Contents lists available at ScienceDirect





## **Tribology International**

journal homepage: www.elsevier.com/locate/triboint

## Tribological performance and conductive capacity of Ag coating under boundary lubrication



### Junhuan Chen, Yangiu Xia\*, Yichao Hu, Buyi Hou

School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China

### ARTICLE INFO

Keywords: Ag coating Electrically conductive grease Electrical wear Electrical contact resistance

### ABSTRACT

To achieve simple, stable and long-life sliding electrical contact pairs, a kind of fine silver coating on electrical contact components was designed and prepared. In this article, electrodeposited fine silver (Ag), heat treated Ag and silver-graphite (Ag/C) composite coatings based on copper (Cu) substrate were prepared. The polyaniline (PAN) was doped as a conductive additive to afford the conductive grease. Compared with the Cu, Ag, treated Ag and Ag/C coatings, the Ag coating lubricated by PAN grease exhibited superior conductive capacity and excellent boundary-lubricated friction behavior. Through analysis of worn surface, the good tribological characteristics of Ag coating are ascribed to mechanical effect of the PAN particles and the protective film generated by PAN grease.

#### 1. Introduction

Electrical contact components, also known as contacts, are the key elements of high and low voltage electrical appliances, which play the important role in connecting, breaking, diversion and isolation of the current [1]. Electrical contact elements are mainly made of electrical contact materials that are vital factors affecting the reliability of the contact system. Thus, these materials have to maintain good electrical conductivity, thermal conductivity, arc-resistance, anti-welding, antiwear, low and stable contact resistance, corrosion resistance and considerable mechanical strength and easy processing characteristics [2,3]. The sliding contact is one of the most complicated electrical contacts, whose electric wear behavior depends on the interaction of electricity, electromagnetism and tribological factors. Consequently, most used pure metals that possess relatively high conductivity are difficult to meet the requirements because of unsatisfactory antioxidativity(Cu), high cost(Au, Ag, Pt and other precious metals) or inferior wear resistance (Cu, Ag, Au et.al) [4-6]. For this reason, copper-based and silver-based composites are widely used in the production of electrical contact elements owing to well lubricity, antioxidation and welding resistance [7–9]. However, compared with fine silver, the preparation of silver-based composite materials is quite complex or has intrinsic defects [10-12]. The performances of electrodeposited Ag-based materials depend on the stirring speed, temperature, current density, dispersant and what not in the plating process [13]. Besides, the composite materials fabricated via powder metallurgical routes usually have low density and large coarse oxides,

and therefore they are easily corroded by arc [14]. For the spray deposition, it can inhibit the precipitation and growth of the second phase, but there are the main problems in the process, like "overspray phenomenon", uniformity of the product size and complicated process parameters [15]. Meanwhile, the second phase acting as lubricating function will weaken mechanical strength and conductivity of composites [16,17]. Moreover, contacts cannot be repaired under dry sliding electrical contact. Therefore the design of sliding contacts is still a challenging work.

To solve problems above, the coating contact pairs under boundary lubrication is promising as an alternative approach of dry friction on electrical contact interface if the boundary lubricating film could function as a versatile film that can increase the abilities of friction reducing and anti-wear, arc and corrosion resistance and can perform low and stable resistivity. It can be a desirable design of sliding electrical contacts for the following reasons: Nobel metallic coatings (such as Ag, Au and Pt coatings) can lower the cost and contact resistance and have better mechanical properties than pure metals [17]. Thus, these highly conductive coatings are commonly applied to electronics industry and electric equipments. As is well known, the lubricating oil or grease can significantly reduce friction and wear under boundary friction than dry sliding, and easily renew without needing replacement of friction pairs. Interestingly, now more and more researches concentrate on conductive grease because it can enhance lubrication efficiency, decrease contact resistance, and extend service life, thereby save energy [18]. XIA et al. found that ionic liquids, carbon nanotubes, nano-ATO, carbon fiber and Ketchen black as

E-mail address: xiayq@ncepu.edu.cn (Y. Xia).

http://dx.doi.org/10.1016/j.triboint.2017.02.006

Received 28 November 2016; Received in revised form 22 January 2017; Accepted 4 February 2017 Available online 06 February 2017

0301-679X/ © 2017 Elsevier Ltd. All rights reserved.

<sup>\*</sup> Corresponding author.

conductive additives can greatly improve the electrical conductivity and tribological characteristics of conductive grease [19-22], but they only investigated conductivity and tribological performances under no friction or no current instead of electrical contacts that are more closed to real conditional operation. That could be insufficient because the friction behavior under electric current might be even opposite to that under no current.

