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Characterisation of wear particles from biomedical carbon/carbon composites with different preforms in hip joint simulator

ZHANG Lei-lei[1], LI He-jun[1], ZHANG Shou-yang[1], LU Jin-hua[1], ZHANG Yu-lei[1], ZHAO Xue-ni[1], GU Cai-ge[1], ZENG Xie-rong[2]

1. State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China;
2. Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen 518060, China

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Abstract: A hip joint simulator was employed to predict the clinical wear behaviour of carbon/carbon (C/C) composites with needled carbon cloth preform and carbon felt preform. Wear particles generated from the two kinds of C/C composites were isolated and characterised by the size distribution and morphology. The evolvement of wear particles in the hip joint simulator was proposed. The results show that the wear particles from two kinds of C/C composites have a size ranging from submicron to tens of micrometers. The wear particles have various morphologies including broken fiber, fragment fiber, slice pyrolytic carbon and spherical pyrolytic carbon. C/C composites with needled carbon cloth preforms have larger size range and more broken fiber particles and slice pyrolytic carbon particles in comparison with C/C composites with carbon felt preforms. The evolvement of pyrolytic carbon particles is caused by surface regularization, whereas, the evolvement of carbon fiber particles is related to stress direction in the hip joint simulator.

Key words: carbon/carbon composites; particle shape; bio-tribology; hip joint

1 Introduction

Carbon/carbon (C/C) composites consisting of carbon fiber reinforcement embedded in carbon matrix are playing an important role in engineering and biomedical applications [1−5]. They are porous materials and posses excellent mechanical properties and stability. Their physical properties, such as density, porosity and elastic modulus, are advantages for hard tissue surgery because these parameters can be tailored to be close to those of the bone [6−8]. Therefore, C/C composites are being developed for bone substitution, bone fixation, joint replacement and osteosynthesis, especially for hip joint arthroplasty [9−11]. However, the further application of C/C composites in hard tissue surgery is limited by the release of carbon particles into the surrounding tissue.

Some researchers have investigated the morphology, surface structure and physicochemical properties of wear particles of C/C composites. But they always focused on the C/C composites used for brake technology [12−14]. Only a few reports focused on the application in hip arthroplasty. PESAKOVA et al [15] have reported that carbon particles were located both inside the compact bone and in the lymphatic node. LEWANDOWSKA-SZUMIEL et al [10] have confirmed that the carbon particles were observed only in the tissue immediately adjacent to the implants without inflammatory reaction, foreign body cell formation, or the presence of wear particles in lymph nodes and spleen. BACAKOVA et al [2] have found that no particles were released spontaneously into the cell culture medium during the cell culture process. Only when the C/C composites were treated with incubation and washing in trypsin solution, the wear particles were released with a size of 0.5−10 μm. HOWLING et al [16] have found that the wear particles of C/C composites have significantly less cytotoxicity for L929 fibroblasts than wear particles of metal. They also found that C/C composite wear particles did not significantly stimulate TNF-α production at a particle volume to cell number ratio of 80:1, indicating

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Corresponding author: LI He-jun Tel: +86-29-88495004; Fax: +86-29-88495764; E-mail: lihejun@nwpu.edu.cn
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that the wear particles had a low osteolytic potential.

Hip joint simulators are developed to predict in vivo wear behavior of hip joint replacements by means of laboratory tests. In these tests, the load, lubrication, motion and geometries of the articulation are more similar to those found clinically than those in conventional wear test devices [17,18]. In this work, a hip joint simulator was employed to generate the wear particles to predict the characteristics of wear particles from hip joints fabricated of biomedical C/C composites in vivo. The size and morphology of the wear particles were investigated and the mechanism by which the wear particles were generated was proposed.

