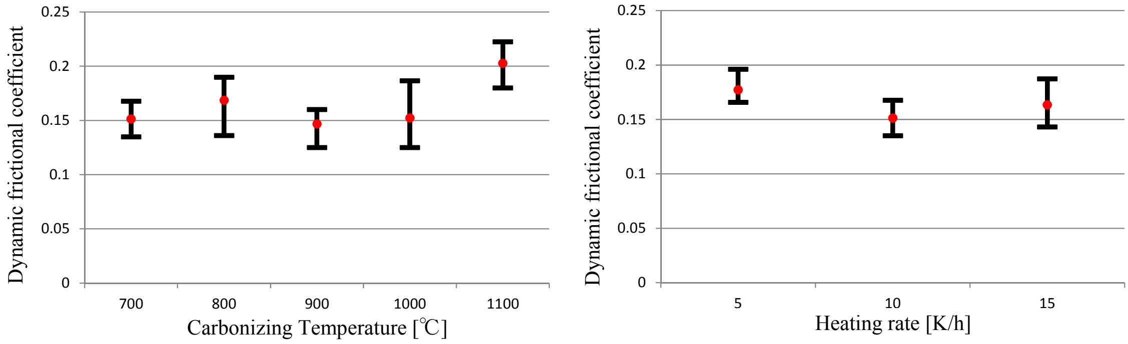


Figure 4. Change of dynamic frictional coefficient against carbonizing temperature and heating rate at 973K.

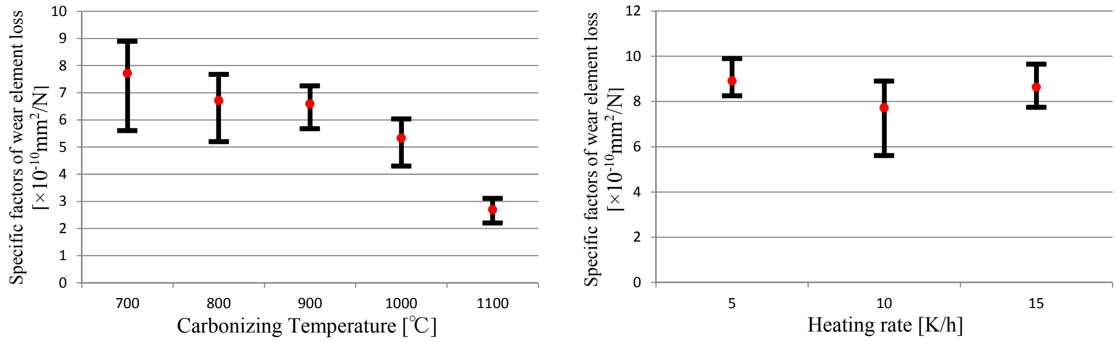


Figure 5. Change of specific factors of wear element loss against carbonizing temperature and heating rate at 973K.

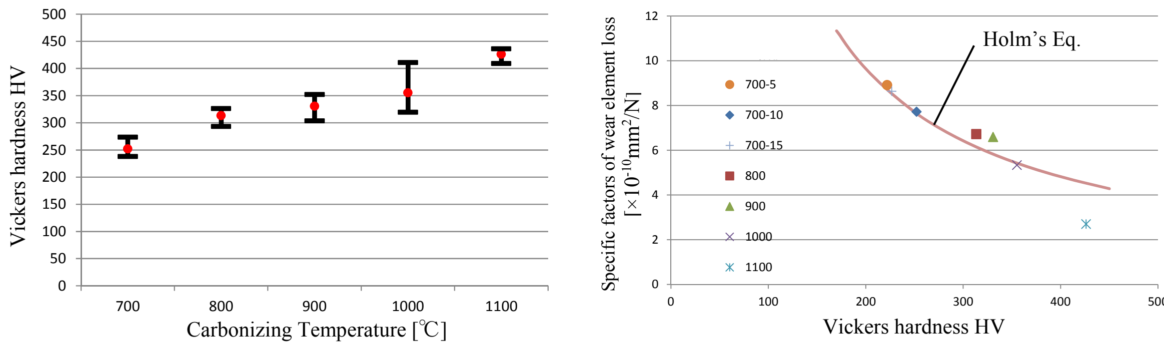


Figure 6. Change of Vickers hardness HV of nano-C/C composites against carbonizing temperature, and the relationship between specific factors of wear element loss and Vickers hardness HV.

Viewing Fig. 4 and 5, as increasing the carbonizing temperature, the specific factors of wear element loss decreases monotonically whether the dynamic frictional coefficient indicates the almost constant against carbonizing temperature. On the other hand, there are no large change in both properties against the change of heating rate at the carbonizing temperature of 973K.

