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Tribological Properties of High Temperature Oxidation Film on Bearing Steel Sliding Against Copper-Graphite

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Keywords：Cu/C, oxide film, water lubrication, liquid rocket turbo pump, mechanical seal.

ABSTRACT

Copper-graphite (Cu/C) materials are used as stationary ring in the mechanical contacted seals of liquid rocket turbo pumps due to their advantages including high thermal conductivity, excellent anti-corrosion and lubrication behaviors. However, the Cu/C stationary ring is subjected to severe wear at startup stage under the real working condition. To solve the problem, this study puts forward a method to modify the surface of the mating pair by high temperature oxidation films. The oxidation films were prepared under different temperatures and the tribological tests were conducted to verify the lubrication effect of the films. Furthermore, the influence of applied load and surface roughness on the tribological behaviors was investigated. In general, the oxidation film played a major role in improving tribological behavior between bearing steel and Cu/C under water lubrication condition.

INTRODUCTION

The mechanical contacted seal is the necessary component of liquid rocket engine turbo pump which works under the severe conditions including high speed, high pressure, high vibration and sealing medium (Wang et al, 2012; Zhang et al, 2008). This kind of mechanical contacted seal is composed of stationary ring and the rotating ring and this pair adopts the hard-soft pattern as shown in Fig.1. Copper-graphite (Cu/C) composite made by adding graphite as a solid lubricant to the copper material is the main material of stationary ring. And the main material of rotating ring is bearing steel. Cu/C combines excellent properties of copper and graphite so that it has high thermal conductivity and good lubrication properties (Grandin et al, 2018). However, for the actual working condition, Cu/C stationary ring showed serious wear during the startup stage of the engine machine. The wear of the Cu/C stationary ring is bound to cause the leakage of the seal medium in the engine turbo pump, and thus giving rise to some safety risks. Therefore, it is urgent to enhance the anti-wear ability of Cu/C materials when sliding against steels and improve the working reliability of the mechanical seals in engine turbo pump.

In recent years, many efforts have been made to reduce the friction and wear of metal materials. Preparing oxide layer on the steel is one of the effective methods. it is found that the Cr bearing steel can form nanoscale iron composite oxides, and these substances contain Cr and Si in inner rust, which is used to protect the surface and prevent further re-oxidation (Levitin et al, 1988; Cote et al, 2000; Nishimura et al, 2015). Also, the oxidation film has the function of reducing friction and wear when friction pairs rub against each other (Guan et al, 2016). The dense, passivated Cr_2O_3 and SiO_x on the surface of the bearing steel is known as a type of ceramic material (Dong et al, 2013; Luo et al, 2009; Yang et al, 1999), which is often used as a protective layer for wearing parts (He et al, 2001; Sourty et al, 2003). Considering the lubrication property of oxide film, the friction between Cu/C and oxide bearing steel surface is worthy of further study.

In this study, we present a facile method of utilizing the oxide film on bearing steel to reduce the wear of Cu/C. Oxidized surfaces containing Cr_2O_3 were formed by high temperature oxidation of bearing steel. Tribological experiments were conducted under dry condition and water lubrication condition. The experimental results demonstrate that this oxidized film is able to improve tribological behaviors compared to the original surface especially

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under water lubrication condition. Furthermore, the lubrication mechanisms of the oxidized film were discussed.

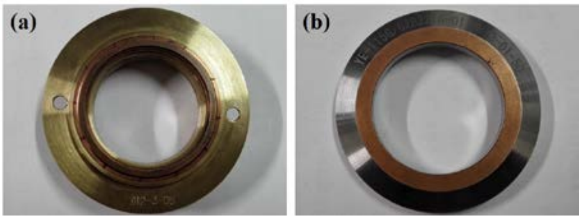


Fig. 1. (a) the image of Cu/C stationary ring, (b)the image of steel rotating ring

EXPERIMENTS

Materials

Cu/C (hardness 50 HV with the standard deviation of 6.48, density 6.61 g·cm^{-3}) and bearing steel disk (Φ30 mm, hardness 699.2 HV with the standard deviation of 53.6) were provided by Xi'an Institute of Dynamics (Shaanxi Province, China). The chemical compositions of both materials are shown in Table 1.

Preparation of Cu/C and oxidized surfaces

Copper-graphite(Cu/C) composite was processed into ball sample by wire-electrode cutting, with the diameter of 6 mm. Cu/C composite's ball was ground and polished until the roughness Ra was within 0.065 μm.

The bearing steel disks were polished with polishing liquid and flannel to ensure its surface roughness under 0.012 μm, and dried at room temperature. Then these disks were oxidized separately in the air environment with the temperature of 100, 120, 140, 160, 180 and 200ºC in for one hour, and cooled at room temperature. And then, took out two of polished disks and ground with #800 sandpaper for 30 minutes. Also, took out two of polished bearing steel disks and ground with #240 sandpaper for 30 minutes. These four disks were treated with different types of sandpaper to simulate the different surface microstructures of machine seal parts. After this treatment, oxidized each of them at the temperature of 200ºC for one hour. When the temperature is high, the surface color turns brown and the roughness Ra increases; When the temperature is low, the blue film is not uniform and dense enough to play the role of anti-friction and anti-wear. When the bearing steel is oxidized at 100-200ºC, it will form a blue dense oxide film similar to ceramic, with smooth surface and low friction coefficient.