2 Experimental

2.1 Sample preparation

Two kinds of preforms includling needled carbon cloth preform and carbon felt preform were used in this research. The needled carbon cloth preforms were fabricated by stacking carbon cloth which consisted of continuous long polyacrylonitrile based carbon fibers. They are pierced with polyacrylonitrile based carbon fiber bundles in *Z* direction, as shown in Fig. 1(a). These preforms are 0.80 g/cm^3 in density and 46.5% in fiber volume fraction. The carbon felt preforms were prepared by hot pressing of the chopped short polyacrylonitrile based carbon fiber infiltrated with the phenolic resin. The schematic diagram of the preforms is shown in Fig. 1(b). These preforms have a density of 0.18 g/cm^3 and a fiber volume fraction of 10.5%.

C/C composites were prepared by densification of two preforms using a thermal gradient chemical vapor infiltration (TCVI) process using methane as the precursors with a deposition temperature of 1 173−1 473 K. The details of TCVI process were given in Ref. [19]. The resulting C/C composites with needled carbon cloth preforms and carbon felt preforms are named as C_c and C_f, respectively. The properties of the two kinds of C/C composites are listed in Table 1. Besides, as a precondition to begin a biotribological test, the biocompatibilities of the two C/C composites were tested by cell culture experiment in vitro. The results show that both two C/C composites are suitable for biomedical use with no cytotoxicity.

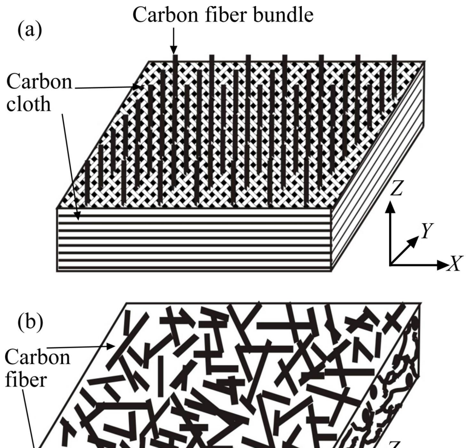

Fig. 1 Schematic diagrams of preform structures of C/C composites: (a) Needled carbon cloth preform; (b) Carbon felt preform

Table 1 Properties of C/C composites with different preforms

C/C composite	Preform	Microstructure of pyrolytic carbon	Density/ (g·cm^{-3})	Porosity/ %
C_c	Needled carbon cloth	Smooth laminar	1.75	7.90
C_f	Carbon felt	Smooth laminar	1.72	8.10

2.2 Wear test

For the wear test, the C_c was machined to spherical femoral heads and acetabular cups (Fig. 2), forming the friction pair of C_c/C_c. The C_f was also machined to spherical femoral heads and acetabular cups with the same size to the C_c, forming the friction pair of C_f/C_f. The surface of both C_c/C_c and C_f/C_f friction pairs was polished by SiC paper and diamond paste to a surface roughness of R_a=0.2−0.5 μm. Then, they were dried in air after being cleaned ultrasonically in turn by acetone, alcohol and deionized water.

The wear tests were performed on a hip joint simulator produced by China University of Mining and Technology. The schematic diagrams of the hip joint simulator and the detailed information of wear test were given elsewhere [11].

2.3 Isolation and characterization of wear particles

After the wear test, the bovine serum lubricants from the wear tests were collected and wear particles generated were isolated from the bovine serum lubricants using the method described by TIPPER et al [20]. Briefly, 50 mL of the bovine serum lubricants were diluted with 50 mL deionized water and centrifuged at 2000*g* for 30 min at room temperature. The supernatant was discarded and 12 mol/L potassium hydroxide was added and maintained at 333 K for 96 h with continuous stirring. Then, the resulting solution was centrifuged at 2000*g* for 30 min. After discarding the supernatant, the deionized water was added with centrifugation at 2000*g* for 30 min. Finally, the wear particles were obtained by washing for three times with deionized water and lyophilizing.

