DOI: 10.3901/CJME.2014.0616.111, available online at www.springerlink.com; www.cjmenet.com; www.cjmenet.com.cn

Dry Friction and Wear Characteristics of Impregnated Graphite in a Corrosive Environment

JIA Qian[1, *], YUAN Xiaoyang[1], ZHANG Guoyuan[2], DONG Guangneng[1], and ZHAO Weigang[3]

1 *Key Laboratory of Education Ministry for Modem Design and Rotor-bearing System, Xi'an Jiaotong University, Xi'an 710049, China*
2 *School of Electromechanical Engineering, Xidian University, Xi'an 710072, China*
3 *Xi'an Aerospace Propulsion Institute, China Aerospace Science and Technology Corporation, Xi'an 710100, China*

Received April 18, 2013; revised March 19, 2014; accepted June 16, 2014

Abstract: Tribological properties of impregnated graphite are greatly influenced by preparation technology and working conditions and it's highly susceptible to corrosion environmental impacts, but the experimental research about it are few. In this paper, three kinds of impregnated graphite samples are prepared with different degree of graphitization, the tribological properties of these samples in the dry friction environment and in a corrosive environment are analyzed and contrasted. The tribo-test results show that the friction coefficient of samples is reduced and the amount of wear of samples increase when the graphitization degree of samples increases in dry friction condition. While in a corrosive environment (samples are soaked N_2O_4), the friction coefficient and amount of wear are changed little if the graphitization degree of samples are low. If the degree of graphitization increase, the friction coefficient and amount of wear of samples increase too, the amount of wear is 2 to 3 times as the samples tested in the non-corrosive environment under *pv* value of 30 MPa • m/s. The impregnated graphite, which friction coefficient is stable and graphitization degree is in mid level, such #2, is more appropriate to have a work in the corrosion conditions. In this paper, preparation and tribological properties especially in corrosive environment of the impregnated graphite is studied, the research conclusion can provide an experimental and theoretical basis for the selection and process improvement of graphite materials, and also provide some important design parameters for contact seal works in a corrosive environment.

Keywords: corrosive environment, impregnated graphite, graphitization, dry friction, coefficient of friction, amount of wear

1 Introduction

Contacting mechanical face seal is a common form of shaft end seal for liquid rocket engine turbopumps[1–2]. Currently, contacting mechanical seal pairs are made up of combinations of soft & hard materials, with rotor materials of stainless steel or hard alloy, and stator materials of graphite[3–4]. The performance of graphite stators is affected by the process parameters and structure parameters of the graphite. Many researchers have studied the preparation and properties of carbon graphite materials for different application environment. The process for impregnating carbon–graphite with copper-based alloys and the structure and properties of the resulting composites have been described by GULEVSKII, et al[5]. SAVCHENKO, et al[6], have improved the graphite manufacturing process by rolling the expanded graphite, when impregnated with boron oxide, has greater tensile strength. LIU, et al[7], recently developed a manufacturing process to obtain an activated carbon in the form of a thin layer, and analyzed the effect of impregnation ratio and temperature to the porosity. Graphite-impregnated pads formed by nano-graphite particles impregnated with polyurethane were found to significantly reduce pad repair rate by 40% and improve pad longevity[8]. A process of impregnating graphite has also been developed for manufacturing the mechanical grinding wheels, test results showing that not only produces better surface roughness and lower grinding temperature and grinding forces but also lower wheel consumption[9]. GUAN, et al[4], studied the frictional properties of a multilayer graphite-like coating for mechanical seals in aquatic environment, which gained the friction coefficients of the coating and the wear rate by the pin-disc test.

ROE developed a finite element model to predict the response of exfoliated graphite to stress[10–11]. HIRAI, et al[12], obtained the friction and wear characteristics of antimony carbon graphite mechanical seal materials used in rotary joints in tests under dry friction, water and steam environments. ROE, et al[13], measured the friction and wear of seals against steel sliders in a controlled atmosphere. In recent years, with the rapid development of high-speed turbopump seal technology, the needs to

* Corresponding author. E-mail: jiaqian@stu.xjtu.edu.cn
Supported by National Natural Science Foundation of China (Grant No. 51175408)

improve seal life and reduce wear rate and coefficient of friction have increased. In order to adapt to this trend, Researchers have studied the seal face coating technology and proposed DLC coating to improve wear resistance[13–14]. A new non-contact mechanical seal structure has been proposed and been development[15–16]. The result from related studies shows that improvement of the existing carbon graphite preparation process is necessary in order to meet the requirements for high-speed turbopumps and other extreme environments.