Table 1. The chemical compositions of Cu/C and GCr15 obtained by EDS.

Samples	Chemical composition (wt%)								
	Fe	C	Mn	Si	S	Cr	Ni	Cu	Mo
Cu/C	0.25	36.97	0.06	0.07	0	0.19	0.25	62.15	0.05
GCr15	93.04	3.36	0.62	0.34	0	1.53	0.3	0.28	0.19

Frictional tests

Tribology experiments were performed by a ball-on-disk tribometer (UMT-2, CETR Corporation Ltd, USA) in reciprocating motion mode. They were conducted at room temperature (25ºC). All experimental data were the average of five experiments. On the one hand, in order to verify the lubricity of the oxidized surface, the Cu/C ball samples moved against the disk with the load of 5 N, the time of 15 minutes and the speed of 24 mm/s under dry and water condition. On the other hand, to explore the effect of applied load on the lubricity of oxidized film, the Cu/C ball samples moved against the disk with the load of 5 N, 10 N, 15 N in sequence and with the speed of 24 mm/s. Each individual test last for 15 minutes. The ball was made of Cu/C composites and the disks were polished bearing steel and bearing steel with oxidized film.

Characterizations

X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD, Kratos, England) was adopted to analyze the chemical state and surface chemical composition of the original and oxidized disk samples. Scanning electron microscopy (SEM, SU-8010, HITACHI, Japan) was utilized to observe the morphology of the wear scars on the disks. Contact Angle Meter (JC2000D2A, POWEREACH, China) was used to measure the contact angle of the bearing steel surfaces. Laser Scanning Confocal Microscope (LEXT OLS4000, Olympus Corporation, Japan) was used to measure the surface roughness of Cu/C balls and GCr15 disks. MoPao 2DE Metallographic Sample Grinder (Laizhou Weiyi Test Instrument Manufacturing Co., Ltd. Laizhou City, Shandong Province, China) was adopted to grind and polish disks.

INTRODUCTION

The chemical analyses of oxidized surfaces

X-ray photoelectron spectroscopy (XPS) were used to study the chemical properties of the original and oxidized bearing steel surfaces. And the oxidized bearing steel surface is polished and at the temperature of 200ºC. For the Fe element, the characteristics of the excitation of electrons from the core level of 2p are discussed with consistency within the Fig. 2(a). The small peak observed at about 704.5 eV is ascribed to zero-valent iron. In the original surface, there are peaks at 708.2 eV and

721.4 eV, which means the surface iron oxide was mainly Fe^{2+} (Baykan et al, 2012; Zollfrank et al, 2008). The oxidized surface's $2p_{3/2}$ photoelectron line ca. 710 eV shows this surface is full of Fe^{3+} (Gerber et al, 2018), and the satellite peak also proves that there is little Fe^{2+} in the disk surface (Aronniemi et al, 2005; Yamashita et al, 2008).

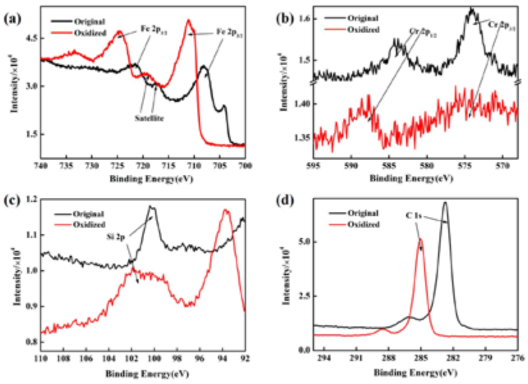


Fig. 2. XPS spectrum of (a) Fe 2p, (b) Cr 2p, (c) Si 2p, (d) C 1s on bearing steel surface of original and oxidized disks.

Fig. 2(b) shows XPS spectrum of Cr 2p. A main purpose of the interpretation of Cr 2p XPS is to determine the valence of Cr in oxidation state, thus contrasting it between the original and oxidized bearing steel disks. The Cr $2p_{3/2}$ peak of original disk is 574.1 eV, and this suggests a thin layer of Cr_2O_3, $Cr(OH)_3$ and Cr mental (Galtayries et al, 2006; Merryfield et al, 1982). The treated disk's Cr 2p peak span is very wide, which means that the valence of Cr became very complicated after oxidation. The major constituent is Cr_2O_3 and the chromium oxides contributes to the wide peak span (Gaspar et al, 2005).

Fig. 2(c) tells the XPS spectrum of Si $2p_{3/2}$ taken from oxidized and unoxidized bearing steel disks. The peak at 100.4 eV is formed by two peaks at 99.1 and 101.7 eV, respectively, which are considered to originate from the element Si and SiO_2 (Park et al, 2003). After oxidation treatment, the change trend of Si $2p_{3/2}$ peak becomes similar to Cr $2p_{3/2}$, and both of them are wider than untreated disks. Therefore, this indicated that the presence of Si after oxidation is SiO_x, with x varying from 0 to 2 (Sahota et al, 1996).