It is noted that valid experimental results could not be obtained from the wear test due to low carbonizing temperature, internal voids, cracks and rough surface of the specimen carbonized at 773K(500°C).

Figure 6 shows the change of Vickers hardness HV of nano-C/C composites against carbonizing temperature, and the relationship between specific factors of wear element loss and Vickers hardness HV. Vickers hardness increases linearly as increasing the carbonizing temperature. Let us examine the Holm's equation;

$$W = k \times P \times L \ / H \quad (3)$$

where k indicates a value of coefficient and H shows the hardness. It can be seemed that the agreement between the values estimated by Holm's equation and the experimental ones are fairly good and the equation (3) is valid in the case of wear condition for C/C composites.

Table 2 and 3 show the experimental results of nano-C/C composites and nano-SiC/C/C composites with Bamboo Charcoal Powder, respectively. At the carbonizing temperature 973K, 1073K and 1173K, the values of wear properties for SiC/C/C composites with BCP took relatively lower than that of C/C composites whether the density indicates higher values. The SiC additive from BCP could be contributed for low coefficient of wear.

Temp.[K] (rate[K/h])	Specific factors of wear element loss [mm2/N]	Friction coefficient	Density [g/cm^3]	Vickers hardness[HV]
973(10)	7.72×10^{-10}	0.15	0.95	253.8
1073(10)	6.72×10^{-10}	0.15	1.10	313.0
1173(10)	6.59×10^{-10}	0.14	1.01	330.7

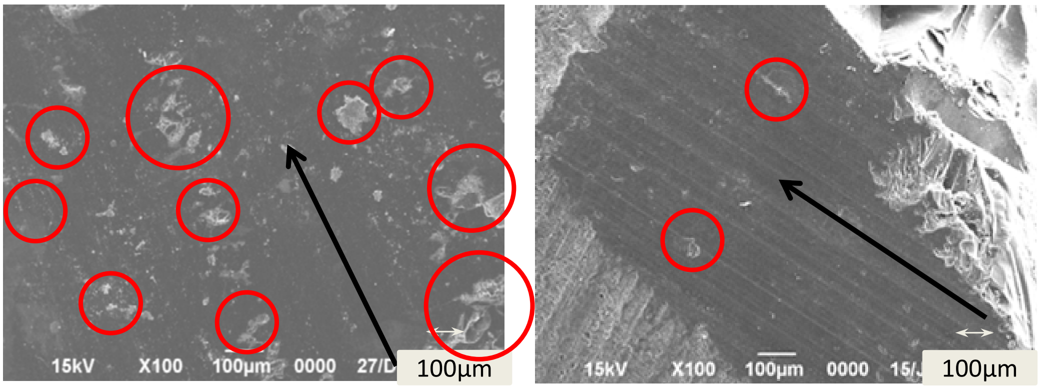
Table 2. Wear properties of nano-C/C composites.

Temp.[K] (rate[K/h])	Specific factors of wear element loss [mm2/N]	Friction coefficient	Density [g/cm^3]	Vickers hardness[HV]
973(10)	6.52×10^{-10}	0.03	1.24	299.0
1073(10)	4.09×10^{-10}	0.05	1.42	365.8
1173(10)	5.04×10^{-10}	0.03	1.34	380.2

Table 3. Wear properties of nano-SiC/C/C composites with BCP.

3.3. SEM observation of the specimens and consideration

Figure 7 shows SEM photograph for observation of sliding surface of C/C composites specimens observed at 100 magnification (a) at 1073K-10K/h and (b) at 1373K-10K/h after wear tests. In these figures, the arrow indicates the sliding direction in the wear test. Observing in Fig. 7(a), microcracks occurred at the sliding surface, propagating into the inside and then many small piece of the material were dropped off. On the other hand, it is seen from Fig. 7(b) that there is less drop off from the specimens at 1373K.



(a) at 1073K-10K/h

(b) at 1373K-10K/h

Figure 7. Sliding surface of C/C composites at 100 magnification (a) at 1073K-10K/h and (b) at 1373K-10K/h.