Polymer was once considered to be non-conductive as its atoms are mainly contacted by covalent bonds. Nevertheless, conductive polyacetylene films were synthesized by high-concentration catalytic synthesis in the 1970s, which led people to pay attention to this new type of conductive materials and successively synthesized a series of conductive polymer materials [23]. Among them, polyaniline (PAN) became the fastest-growing conductive polymer because of its raw materials easy to obtain and synthesize. Only when treated by chemical or electrochemical methods, conductive PAN can exhibit conductivity, for example the industry commonly used proton acid (such as hydrochloric acid) is doped to produce electrical conductivity [24]. Conductive PAN has been widely employed in metal and non-metallic surface coating to increase the conductivity. In addition, it is possible to prevent the oxidation of metals as the PAN reacts with the substrate metal to produce chemically inert films [25,26].

In this paper, the conductive grease was obtained by selecting PAN powder as conductive additive of a synthetic grease. Ag, heat treated Ag and Ag/C composite coatings based on Cu substrate were fabricated by electroplating. Compared with tribological characteristics and conductive capacity of Cu substrate and Ag/C coating under different lubricating states, the Ag coating under boundary lubrication were studied. Furthermore, this paper mainly reports the effects of load, current intensities and temperature on tribological properties and conductive capacity of the Ag coating under boundary lubrication. Conductive and electrical wear mechanisms of Ag coating under boundary lubrication were studied for the new design of sliding electrical contacts.

#### 2. Experimental details

#### 2.1. Materials

#### 2.1.1. Conductive grease

PAN powders (provided by Taizhou Yongjia Trading Co., Ltd) were used as a conductive additive. In addition the conductive graphite powders (grain size  $1-15 \mu$ m, density  $1-2.4 \text{ g/cm}^3$ , Qingdao Tianheda Graphite Co., Ltd) were as a comparative additive. PAO, bought from Dow Chemical, was applied for the base oil to prepare conductive grease. The thickener was formed by saponification of Lithium hydroxide, sebacic acid and 12-hydroxy stearic acid, and then was used to thicken the base oil into grease. Acetone was used as the polar dispersant. All the chemical reagents employed are analytical grade and used as-received. Two commercial conductive greases were used as reference greases. In this paper they are named C1 and C2. The C1 was provided from Beijing Guodianfutong Science and Development Co., Ltd., and C2 was provided from Changsha Zhongcheng Petrochemical Co., Ltd. Table 1 lists the physicochemical characteristics of the PAN, and Fig. 1 shows its SEM images.

Table 1Physicochemical properties of PAN.

Sample	Grain size	molecular weight	Density	Conductivity	doping ratio (molar ratio)
PAN	1–10 µm	50000– 60000	0.3–0.5 g/cm <sup>3</sup>	2 S/cm	> 30%



Fig. 1. SEM image of PAN powder.

#### 2.1.2. Coatings

Oxygen-free copper (diameter:100 m×50 mm×1 mm, hardness:125 HV) obtained from Shanghai Songyoushiye Company was used as substrate of coatings. Graphite powder(grain size: <5  $\mu$ m) and VP06-122/123 dispersant (purchased from Germany Schloss company) were introduced for coating process. Silver salt solution for silvering was bought from China Aviation Industry Hongdu Group.

#### 2.2. Preparation and characterization

#### 2.2.1. Preparation and characterization of conductive greases

The lithium complex grease (as the base grease) was produced in accordance with the literature [22]. 1 wt% PAN and graphite as additives were respectively added into the base grease by uniformly mixing the powders into the base grease. The base grease adding PAN (PAN grease for short) and graphite (graphite grease for short) were obtained after fine grinding. The anticorrosion behavior, the penetration capacity, and the dropping point of all greases were examined by Chinese National Standards GB/T 7326 (copper strip test), GB/T 269, and GB/T 3498, respectively. A HLY-200A circuit resistance apparatus was utilized to assess the volume resistivity of the greases.

# 2.2.2. Preparation and characterization of Ag, heat treated Ag and Ag/C composite coatings

The Cu substrate was polished with the sandpaper to remove scale and dirt, and then pre-plated silver aimed to promote the bond strength of coating and substrate. After these two steps, Ag coating and Ag/C composite coating were electroplated on pre-plated samples in plating solution, respectively. Eventually, two coatings were obtained by washing with distilled water and dried in ambient temperature. It is important to investigate the influence of temperature on electrical friction behavior of Ag coating because specific contacts need to withstand intermittent high temperatures such as disconnectors. So treated Ag coating was made by heated to 240 °C for 1 h and cooled to room temperature with the furnace cooling.