The XPS C 1s spectrum for bearing steel original and oxidized is shown in Fig. 2(d). The C 1s peak's binding energy of the processed sample is higher than untreated one. It is believed that the development of an sp3 bonded component within the matrix lead to the binding energy increase, which contribute to the strength of the C 1s enveloped in different binding energies (Jackson et al, 1995). This means that after oxidizing, new chemical bonds were formed between carbon and oxygen (Hoffmann et al, 2005).

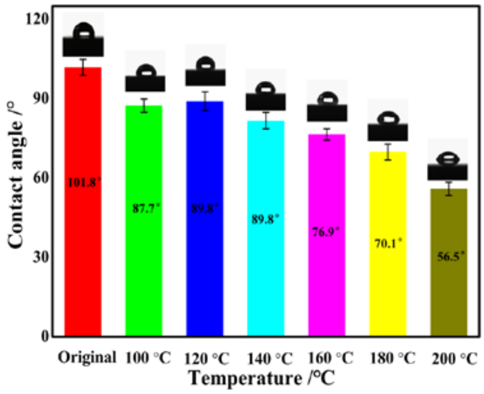


Fig. 3. Contact angle of disk surfaces oxidized at different temperatures.

The contact angles on the surfaces of the original disk and the fixed temperature gradient oxidation disks were measured by using a Contact Angle Meter with distilled water. Contact angle of the original surfaces is about 101.8°, which is higher than that of disk surfaces with oxidized treatment at different temperatures in the air, as it is shown in the Fig. 3, and with the increase of temperature, there is a continuous reduction of contact angle. Because of the compact structure of oxide particles on surface of steel and annealing treatment, the morphology became interconnected particles and surface energy increased, which caused low contact angle. When the oxidation temperature reached 200ºC, the contact angle was the smallest, and it indicated that the water lubrication film was more easily formed on the oxidized disk.

The friction coefficients in dry and water conditions

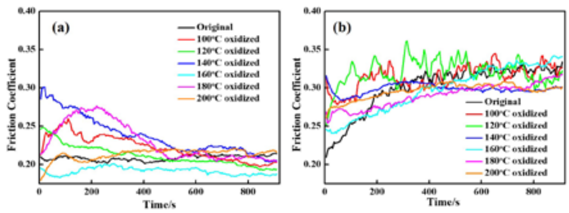


Fig. 4. The friction coefficient on original and oxidized surfaces under (a) dry condition, (b) water lubrication condition at a load of 5 N.

Cu/C has excellent self-lubrication performance. These experiments were repeated five times under dry and water conditions to get average friction coefficient. Fig. 4(a) shows the friction coefficient of original surfaces and oxidized treatment surfaces with dry friction. As temperature increased, there was no obvious rule of friction coefficient. Even though the number of friction coefficient fluctuated greatly in the initial stage, it eventually became very stable, near 0.22.

In water lubrication condition, the distinction of tribological curves is more obvious. Fig. 4(b) shows that the friction condition of that Cu/C sliding against untreated bearing steel disk surfaces is not as good as dry condition, and the friction coefficient has a great undulation. It is the same with surfaces under lower temperature (100ºC, 120ºC) oxidation. But the lubrication environment has changed a lot when it comes to high temperature oxidized surfaces. As Fig. 4(b) shows, the friction coefficient of 180 and 200ºC oxidized treatment surfaces eventually tend to be stable, and it is lower than untreated and low temperature treated surfaces.

It can be seen from Fig. 4 that the oxidation treatment of bearing steel has little effect on the friction coefficient of dry friction. The friction coefficient of each group fluctuates within an acceptable range. Under water lubrication, the friction coefficients fluctuation of the oxidized bearing (140-200ºC) steel surfaces diminish obviously and become more stable compared with the original one, which indicates that the friction mechanism of the oxidized bearing steel may change under water lubrication.

The worn surfaces conditions

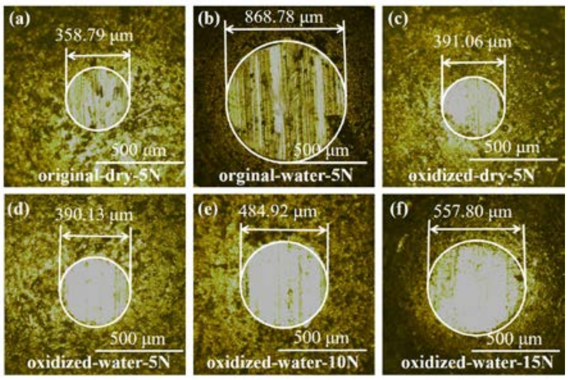


Fig. 5. Worn surfaces of Cu/C ball in different lubrication conditions.