The obtained wear particles were diluted with deionized water and ultrasonic dispersion to analyze the

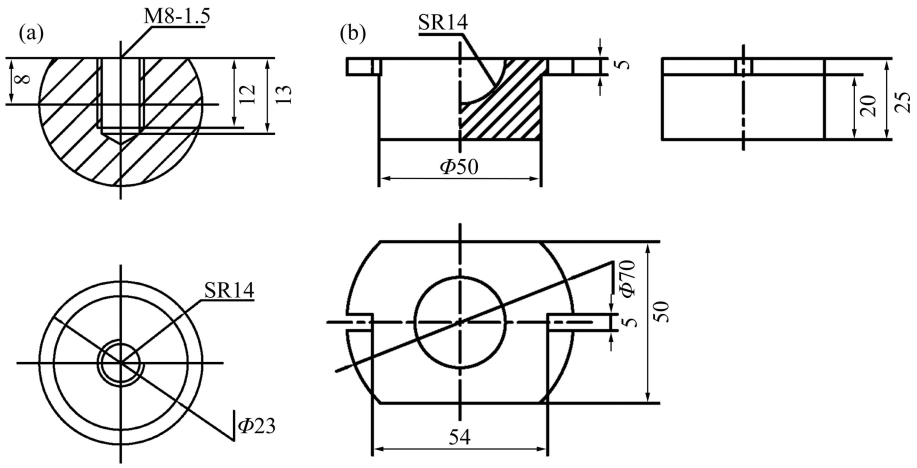

Fig. 2 Dimensions of femoral head (a) and acetabular cup (b) in hip joint simulator (Unit: mm)

size distribution by laser particle size analyzer (BN-01S). And the morphologies of particles coated with gold were observation by scanning electron microscopy (SUPRA55).

3 Results and discussion

3.1 Size distribution of wear particles

The size distributions of the wear particles from C/C composites with different preforms are shown in Fig. 3. Three regions are identified during analyzing the particle size. Small particle size less than 5 μm is designated as region S. Medium particle size ranging from 5 μm to 30 μm is designated as region M. Large particle size above 30 μm is designated as region L. For the C_c/C_c friction pairs, the wear particles have a size ranging from 0.3 μm to 93.9 μm. The peak value of the size distribution is at 6.1 μm. The percentage of particles in the regions S, M and L are 24.8%, 67.7% and 7.5%, respectively. For the C_f/C_f friction pairs, the size of the wear particles is from 0.2 μm to 60.9 μm with a peak value of 5.1 μm. The percentage of the particles in regions S, M and L are 36.4%, 59.8% and 3.8%, respectively. A comparison of the frequency distribution between the particle size for C_c/C_c and C_f/C_f friction pairs shows that the former has a larger range of size distribution with more particles in regions L and M and less particles in region S.

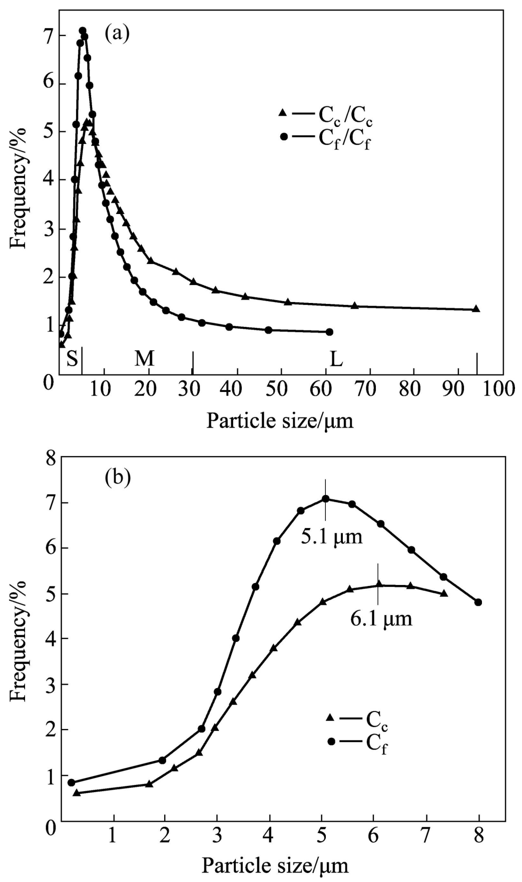

Fig. 3 Size distributions of wear particles from C/C composites with different preforms in hip joint simulator