This paper intends to research the preparation process and dry friction and wear characteristics (e.g., coefficient of friction, wear rate) of impregnated graphite in a corrosive environment. The purpose of this article is to understand the performance of this material for use as seal material in aerospace engineering better. The results will provide the experimental basis for designing high-reliability and high-stability mechanical seals.

2 Preparation of Graphite Material

2.1 Manufacturing process of impregnated graphite

Graphite is a material which has good self-lubricating properties, temperature resistance and corrosion resistance. It is particularly suitable in environments where lubricant is difficult to use, including corrosive or high temperature environments. As a porous material, graphite has drawbacks of poor air-tightness and low material strength. Therefore, before using it for seals, graphite must be immersion treated. The impregnated reinforcing of graphite is usually carried out under high temperature and pressure. The impregnated material determines the impregnation process to be used, the difficulty and the cost of production of the sealing material. A traditional process of manufacturing carbon graphite material, as shown in Fig. l, includes mixing, forming, calcination and graphitization, and dipping.

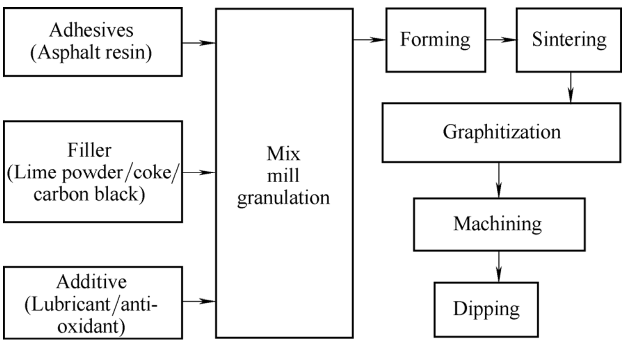


Fig. 1. Flow diagram of the typical manufacturing process for impregnated graphite

In general, the dipping materials of impregnated graphite can selectable phenolic resin, carbon, antimony, silver, and babbitt so on. In this paper impregnated graphite dipping with phenolic resin.

Because of the special conditions in this paper, such as high temperature and strong corrosion, graphite should be denser, a second impregnation process is needed. Graphite material for this study was produced according to the process shown in Fig. 2. The secondary impregnation process includes total roughing, quality inspection, impregnation, curing, rough inspection, airtight inspection and finished product inspection.

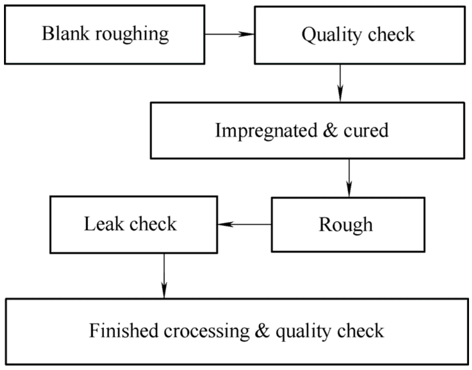


Fig. 2. Flow diagram of the secondary impregnation process for graphite used in seals

Graphite material in this study was impregnated with a phenolic resin using an impregnation temperature of 60 °C and resin curing temperature of 180 °C. The microscopic parameters of density, open porosity, and degree of graphitization are controlled during manufacturing. The material's density depends on the bulk density and firing conditions of the raw graphite, the temperature of the impregnation process and the curing temperature of the resin. The degree of graphitization is mainly related to the firing temperature of the raw graphite. Three kinds of samples are prepared for test named as #1, #2 and #3 with differences in firing temperature as shown in Table 1. The preparation process route for the samples, included mixing, molding, roasting and dipping.

Table 1. Preparation process parameters of the three graphite samples

Sample No.	Material formulations	Firing temperature T / ℃
#1	77% of coke, 8% carbon	1000
#2	black, 10% earthy graphite	1500
#3	powder, 5% iron oxide red	3000

2.2 Physical parameters of samples

Mechanical seal rings and test samples were prepared, as shown in Fig. 3. Test samples included graphite pins and metal plate, where the material of the pins and stationary ring were the same. The plate and snap ring were both made of the same stainless steel material. The pin as shown in Fig. 3(a) is made of graphite, used for the friction and wear experiment. Fig. 3(b) shows the mechanical seal rotary ring, is made of 9Cr18. Fig. 3(b) shows the mechanical seal stationary ring, the material of its friction surface is impregnated graphite.