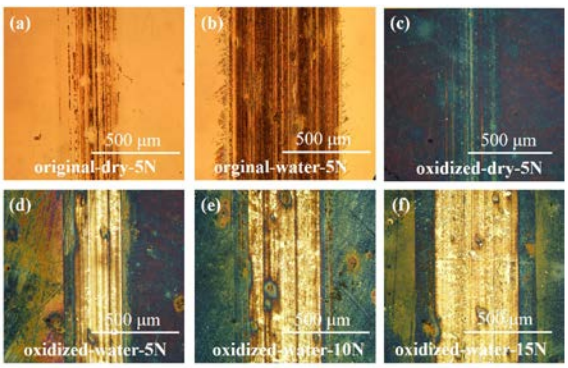


Fig. 6. Worn surfaces of bearing steel disks in different lubrication conditions.

The worn surfaces are of great concern in tribology. And then the disks and balls were cleaned with acetone by ultrasonic wave for 10 minutes after frictional tests. Fig. 5 shows the worn surfaces of Cu/C balls sliding against original and oxidized bearing steel disks on the condition of dry friction and water lubrication. Fig. 5(a) represents the wear scar of Cu/C ball sliding against the original disk under dry friction condition and the diameter is 358.79 µm, which is much smaller than 868.78 µm under the water lubrication in Fig. 5(b). Fig. 5(c), (d), (e), (f) are wear scars of Cu/C balls sliding against the oxidized disks and Fig. 5(c) is under dry friction while the other three are under water lubrication condition. In Fig. 5, the diameter of the Fig. 5(a), (c) and (d) are nearly the same, but Fig. 5(b) and (d) differ very much, which means that in the case of water lubrication, the oxidized disk has much less wear to Cu/C. Fig. 5(d), (e) and (f) are the wear scars at the load of 5 N, 10 N, 15 N under water lubrication, and the diameter rises with the increase of load. Fig. 6 is the scratches of the disk's surfaces corresponding to Fig. 5, respectively. It is clear that there is much Cu/C adhesion on the surface, and thus forming a transfer film in Fig. 6 (a) and (b). In Fig. 6(d), (e) and (f), the oxidation layer was destroyed and there was little Cu/C residual on the surface. That is to say, the water acting as a bad factor in lubrication for original bearing steel disk would promote the lubrication when the disk is oxidized.

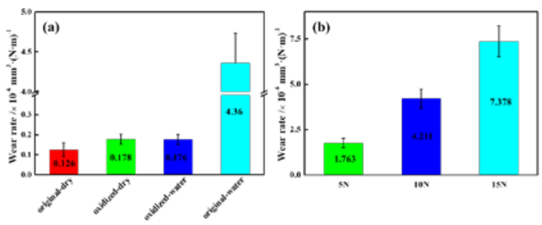


Fig. 7 (a) Cu/C ball wear rate of original and oxidized disks with dry friction and water lubrication; (b) Cu/C ball wear rate of oxidized disk with water lubrication at different load.

Cu/C composites wear easily under water lubrication. Fig. 7(a) shows the wear rates of Cu/C balls with the counterface of original and oxidized bearing steel disk on the condition of dry friction and water lubrication. The wear rate is 0.126×10^{-6} $mm^3\cdot(N\cdot m)^{-1}$ with dry friction for untreated disks, while it is 4.36×10^{-6} $mm^3\cdot(N\cdot m)^{-1}$ on the water lubrication condition in the same circumstances. After oxidation treatment, the wear rate on dry friction condition does not change significantly and it is 0.178×10^{-6} $mm^3\cdot(N\cdot m)^{-1}$, but it becomes 0.176×10^{-6} $mm^3\cdot(N\cdot m)^{-1}$ under water lubrication, and the wear rate is reduced by 96%, compared with the original disk. It suggests that the existence of oxidation film has little effect on lubrication under dry friction condition, but it has remarkable effect on reducing wear rate under water lubrication condition. Furthermore, Fig. 7(b) tells us that the wear rate of Cu/C ball varies with the load.

The influence of applied load on tribological behaviors

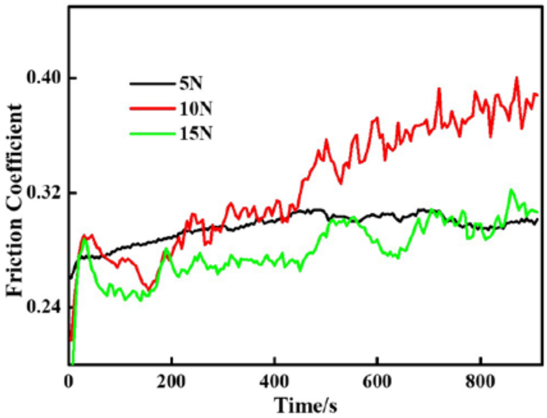
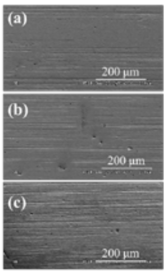


Fig. 8. The friction coefficient in water condition on oxidized treatment surfaces with different loads.