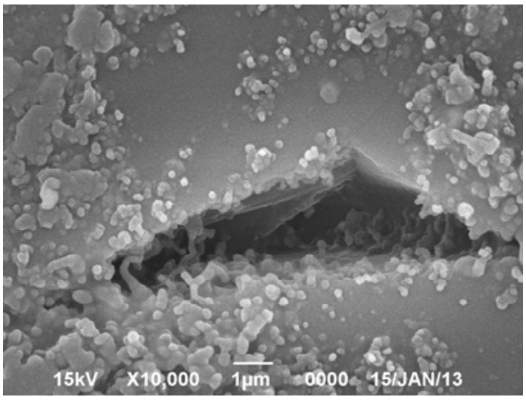
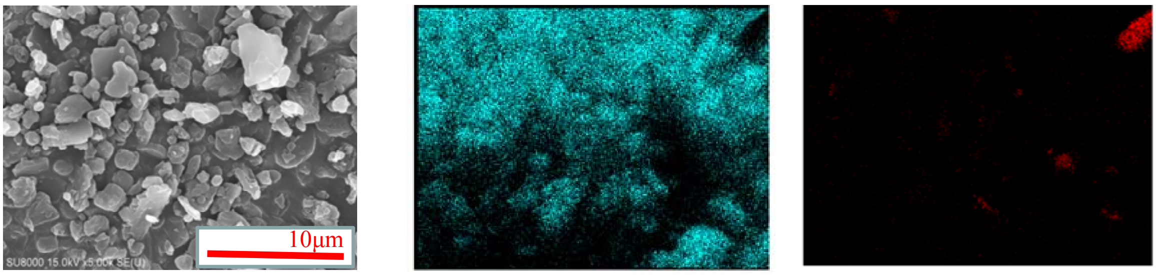
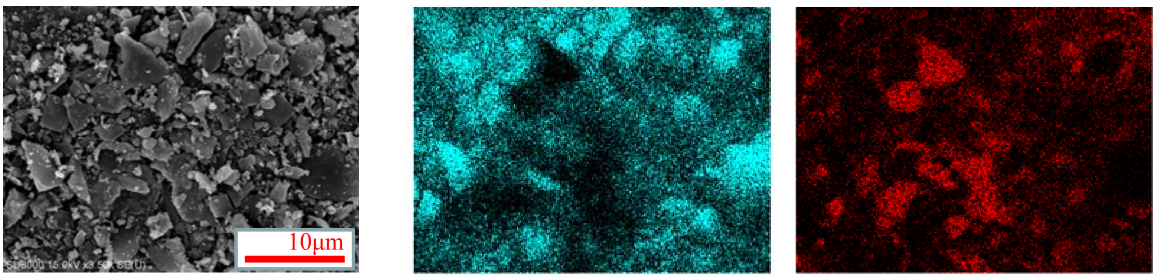


Figure 8. BC fibre bridging observed in a microcrack on sliding surface of C/C composites at ×10000.



(a) SEM photo at 973K(10K/h) Carbon image Iron image



(b) SEM photo at 1173K(10K/h) Carbon image Iron image

Figure 9. Wear element loss powder of SiC/C/C composites (a) at 973K(10K/h) and (b) at 1173K(10K/h).

Sliding surface of C/C composites is shown in Fig. 8 observed at 10000 magnification. It is easily observed the fibre bridging by carbonized BC fibres in the microcrack. When the wear element loses by sliding force in tests, the fracture pass was affected by fibre bridging of carbonized BC microfibrils, and large energy was absorbed during microcrack propagation.

Figure 9 shows SEM photographs for wear element loss powder of nano-SiC/C/C composites (a) at 973K(10K/h) and (b) at 1173K(10K/h). From Fig. 9(b) for SiC/C/C composites carbonized at 1173K(10K/h), you can easily see the fine powder of wear element loss in the photograph at left hand side, and the image of iron contents is detected over the observed area. It can be said that SiC/C/C composites has relatively high hardness and then, in the sliding on the SUS304 drum surface, the composites attack the drum surface aggressively. Therefore, the wear element loss powder of SiC/C/C composites consist of iron materials from the rotating drum surface made by SUS304. This phenomenon is only observed for the SiC/C/C composites burned at higher temperature over 1173K.

The BC microfibrils, which were combined together with the matrix of polymer, worked and had some effects on the higher value of the fracture toughness of BC composites, and then the specific factor of wear element becomes lower in tests. The SiC additive from BCP could be contributed for low coefficient of wear. It is found that these constituents contribute to extremely low values of the specific factor of wear element loss and the frictional coefficient.

4. Conclusions

As main conclusions, it was found that:

(1) A fabrication method of nano-C/C composites and nano-SiC/C/C composites with BCP, in which BC microfibril network of three dimensional structure and their bonding condition remain was successfully developed.

(2) The effect of carbonizing temperature and heating rate on the wear properties of C/C composites is clarified.

(2) For the SiC/C/C composites, the frictional coefficient took the low values of 0.03-0.05 during the tests, and the specific factor of wear element loss is $4.09 - 6.52\times10^{-10}$ mm^2/N. The SiC/C/C composites have excellent wear properties, and the carbonized BC fibres and SiC additive from BCP could be contributed for low coefficient of wear properties.

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