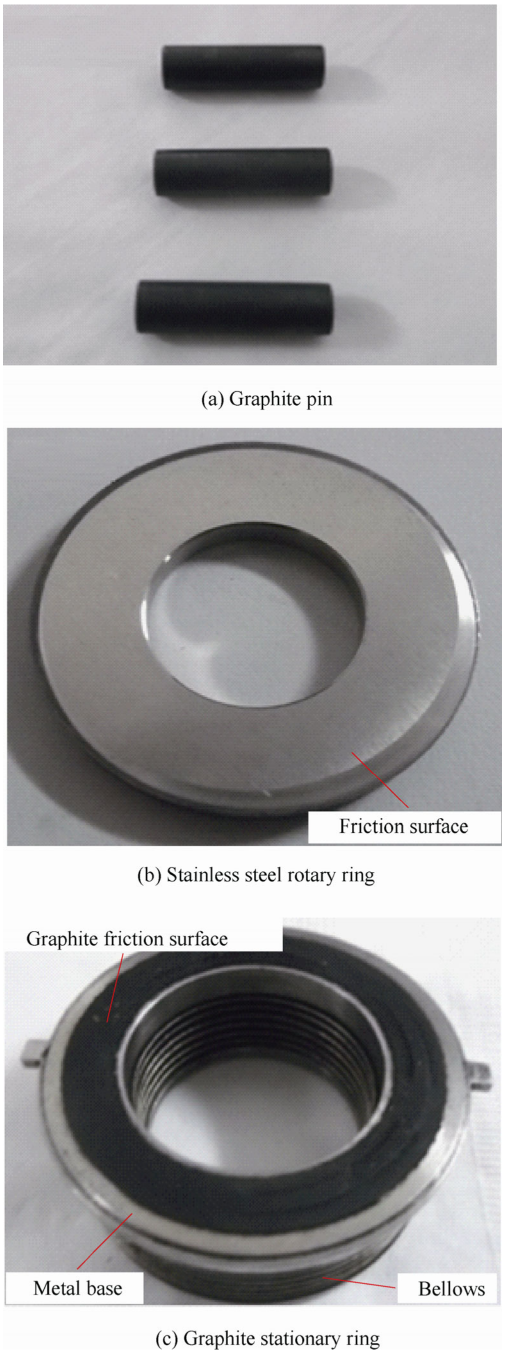


Fig. 3. Graphite pin stainless steel plate and graphite stationary ring of mechanical seals

The physical parameters of the graphite pins are listed in Table 2. Open-cell porosity and product volume ratio were determined according to the standard “JB/T8133.15-1999, electric carbon products chemical and physical properties test methods porosity”. This standard is used for the quantitative analysis of materials using boiled openings porosity of open porosity, indicating the effect of resin impregnated. Degree of graphitization refers to the amount of graphite crystalline growth upon heating of a carbon-containing material, which determines the hardness of the graphite material and the film lubrication performance. This was determined using the standard “JB/T4220-1999, artificial graphite lattice parameter determination method”.

Table 2. Physical performance parameters of samples

Physical parameter	#1 graphite	#2 graphite	#3 graphite
Shore hardness HB/HBW	93.4	91.5	80.8
Compressive strength RM/MPa	216.11	205.45	179.40
Flexural strength σ_{bc}/MPa	78.20	76.46	55.71
Bulk density $\rho/(\mathrm{g \cdot cm^{-3}})$	1.904	1.943	1.995
Open-cell porosity P_O/%	0.481	0.286	0.169
Degree of graphitization G/%	6–14	40–44	80–85
Linear expansion coefficient when 500℃ $\alpha_l/(10^{-6} \cdot ℃^{-1})$	7.578	8.226	6.282
Thermal conductivity in 0–500 ℃ $\lambda/(\mathrm{Wm \cdot K^{-1}})$	36.08	50.33	45.54

2.3 Preparation of the impregnated graphite in the corrosive environment

The graphite seal ring tested here must be effective in containing liquid N_2O_4, a rocket engine propellant. Because of its strong corrosivity and volatility, liquid N_2O_4 is difficult to directly use in machine etching friction experiments. Mechanical seal friction tribological tests fall into two categories, lubrication test and dry friction test. Static and dynamic characteristics of seal are obtained by the lubrication test. In the condition of lubrication, water is instead of lubricants N_2O_4, because both of them have similar viscosity values. Friction coefficient and wear amount are obtained by the dry friction test. Wear occurs mainly in the condition of dry friction. In this case, the friction coefficient of seals is higher than that under the condition of liquid lubrication. N_2O_4 can corrodes phenolic resin, take samples immersion in N_2O_4 then carry on the tribo-tests can assess the impact of corrosion to the samples and do not damage the testing machine.

In order to simulate the class of seal ring applications relevant for aerospace equipment conditions, therefore, immersed the impregnated graphite samplescan in N_2O_4 solution for 4 h before each experiment. The immersion medium was water and N_2O_4 in a ratio of 1:1.2, similar to actual use conditions.