(d)

Element \ wt% \ Load	5 N	10 N	15 N
Fe	88.01	87.66	85.04
Cu	0.3	0.6	3.54
C	1.75	1.92	1.77
O	6.84	6.65	6.67
Si	0.75	0.72	0.48
Cr	1.53	1.58	2.03
Mn	0.82	0.87	0.47

Fig. 9 SEM images of scratches at the load of (a) 5 N, (b) 10 N, (c) 15 N and (d) the chemical composition of worn surfaces of bearing steel disks at different loads.

The experiments about the effect of different loads on friction coefficient were carried out on oxide surfaces in water lubrication condition. Fig. 8 shows that the friction coefficient is related to the load. The contact pressure increases with the increase of the load. In the initial stage of reciprocating friction, the point contact pressure is too large and the Cu/C is relatively soft, which leads to serious adhesion wear, and the debris is closely bound to the surface of the disks. At this time, Cu/C will play a lubricating role. So, the friction coefficient of the experiments was low at the beginning under water lubrication. At the load of 10 N, the friction coefficient was going up. The average friction coefficient is higher than that of 5 N. while at the load of 15 N, the friction coefficient fluctuated greatly and was lower than that of 5 N. Fig.9 shows the SEM images and EDS analysis of the worn scratches at different loads. These scratches have obvious abrasive wear marks, and wear becomes serious with the increase of load. As Fig.9 (d) shows that the chemical composition of worn surfaces and the Cu content increases with the load. So, the oxide film demonstrated good lubrication performance at the load of 5 N, and the coefficient of friction remained steady and low. At 10N, the oxide film was destroyed, and the specific pressure was small, so a large amount of Cu/C could not be adhered to the friction surface to form a good lubrication and made friction coefficient rise. While at the load of 15 N, Cu/C content was high, even if the oxide surface was destroyed, high specific pressure could make the Cu/C form transfer film, so the friction coefficient was relatively low. This result is consistent with previous study that when the Cu/C slid against the surface of bearing steel under water lubrication, the friction coefficient and wear would be reduced by increasing the load appropriately (Zhang et al, 2017).

The influence of surface roughness on tribological behaviors

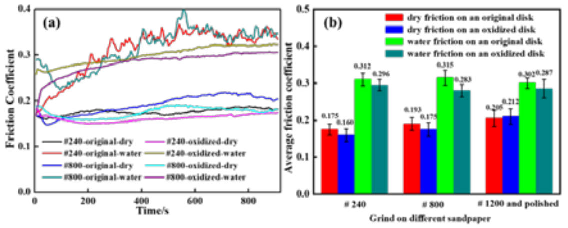


Fig. 10. The (a) friction coefficient and (b) average friction coefficient under dry friction and water lubrication of Cu/C balls and bearing steel disks treated with different types of sandpaper.

In the actual sealing application, the contact surface will not be so smooth. The steel disks treated with different types of sandpaper represents the original sealing surface with different roughness. Effect of surface roughness on friction coefficient was studied by using disks ground with ＃240, ＃800 and ＃1200 sandpapers, respectively. Fig. 10(a) shows the friction coefficient of Cu/C ball and ground bearing steel disks changing with time under different lubrication condition. With dry friction, no matter it is ＃240, ＃800 disk, or it is not oxidized, the average friction coefficient is steadily concentrated below 0.20 in Fig. 10(b). In addition, the friction coefficient of oxidized disk is slightly lower than that of the original disk. But the ＃1200 and polished with polishing liquid and flannel disks with the lowest roughness have the highest average friction coefficient of the three group. That due to some degree high roughness surface can adhere more soft Cu/C particles and form a thick lubricant film under dry friction condition. In water lubrication, ＃240 and ＃800 disks are the same as previous experiments, and the oxidized disk has a lower coefficient of friction than the original disk.

The average friction coefficient of ＃800 and ＃1200 oxidized disk is 0.28, lower than ＃240 oxidized disk 0.31 because of its smoother surface.

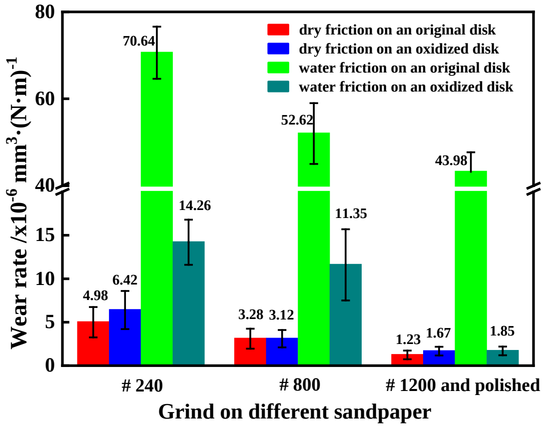


Fig. 11. The wear rate under dry friction and water lubrication condition of Cu/C balls when sliding against bearing steel disks treated with different types of sandpaper.