3.2 Morphologies of wear particles

Figure 4 shows the SEM images of the wear particles from C/C composites with different preforms in the hip joint simulator. The wear particles of both C_c/C_c and C_f/C_f friction pairs have various morphologies, such as integrated fiber, broken fiber, fragment fiber, slice pyrolytic carbon and spherical pyrolytic carbon. The C_c/C_c friction pairs have more broken fiber particles with a large size compared with the C_f/C_f friction pairs, which is caused by the different preform structures. The C_c/C_c friction pairs have a preform made up of carbon cloth with long carbon fibers, and volume fraction of the carbon fibers is 46.5%. Whereas, C_f/C_f friction pairs have a preform composed of short carbon fibers with a volume fraction of 10.5%. C_c/C_c friction pairs have more and longer carbon fibers than C_f/C_f friction pairs, leading to the more broken fiber particles found for C_c/C_c friction pairs.

Figure 5 shows the magnified images of the wear

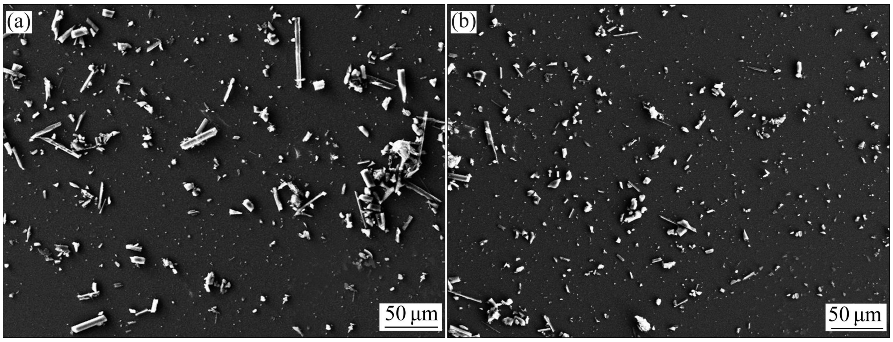

Fig. 4 SEM images of wear particles from C/C composites with different performs: (a) Needled carbon cloth preform; (b) Carbon felt preform