3 Test Methods

Three tribological properties of the graphite samples were investigated: the coefficient of friction, wear and the transfer film.

3.1 Acquisition of the coefficient of friction

The equipment used to quantify coefficient of friction is the UMT-2 multifunctional tribo-tests machine. The rotating module of UMT-2 is used for tribo-test in this study, the pin and disc as the friction pair. The material of pin is graphite, $\Phi6\times18$ mm in size. The material of disk is 9Cr18, $\Phi40\times5$ mm in size. 9Cr18 is also the material of mechanical seal rotary ring. The disk is fixed on the work bench and connected to the motor. During testing, the pin was held stationary and the disk is rotated by a motor, as depicted in Fig. 4. The force sensor monitors the load force N and the level of the friction force F are converted them into an output signal during the work. The friction coefficient is obtained by the computer automatically, according to the formula $\mu=F/N$. The rotating line speed of UMT-2 is 0 to 2500 r/min and load range is 5 N to 150 N. Surface contact is dry friction in tests, line speed v=1 m/s, radius of gyration r=10 mm; these and other test parameters are shown in Table 3.

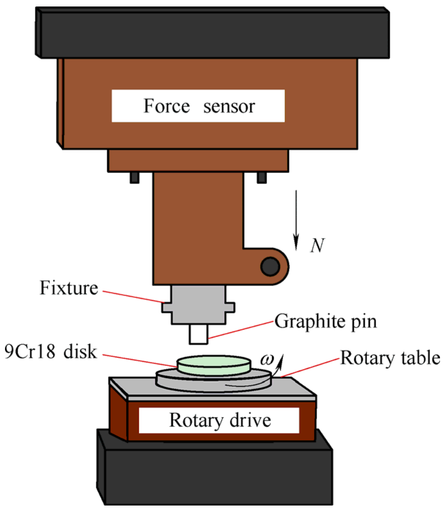


Fig. 4. UMT-2 tribo-tests experiment

Table 3. Tribo-tests parameters

pv/(MPa • m • s^{-1})	Pressure P/MPa	Load N/N
10	10.00	31.42
20	20.00	62.83
30	30.00	94.25
35	35.00	109.96

3.2 Determination of wear

In the tests, wear is considered as the amount of change in the volume of material, the symbols of it is W_V and it is shown in Eq. (1):

$$W_V=\frac{\Delta G}{d}, \tag{1}$$

where W_V indicates the amount of wear in material volume (cm^3), ΔG is the material wear quality (g), d is bulk density (g/cm^3). The quality of wear is weigh by an electronic balance, it accuracy up to 0.1 mg.

3.3 Transfer film analysis

The differences in abrasion resistance in the test samples are analyzed by visualizing the transfer film of graphite, using scanning electron microscopy jsm-64601v. The magnification of the electron micrographs is 3000, sample is the disks after tribo-test under pv=30 MPa • m/s. The micrograph allows the inspection of the samples' surface topography.

4 Results of Dry Friction Experiments

4.1 Coefficient of friction results

Fig. 5 and Table 4 show the coefficients of friction of the three samples under different pv conditions. The coefficient of friction decreased with the increase in degree of graphitization under the dry friction conditions. With an increase of pv value, the coefficient of is reduced. In particular, when pv is decreased from 35 to 10 MPa • m/s, the coefficient of friction of the #1 graphite material is reduced by 31.5%, by 9.6% in #2, and by 14.3% in #3.