Fig. 11 shows the wear rate of Cu/C balls when sliding against different surface roughness disks. It indicates that the high the roughness is, the greater the wear rate is. And in water lubrication, the wear rate of ＃1200 and polished disk after oxidation is 96% smaller than the original, and the ＃800 and ＃240 disks are 78% and 80% smaller than original disk, respectively. The reason is that there is an adhesive wear when Cu/C balls slide against bearing steel disks, and it will be a lot of Cu/C sticking to the surface if it has a high roughness. In water lubrication, the peeled Cu/C is hard to retain, and the water will continue scour, making it difficult to form a stable transfer film on the original disk surface. But when it comes to an oxidized disk, the plow formed on the surfaces by the sandpaper will cause more serious Cu/C wear. However, the combined action of the oxidation layer and water will form a new film to improve the lubrication condition and reduce the wear of Cu/C.

Relevant mechanisms

As a kind of self-lubricating material, Cu/C forms a transfer film on the scratch surface when sliding against bearing steel. Fig. 12(a) and Fig. 12(b) show the SEM images and EDS analysis of the surface scratches on original disks under dry friction condition and water lubrication condition. Compared with Fig. 12(b), the scratch produced in Fig. 12(a) is more uniform and smooth, and the EDS analysis of the two graphs show the surface scratches contain Cu which comes from Cu/C composite. The element weight of Cu in Fig. 12(b) is 24.47 wt%, much greater than 8.62 wt% in Fig. 12(a). This data means that Cu/C has great wear in water lubrication, which indicates that it is easier to form stable transfer film under dry friction than water lubrication.

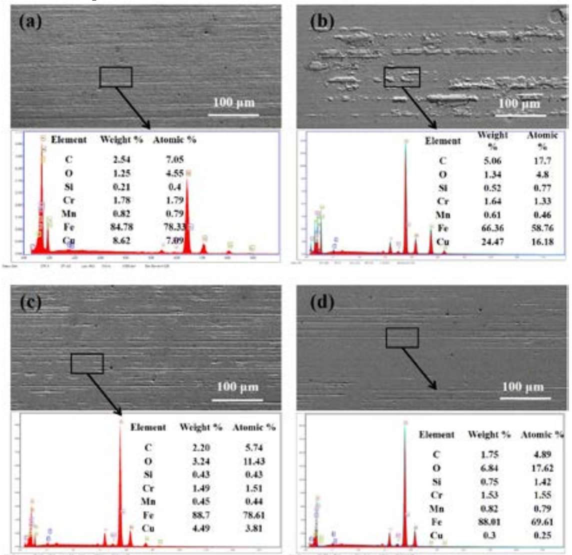


Fig. 12. The SEM images and EDS analysis of the surface scratch on the (a)original disk in dry friction, (b)original disk in water lubrication, (c)oxidized disk in dry friction, (d)oxidized disk in water lubrication.

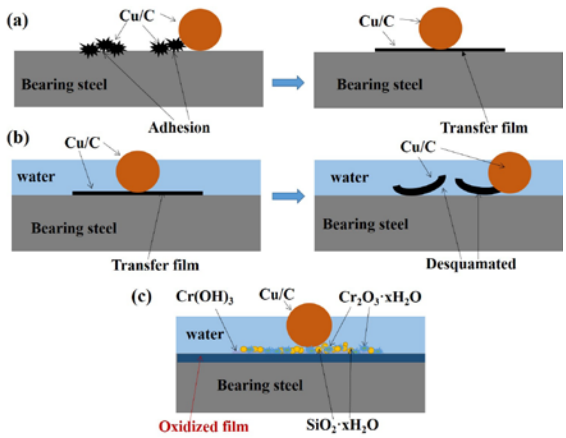


Fig. 13. (a) The forming process of transfer film, (b) the forming and breaking of transfer film, and (c) The transfer film on oxidized disk surfaces formed by tribo-chemical reaction products.

Fig. 12(c) and Fig. 12(d) show the SEM images and EDS analysis of the surface scratches on oxidized disks. It can be seen clearly that Fig. 12(a), Fig. 12(c) and Fig. 12(d) almost have the same flatness, so the friction under these three conditions has been well lubrication. The EDS analysis of Fig. 12(c) and Fig. 12(d) tells that the element weight of Cu content in the scratches after oxidation is less than that in Fig. 12(a) and Fig. 12(b). What’s more, comparing with the Cu content of original surface 0.28 wt%, there is little Cu residue on the surface of the oxidized disk under water lubrication. This suggests that the lubrication mechanism of the oxidized surface has changed.

Cu/C transfer film is able to be formed because of the self-lubricating property of this composites in dry friction, just as Fig. 12(a) shows. But in Fig. 12(b), this film will be broken and desquamated in water, and then the adhesion behavior can cause Cu/C to form a film on the surface of bearing steel again and desquamated. The recurrence of this situation will result in severe wear of Cu/C. In dry friction, the friction interface of the composite material is heated to soften, and Cu/C dust clings to the bearing steel plate easily, which will promote the formation of a layer of compact lubrication film. While in the water environment, due to the cooling water, it will make the Cu/C dust adhesion decrease, and the formation of the porous membrane proceeds, which is easy to be damaged and unable to form a good lubricating environment, and as it shows in Fig. 12(b) whose worn surface is rougher than others. This process can explain why the wear scar of Cu/C in water is large and the friction coefficient remains unstable.