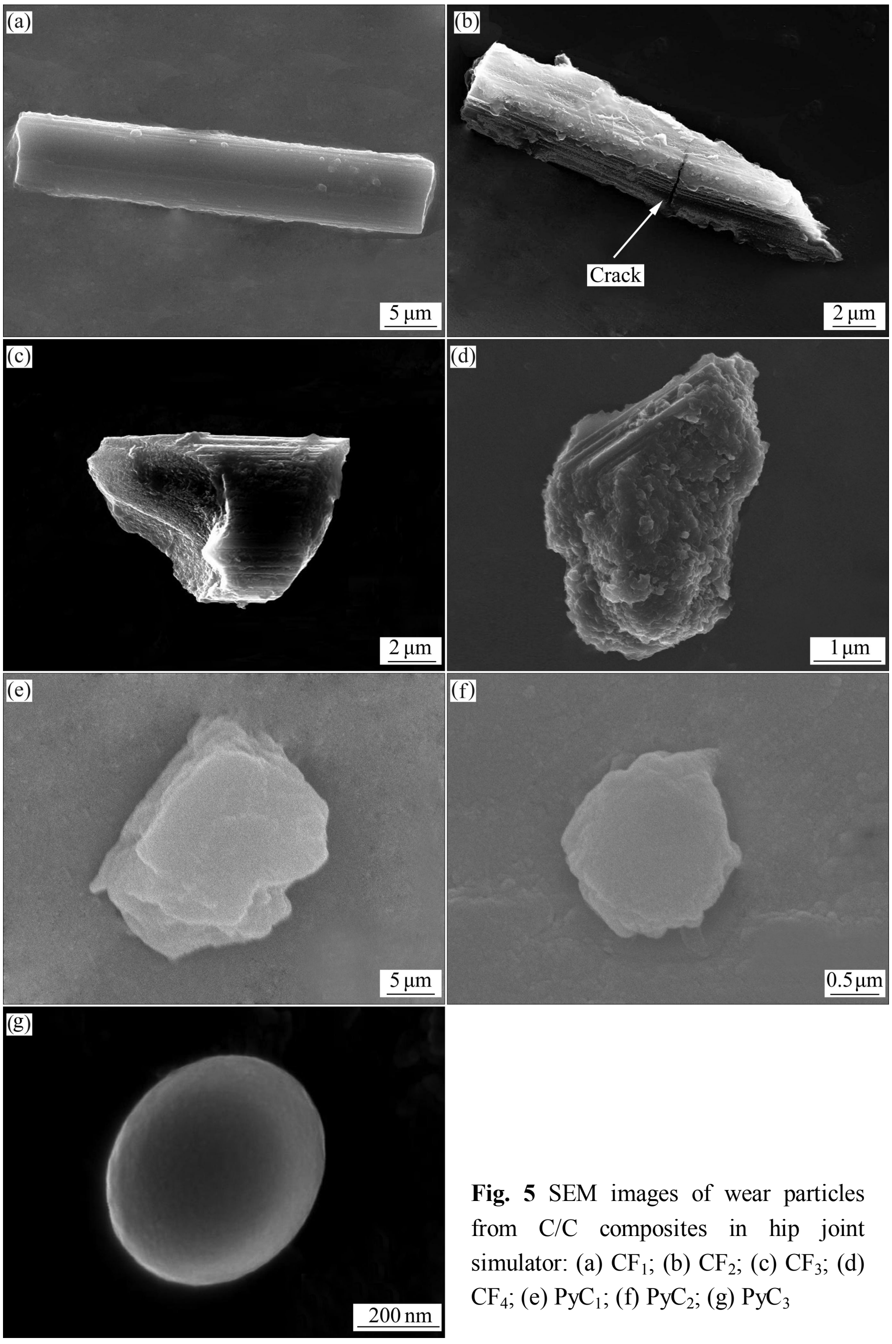

Fig. 5 SEM images of wear particles from C/C composites in hip joint simulator: (a) CF_1; (b) CF_2; (c) CF_3; (d) CF_4; (e) PyC_1; (f) PyC_2; (g) PyC_3

particles from C/C composites in the hip joint simulator. According to the reinforcement phase and matrix phase in C/C composites, the wear particles are classified into carbon fiber particles (Figs. 5(a)−(d)) and pyrolytic carbon particles (Figs. 5(e)−(g)). The carbon fiber particles have four kinds of morphologies, namely CF_1, CF_2, CF_3 and CF_4. The CF_1 particles show integrated fiber morphology with a smooth surface in the axial direction and regular fracture in the radial direction (Fig. 5(a)). The particles have an axial length of tens of micrometers and a radial length equal to the diameter of the carbon fiber. The sizes of these particles are the largest among all kinds of wear particles. The CF_2 particles have broken fiber morphology with an irregular fracture and some cracks in the radial direction (Fig. 5(b)). The particles have length of 10−50 μm in the axial direction. The particles retain the morphologies of the carbon fibers with an axial damage at the end of the particles. The CF_3 particles only retain part of fiber morphology with a short radial and axial length (Fig. 5(c)). The CF_4 particles are fragment particles with a size from submicron to several micrometers, showing an irregular morphology (Fig. 5(d)). The pyrolytic carbon particles have three kinds of morphologies denoted by PyC_1, PyC_2 and PyC_3. The PyC_1 particles show blocky or slice morphologies with a complicated shape and an irregular boundary (Fig. 5(e)). The PyC_2 particles retain the shape of the PyC_1 particles, but having a smooth surface and a regular boundary (Fig. 5(f)). The size of the PyC_2 particles is about several micrometers. The PyC_3 particles are spherical in shape with a size of submicron, the smallest size among all kinds of wear particles (Fig. 5(g)).