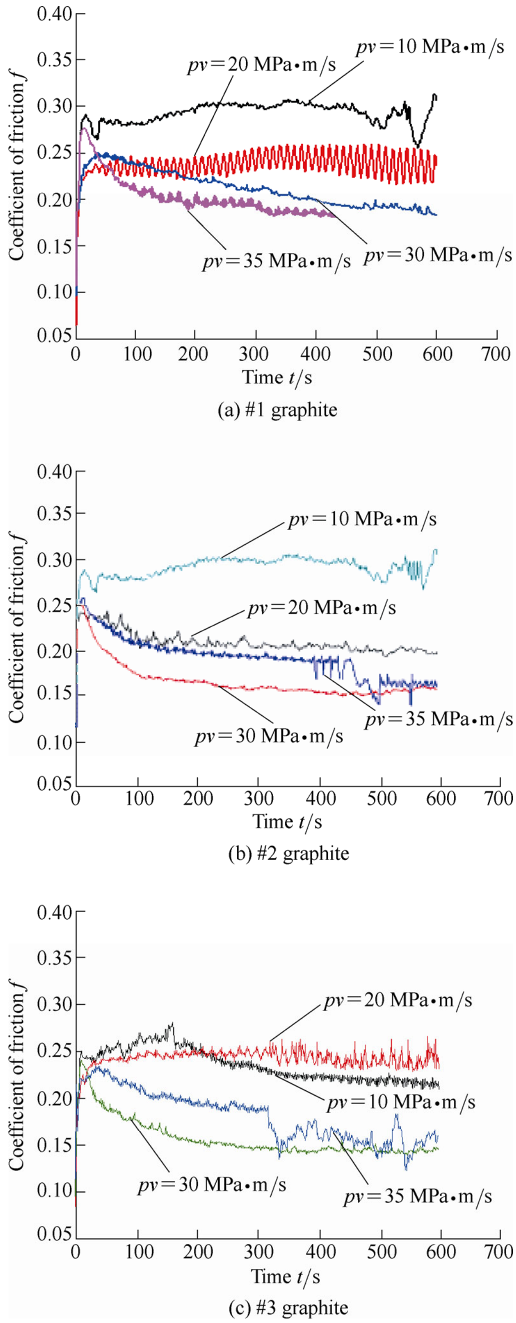


Fig. 5. Curve of the coefficients of friction from three materials in different pv conditions

Table 4. Results of friction characteristic testing for graphite materials under different *pv* conditions

pv/(MPa • m • s^{-1})	Friction coefficient f		
	#1 graphite	#2 graphite	#3 graphite
10	0.295	0.237	0.210
20	0.245	0.215	0.208
30	0.226	0.203	0.200
35	0.204	0.193	0.180

In summary, the coefficient of friction is less affects by the *pv* changes if the degree of graphitization are high.

4.2 Wear test results

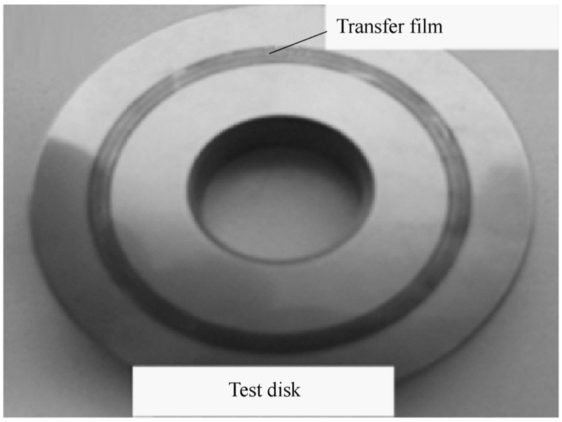
The condition of wear test is pv=30 MPa • m/s and test time t=20 min. The amount of wear is the amount of graphite volume change before and after test, with average volume wear in three experiments shown in Table 5. As can be seen in the table, the wear increased with increasing degree of graphitization in the samples. This is likely because a greater degree of graphitization produces a more complete graphite hexagonal layer sheet structure under shear stress, leading to easier shedding.

Table 5. Wear characteristics of graphite materials under *pv*=30 MPa/ms

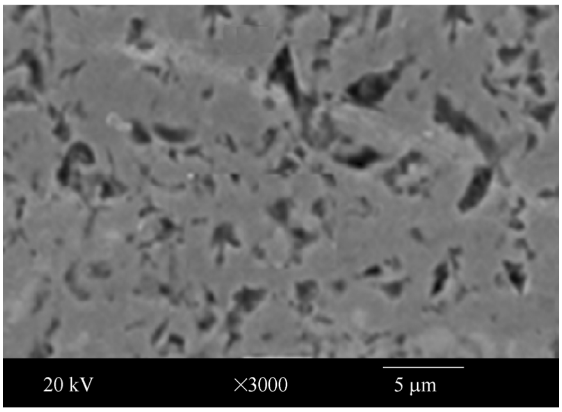
pv/(MPa • m • s^{-1})	Average volume of abrasive volume W_V/mm^3		
	#1 graphite	#2 graphite	#3 graphite
30	0.26	0.27	0.42