Fig. 12(d) indicates there is little Cu/C residues and a new lubricant film have been formed on oxidized disk under water lubrication. After being oxidized, the composition and surface properties of bearing steel have changed a lot. The XPS analysis in Fig. 2 shows the surface was full of Fe^{3+}, Cr^{3+}, C-O, Si-C, Si-O and a mixture of some elementary substance. And Fig. 3 shows that the surface's contact angle became smaller and the hydrophilicity was enhanced. It is believed that at a certain temperature, the glaze layer is completely formed and exhibits good lubricating properties, thereby reducing friction coefficient and wear rate (Rybiak et al, 2010).

For the glaze layer, earlier study demonstrate that Cr_2O_3 can react with water and form chromic oxide hydrate under boundary lubrication conditions ($Cr_2O_3{\cdot}xH_2O$) (Wei et al, 1996). Therefore, this chemical reaction must occur when tribological experiments are carrying out on the oxidized disks in water lubrication. $Cr_2O_3{\cdot}xH_2O$ is a soft, easy to shear substance and acts as a kind of lubricant. Beyond that, there are some other chemical reaction occurring. The materials produced by these reactions (equations 1-3) are used as a lubricant additive in water. Silica gel, chromic oxide hydrate and hydroxide reaction film (Liu et al, 2013) prevent further contact between bearing steel and Cu/C, and avoid higher wear rate as it is shown in Fig. 13c.

$$Cr2O3 + xH2O \rightarrow Cr2O3{\cdot}xH2O \quad (1)$$

$$SiO2 + xH2O \rightarrow SiO2{\cdot}xH2O \quad (2)$$

$$Cr2O3 + 3H2O \rightarrow 2Cr(OH)3 \quad (3)$$

Clearly, the tribo-chemistry interactions can play a critical role during the friction process when Cu/C ball sliding against oxidized bearing steel. Frictional heat between the friction pairs can bring about the chemical reaction with water, and the tribo-chemical reaction products can be utilized as lubrication medium for further friction process.

CONCLUSIONS

Through the experiments mentioned above, the effect of oxidation film on the friction between Cu/C and bearing steel under water lubrication condition was proved. By using the method of oxidation of bearing steel, the problems of wear and tear of Cu/C in water were solved. In summary, the following conclusions can be drawn in this paper.

1. Friction coefficients of original and oxidized surfaces in dry friction are almost the same. But when the tests are performed under water lubrication condition, the friction coefficients of original surfaces increase and show a fluctuation.
2. Increasing the load of tests and roughness of the disk surfaces would promote the formation of Cu/C transfer film under water condition.
3. High temperature oxidation treatment of the bearing steel can reduce the friction coefficient and make the friction coefficient stable under water lubrication condition.
4. Oxidized bearing steel would produce tribo-chemical reaction in water environment to form lubricating film to reduce the wear rate of Cu/C. Compared with original bearing steel, it would reduce the wear rate of Cu/C by up to 96%.
5. High oxidation temperature increases the hydrophilicity of the oxidized surface. It means that the water lubrication film can be formed more easily on the surface after higher temperature oxidation.

REFERENCES

Aronniemi, M., Sainio, J., Lahtinen, J., "Chemical state quantification of iron and chromium oxides using XPS: the effect of the background subtraction method," *Surf. Sci.*, Vol. 578, pp. 108-123 (2005).

Baykan, D., Oztas, N.A., "Synthesis and characterization of iron orthophosphate by solution combustion method," *Mater. Res. Bull.*, Vol. 47, pp. 4013-4016 (2012).

Cote, P.J., Rickard, C., "Gas-metal reaction products in the erosion of chromium-plated gun bores," *Wear*, Vol. 241, pp. 17-25 (2000).

Dong, Z., Chen, W., Zheng, W. et al., "Effect of yttria addition on the stability of porous chromium oxide ceramics in supercritical water," *J. Nucl. Mater.*, Vol. 432, pp. 466-474 (2013).

Galtayries, A., Warocquier-Clérout, R., Nagel, M.D. et al., "Fibronectin adsorption on Fe–Cr alloy studied by XPS," *Surf. Interface Anal.*, Vol.

38, pp. 186-190 (2006).

Gaspar, A.B., Perez, C.A.C., Dieguez, L.C., "Characterization of Cr/SiO_2 catalysts and ethylene polymerization by XPS," *Appl. Surf. Sci.*, Vol. 252, pp. 939-949 (2005).

Gerber, S.J., Erasmus, E., "Electronic effects of metal hexacyanoferrates: An XPS and FTIR study," *Mater. Chem. Phys.*, Vol. 203, pp. 73-81 (2018).

Grandin, M., Wiklund, U., "Influence of mechanical and electrical load on a copper/copper-graphite sliding electrical contact," *Tribol. Int.*, Vol.121, pp. 1-9 (2018).

Guan, X., Wang, Y., Wang, J. et al., "Adaptive capacities of chromium doped graphite-like carbon films in aggressive solutions with variable pH," *Tribol. Int.*, Vol. 96, pp. 307-316 (2016).