3.3 Evolvement of wear particles

Based on the analysis of the size and morphology of the wear particles of C/C composites with different preforms, the evolvement process of the wear particles in the hip joint simulator was proposed. The evolvement processes of carbon fiber particles and pyrolytic carbon particles are shown in Fig. 6. For the evolvement of carbon fiber particles (Fig. 6(a)), the CF_1 particles are originally formed by the rupture and remove of carbon fibers from the worn surface during the wear process. These particles have a largest size among all kinds of particles. According to the weakest-link theory, the probability of failure of carbon fibers is described by the Weibull distribution [21]:

$$P(\sigma) = 1 - \exp[-L(\frac{\sigma}{\sigma_0})^{\beta}]$$

where $P(\sigma)$ is the fracture probability of the carbon fibers, L is the length of the carbon fibers, σ is the given strength, σ_0 is the scale parameter, and β is the shape

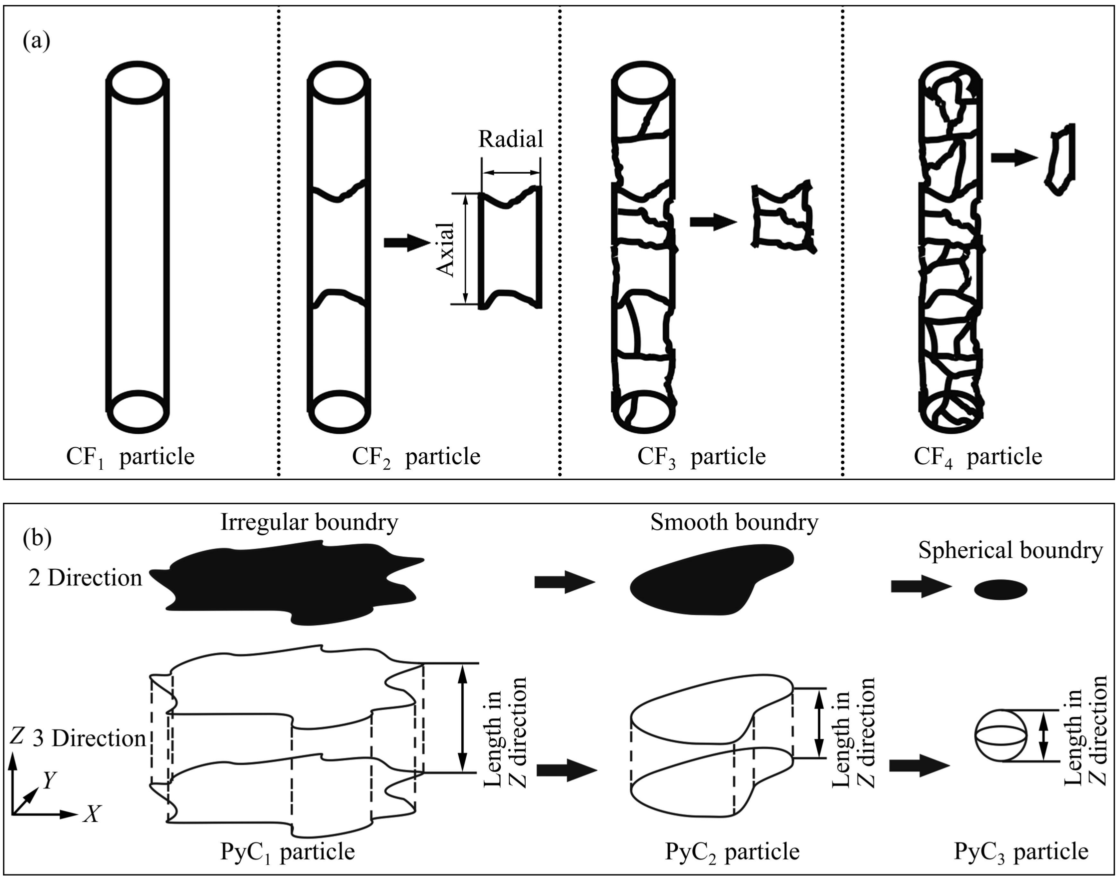

Fig. 6 Evolvement of carbon fiber particles (a) and pyrolytic carbon particles (b) of C/C composites in hip joint simulator

parameter. Both of σ_0 and β keep constant for a certain materials.