4.3 Analysis of SEM micrographs

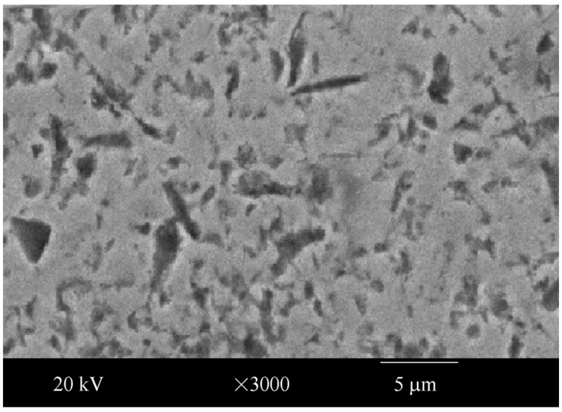
The Shore hardness of graphite is generally 100 or less, it is far less than the number of 9Cr18. Because of friction, the tested surfaces of metal disks will accumulate a layer of graphite transfer film as shown in Fig. 6(a). The black areas are transfer film in Fig. 6(b)–Fig. 6(d). As can be seen from the figure, comparison of three samples, #3 has a maximum transfer film, transfer film amount of #1 and #2 is quite. The amount of transfer is proportional to the amount of wear and inversely proportional to the coefficient of friction.



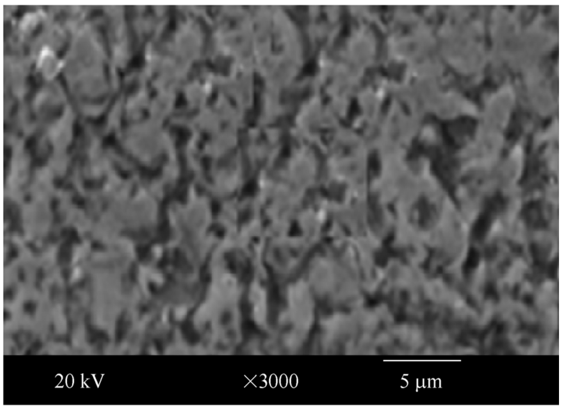
(a) Test disk



(b) #1 graphite



(c) #2 graphite



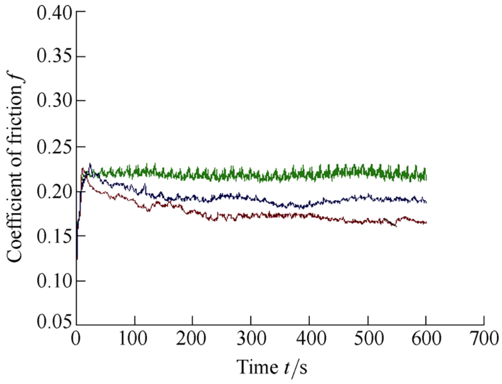
(d) #3 graphite

Fig. 6. SEM micrographs of transfer films

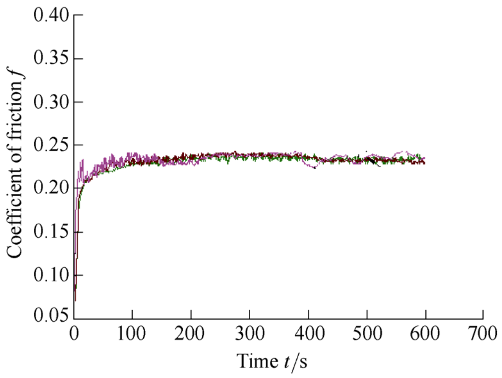
5 Results of Experiments in the Corrosive Environment

5.1 Coefficient of friction results

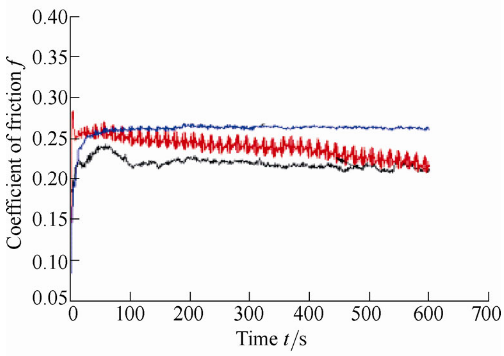
Results of coefficient of friction testing in a corrosive environment at a representative *pv* value of 30 MPa • m/s are shown in Fig. 7. The mean coefficient of friction values obtained from three replicate experiments in the corrosive environment are described in Table 6. Contrast to dry friction environment, the coefficients of friction is increase when tested in the corrosive environment, if the degree of graphitization of sample is increased. Because of the corrosion damage to the resin, the porosity of the material increased, producing rapid declines in the antifriction properties of the material.



(a) #1 graphite



(b) #2 graphite



(c) #3 graphite

Fig. 7. Curves of the coefficients of friction from test materials after soaking medium in a corrosive environment

Table 6. Coefficients of friction in the corrosive environment

pv/(MPa • m • s^{-1})	Coefficient of friction f		
	#1 Graphite	#2 Graphite	#3 Graphite
30	0.205	0.223	0.262

Compared to results for unetched samples tested at pv=30 MPa • m/s, the coefficient of friction for graphite #1 was reduced 9%, for #2 was increased 10%, and for #3 was increased 31%.