He, L.X., Gao, M., Li, C.E., "Effects of Cr_2O_3 addition on the properties of PZT-PMN ceramics," *J. Inorg. Mater.*, Vol. 16, pp. 337-343 (2001).

Hoffmann, E.A., Körtvélyesi, T., Wilusz, E. et al., "Relation between C 1s XPS binding energy and calculated partial charge of carbon atoms in polymers," *J. Mol. Struc-Theochem*, Vol. 725, pp. 5-8 (2005).

Jackson, S.T., Nuzzo, R.G., "Determining hybridization differences for amorphous carbon from the XPS C 1s envelope," *Appl. Surf. Sci.*, Vol. 90, pp. 195-203 (1995).

Levitin, V.S., Zakharov, E.G., Kropachev, V.S., "Use of methods of special electrometallurgy to raise the quality of high-chromium bearing steel," *Metallurgist*, Vol. 32, pp. 70-72 (1988).

Liu, N., Wang, J., Chen, B., Yan, F., "Tribochemical aspects of silicon nitride ceramic sliding against stainless steel under the lubrication of seawater," *Tribol. Int.*, Vol. 61, pp. 205-213 (2013).

Luo, F., Gao, K.W., Tao, C.H. et al., "Tribological behavior of chromium oxide coatings under dry friction and water lubrication conditions," *Mater. Res. & Appl.*, Vol. 45, pp. 1-15 (2009).

Merryfield, R., Mcdaniel, M., Parks, G., "An XPS study of the Phillips Cr/silica polymerization catalyst," *J. Catal.*, Vol. 77, pp.348-359 (1982).

Nishimura, T., "Nano Structure of the Rust Formed on Chromium Bearing Steel in Concrete after Wet and Dry Corrosion Test," *ISIJ Int.*, Vol. 55, pp. 1739-1746 (2015).

Park, S.M., Chang, H.B., Sang, H.N. et al., "The effects of ambient He pressure on the oxygen density of Er-doped SiOx thin films grown by laser ablation of a Si:Er_2O_3 target," *Appl. Surf. Sci.*, Vol. 218, pp. 311-317 (2003).

Rybiak, R., Fouvry, S., Bonnet, B., "Fretting wear of stainless steels under variable temperature conditions: Introduction of a 'composite' wear law," *Wear*, Vol. 268, pp. 413-423 (2010).

Sahota, M.S., Short, E.L., Beynon, J., "An analysis of silicon oxide thin films by computer simulation of Si 2p XPS spectra using the Sanderson technique," *J. Non-Cryst. Solids*, Vol. 195, pp. 83-88 (1996).

Sourty, E., Sullivan, J.L., Bijker, M.D., "Chromium oxide coatings applied to magnetic tape heads for improved wear resistance," *Tribol. Int.*, Vol. 36, pp. 389-396. (2003).

Wang, J., Jia, Q., Yuan, X. et al., "Experimental study on friction and wear behaviour of amorphous carbon coatings for mechanical seals in cryogenic environment," *Appl. Surf. Sci.*, Vol. 258, pp. 9531-9535 (2012).

Wei, J., Xue, Q., "The friction and wear properties of Cr_2O_3 coating with aqueous lubrication," *Wear*, Vol. 199, pp. 157-159 (1996).

Yamashita, T., Hayes, P., "Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials," *Appl. Surf. Sci.*, Vol. 254, pp. 2441-2449 (2008).

Yang, J., Xia, Y. Cheng, J., "Study on friction and wear properties of graphite-ZTA self-lubrication ceramic composites," *Powder Metallurgy Technology*, Vol. 75, pp. 34-38 (1999).

Zhang, G., "Theoretical and Experimental Approach of Separation Speed of Spiral Groove Face Seals," *Chin. J. Mech. Eng-en.*, Vol. 44 (2008).

Zhang, P., Zhao, W., Dong, G., "Investigation into Friction and Wear Behaviors of Copper-Based Graphite Seal Material," *J. Xi'an Jiaotong Univ.*, Vol. 51, pp. 92-97 (2017).

Zollfrank, C., Scheel, H., Brungs, S. et al., "Europium(III) Orthophosphates: Synthesis, Characterization, and Optical Properties," *Cryst. Growth Des.*, Vol. 8, pp. 766-770 (2008).

軸承鋼表面高溫氧化膜對銅石墨滑動的摩擦學改善研究

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摘 要

銅-石墨（Cu/C）材料由於其高導熱性、優異的防腐和潤滑性能等優點，被用作液體火箭渦輪泵機械接觸密封的靜環。然而，在實際工作條件下，Cu/C 靜環在啟動階段會受到嚴重磨損。為了解決這一問題，本研究提出了一種通過高溫氧化膜對配副表面進行改性的方法。在不同的溫度下製備了氧化膜，並進行了摩擦學測試，以驗證氧化膜的潤滑效果。此外，研究了外加載荷和表面粗糙度對摩擦學行為的影響。總的來說，氧化膜在改善軸承鋼和 Cu/C 在水潤滑條件下的摩擦學性能方面起著重要作用。