The failure probability strongly depends on the length of the carbon fibers (L) regarded. The particles with a larger length are easy to be destroyed. Considering that the axial length of CF_1 particles is larger than the radial length, the crack and rupture are easy to form in the axial direction, leading to the decrease of the axial length. Thus, the CF_2 particles are formed. As the length in the axial direction decreases to the similar value of the radial length, the damage of the particles occurs both in the radial and axial directions because there is no orientation advantages for the particles, resulting in the formation of CF_3 particles. Some of the particles are damaged in multi-directions with the fiber shape being lost, forming the CF_4 particles with irregular shape. For the evolvement of the pyrolytic carbon particles (Fig. 6(b)), the pyrolytic carbon originally removed from the worn surface has blocky or slices morphologies with a complicated boundary, forming PyC_1 particles. The PyC_1 particles have a length of 10 μm in the X and Y directions with a length of a few micrometers in Z direction. The particles are sheared and crushed between the femoral head and acetabular cups with their size being decreased. The decrease is more obvious for the X and Y directions than the Z direction due to the fact that the original length of the former is larger than the later. And also, the boundary of particles is gradually smooth caused by the cross-path movement of the hip joint simulator, forming the PyC_2 particles. As the length of the particles in X and Y directions decreases to the similar value in Z direction and the surface of the particles is more smooth, the particles will reach a relatively steady state, forming PyC_3 particles with a spherical morphology.

4 Conclusions

1) The wear particles of C/C composites with needled carbon cloth perform and carbon felt perform in a hip joint simulator have a size ranging from submicron to tens of micrometers.

2) The wear particles of C/C composites show various morphologies including broken fiber, fragment fiber, slice pyrolytic carbon and spherical pyrolytic carbon.

3) C/C composites with needled carbon cloth performs have a larger size range and more broken fiber particles and slice pyrolytic carbon particles in comparison with C/C composites with carbon felt performs.

4) The evolvement of pyrolytic carbon particles is caused by surface regularization, whereas the evolvement of carbon fiber particles is related to stress direction in the hip joint simulator.

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不同预制体炭/炭复合材料在髋关节模拟试验机中的磨损颗粒表征

张磊磊[1]，李贺军[1]，张守阳[1]，卢锦花[1]，张雨雷[1]，赵雪妮[1]，谷彩阁[1]，曾燮榕[2]

1. 西北工业大学 凝固技术国家重点实验室，西安 710072；
2. 深圳大学 深圳市特种功能材料重点实验室，深圳 518060

摘　要：采用髋关节模拟试验机检测穿刺碳布预制体和碳毡预制体炭/炭复合材料的磨损行为。分离提取产生的磨损颗粒，检测颗粒形貌和尺寸分布并提出颗粒的演化过程。结果表明：炭/炭复合材料磨损颗粒的尺寸分布在亚微米至数十微米之间，颗粒形貌呈现破损纤维状、纤维碎片状、片状和球状。穿刺碳布预制体炭/炭复合材料比碳毡预制体炭/炭复合材料的磨损颗粒尺寸分布范围更广泛，磨损颗粒中的破损碳纤维状和片状形貌较多。热解碳颗粒的演变主要是其表面的规则化过程，而碳纤维颗粒的演变主要与髋关节模拟试验机提供的应力方向有关。

关键词：炭/炭复合材料；颗粒形状；生物摩擦；髋关节

(Edited by LI Yan-hong)