5.2 Wear testing results

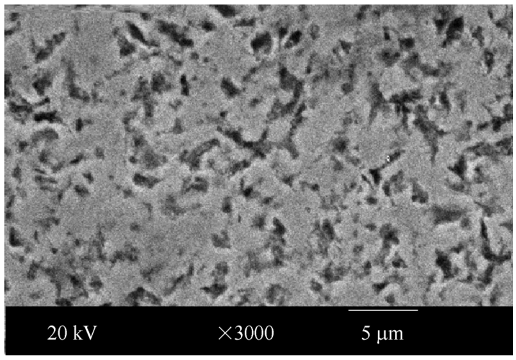
Table 7 shows the wear characteristics of the samples test in corrosive environments, with pv=30 MPa • m/s. When the degree of graphitization was greater, the wear was increased; in the corrosive environment, the wear was increased about 1 to 3 times that seen in the dry friction environment. In particular, compared with the non-corrosive condition at the same pv, wear volume of #1 graphite increased 115%, of #2 graphite increased 215%, and #3 graphite increased 298%.

Table 7. Abrasive volume of samples under the corrosive environment

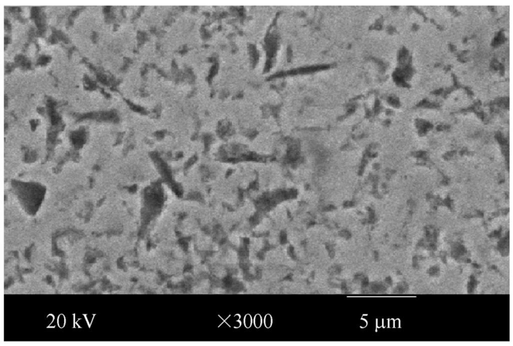
pv/(MPa • m • s^{-1})	Average volume of abrasive W_V/mm^3		
	#1 Graphite	#2 Graphite	#3 Graphite
30	0.56	0.85	1.67

5.3 Analysis of SEM micrographs

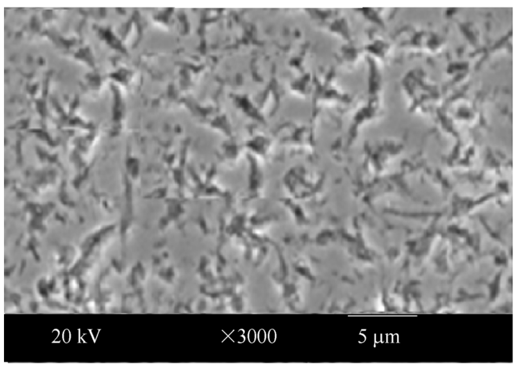
Fig. 8 shows the electron micrographs of disks after tested in the corrosive environment. The transfer film of #1 graphite is most and distributed evenly, and that of #2 graphite is intermediate between #1 and #3, Consistent with the amount of wear measured. However, a large amount of wear does not necessarily lead to more transfer film.



(a) #1 graphite



(b) #2 graphite



(c) #3 graphite

Fig. 8. SEM micrograph of transfer films on test disks treated in a corrosive environment

6 Conclusions

(1) In the dry friction condition, an increased degree of graphitization leads to reduced coefficient of friction and increased wear of impregnated graphite samples. The amount of transfer is proportional to the amount of wear and inversely proportional to the coefficient of friction.

(2) In a N_2O_4 corrosive environment, coefficient of friction and wear of samples are both increased when the degree of graphitization of samples has an increase, friction coefficient and wear of samples changes little when the sample has low degree of graphitization.

(3) In a N_2O_4 corrosive environment, the amount of wear is 2 to 3 times as the samples are test in the non-corrosive environment under *pv* value of 30 MPa • m/s. However, a large amount of wear does not necessarily lead to more transfer film.

(4) The tribological properties of samples shows that the impregnated graphite which friction coefficient stable and graphitization degree in mid level, such #2, is more appropriate to have a work in the corrosion conditions.

References

[1] ZHANG Guoyuan, YUAN Xiaoyang, ZHAO Weigang, et al. Theoretical and experimental approach of separation speed of spiral groove face seals[J]. *Chinese Journal of Mechanical Engineering*, 2008, 44(8): 55–60. (in Chinese)

[2] YUAN Xiaoyang, ZHANG Guoyuan, ZHAO Weigang, et al. Theoretical and experimental approach for the characteristics of water-lubricated, high-speed double spiral-groove face seals[C]// *STLE/ASME International Joint Tribology Conference, IJTC 2006*, October 23–October 25, American Society of Mechanical Engineers, San Antonio, TX, United states, 2006: 362–369.

[3] WANG Jianlei, JIA Qian, YUAN XiaoyangYuan, et al. Experimental study on friction and wear behaviour of amorphous carbon coatings for mechanical seals in cryogenic environment[J]. *Applied Surface Science*, 2012, 258(24): 9531–9535.

[4] GUAN X., WANG L. The tribological performances of multilayer graphite-like carbon (GLC) coatings sliding against polymers for mechanical seals in water environments[J]. *Tribology Letters*, 2012, 47(1): 67–78.

[5] GULEVSKII V A, ANTIPOV V I, KOLMAKOV A G, et al. Designing of copper-based alloys for the impregnation of carbon-graphite materials[J]. *Russian Metallurgy (Metally)*, 2012(3): 258–261.

[6] SAVCHENKO D V, SERDAN A A, MOROZOV V A, et al. Improvement of the oxidation stability and the mechanical properties of flexible graphite foil by boron oxide impregnation[J]. *New Carbon Materials*, 2012, 27(1): 12–18.

[7] LIU C, CHEN Z, CHEN H, et al. Preparation of expanded graphite-based composites by one step impregnation[J]. *Journal of Wuhan University of Technology, Materials Science Edition*, 2011, 26(2): 253–256.

[8] TSAI M Y, YAN L W. Characteristics of chemical mechanical polishing using graphite impregnated pad[J]. *International Journal of Machine Tools and Manufacture*, 2010, 50(12): 1031–1037.

[9] TSAI M Y, JIAN S X. Development of a micro-graphite impregnated grinding wheel[J]. *International Journal of Machine Tools and Manufacture*, 2012, 56: 94–101.

[10] ROE M. Performance prediction of exfoliated graphite seals: 2. A theoretical basis for its optimisation[J]. *Sealing Technology*, 2009(6): 7–9.

[11] ROE M, TORRANCE A. Performance prediction of exfoliated graphite seals: 1. Determination of parameters and verification of model[J]. *Sealing Technology*, 2008, 2008(4): 6–13.

[12] HIRANI H, GOILKAR S. Formation of transfer layer and its effect on friction and wear of carbon-graphite face seal under dry, water and steam environments[J]. *Wear*, 2009, 266(11–12): 1141–1154.

[13] ROE M, TORRANCE A. The surface failure and wear of graphite seals[J]. *Tribology International*, 2008, 41(11): 1002–1008.

[14] ZHANG Guoyuan, YUAN Xiaoyang, DONG Guangneng, et al. The tribological behavior of Ni-Cu-Ag-based PVD coatings for hybrid bearings under different lubrication conditions[J]. *Tribology International*, 2010, 43(1–2): 197–201.

[15] ZHANG Guoyuan, ZHAO Weigang, YAN Xiutian, et al. Experimental study for water-lubricated high-speed controllable spiral-groove face seals[J]. *Journal of Aerospace Power*, 2011, 26(4): 947–953.

[16] ZHANG Guoyuan, ZHAO Weigang, YAN Xiutian, et al. A theoretical and experimental study on characteristics of water-lubricated double spiral-grooved seals[J]. *Tribology Transactions*, 2011, 54(3): 362–369.

Biographical notes

JIA Qian, born in 1981, is currently a PhD candidate at *Key Laboratory of Education Ministry for Modem Design and Rotor-bearing System, Xi'an Jiaotong University, China*. He received his bachelor degree from *Chang'an University, China*, in 2004. His research interests include mechanical design and tribology.
Tel: +86-29-82669152; E-mail: jiaqian@stu.xjtu.edu.cn

YUAN Xiaoyang, born in 1963, is currently a professor and a PhD candidate supervisor at engineer at *Xi'an Jiaotong University, China*. His research interests include mechanical design and tribology.
E-mail: xyyuan@mail.xjtu.edu.cn

ZHANG Guoyuan, born in 1979, is currently an associate professor at *School of Electromechanical Engineering, Xidian University, China*. His research interests include mechanical kinetics and tribology.
E-mail: gyzhang@nwpu.edu.cn

DONG Guangneng, born in 1965, is currently a professor and a PhD candidate supervisor at *Xi'an Jiaotong University, China*. His research interests include mechanical design and tribology.
E-mail: donggn@mail.xjtu.edu.cn

ZHAO Weigang, born in 1977, is currently a senior engineer at *Xi'an Aerospace Propulsion Institute, China Aerospace Science and Technology Corporation, China.*
E-mail: yxxzwg@yahoo.com.cn