The Vickers hardness of the three coatings was measured with a HX-1000TM / LCD microhardness meter (measurement parameters were: load 10 g, loading time 20 s). The surface roughness of the coatings was measured with JB-6C roughmeter before other tests in case the soft surface of Ag was scratched. The bonding strength of the samples was qualitatively tested by bending test according to the GB/T 5270-200X standard: the test piece (50 mm×100 mm×1 mm) was bent 180° on a 1 mm diameter shaft and repeatedly bent until it broke. A D8ADVANCE diffractometer equipped with a Cu Ka X-ray tube was used to perform XRD analysis on the samples and identify the phases formed. Surface and cross-section of coating samples were characterized with an EVO-18 scanning electron microscope (SEM; Zeiss,

#### Table 2

Mechanical properties of as-prepared coatings.

Coatings	Thickness (µm)	Hardness (HV)	Roughness (µm)	Adhesion
Ag	10	99	0.332	
Ag/C	15	36	0.571	
Treated Ag	10	106	0.603	

"-" states that the specimen doesn't peel off according to GB/T 5270-200X test.



Fig. 2. Schematic diagram of ball-on-disk contact and electrical circuit.

Germany) equipped with an EDS attachment. Table 2 lists mechanical characteristics of as-prepared coatings.

#### 2.3. Tribological and electrical conductivity tests

A MFT-R4000 current-carrying friction and wear tester was performed to evaluate the tribological properties and contact resistance of samples in a ball-on-disk configuration. The upper ball (AISI52100 steel; hardness: 710 HV, ø6mm) was driven to reciprocally slide against the lower stationary coating and Cu samples (20 mm×20 mm×1 mm) under boundary lubrication and dry state at a stroke of 5 mm and an ambient temperature of ~25 °C for a duration of 30 min. Before and after each sliding test, the steel ball and samples were ultrasonically washed with petroleum ether for 10 min. For boundary lubrication, approximately 1 g of the to-be-tested grease was introduced to the contact zone of the sliding pair before sliding. The coefficient of friction (COF) was recorded by a computer attached to the tester. The electrical circuit of the tests is illustrated in Fig. 2. In this paper, the circuit resistance values (Fig. 2) calculated by Ohm's law represented the electrical contact resistance (ECR) values of friction pair for other ECR values were constant such as wires' and components'. The contact current between the friction pair was measured and recorded automatically every 1 s by the tester. The resistance waveforms were calculated by current waveforms which were recorded by the computer. An optical microscope was employed to measure the wear width. The sliding test under each preset condition was repeated

#### Table 3

Physicochemical properties of fabricated and commercial greases.

three times to minimize data scattering. The average values of the COF and wear width were reported in association with error bars in this article. The morphology and chemical composition of the wear scars were analyzed with an EVO-18 SEM equipped with an EDS attachment.

#### 3. Results and analysis

#### 3.1. Samples characteristics

#### 3.1.1. Physicochemical characteristics of the conductive grease

Table 3 lists basic physicochemical characteristics of the greases. The conductive grease including fabricated PAN and graphite greases and two commercial greases exhibits good thermostability (>270 °C), and they also exhibit good anticorrosion behavior. PAN grease shows lower volume resistivity and contact resistance than other greases.

#### 3.1.2. Characterization of coating samples

Fig. 3 shows the surface and cross-section morphology of the asfabricated Ag, treated Ag and Ag/C coatings. The structure of Ag coating is very dense (Fig. 3(a)), whereas the surface of Ag/C coating with porous structure consists of bright strips (Ag grains) and dark strips (graphite grains) (Fig. 3(e)). But the treated Ag coating has some visible cracks and much rougher surface than that of Ag coating as a result of oxidation of Ag grains by heat (Fig. 3(d)). The Ag coating and Ag/C composite coating have closely bonded with the Cu substrate and the transition region is natural, indicating that the coatings have good adhesion (Fig. 3(b) and (f)).

Fig. 4 shows the XRD patterns of silver coating and Ag-graphite composite coating. As is observed, the diffraction peaks of Ag and Ag/C composite layers correspond to the Silver-3C diffraction peak [27,28]. It reveals that the crystal structure of silver prepared by electrodeposition is face-centered cubic structure, of which the lattice constant is a=b=c=4.086. Due to the graphite content is very low, graphite diffraction peak of Ag/C layer is very weak. The results of XRD show that the prepared coatings have high purity and no crystalline or heterogeneous phase.

#### 3.2. Tribological and electrical performance

3.2.1. Friction and electrical contact resistance (ECR) results of Cu, Ag and Ag/C samples under the dry friction and boundary lubrication

Fig. 5 shows the COF and ECR values of samples (Cu, Ag and Ag/C) as functions of time and corresponding wear width under different lubrications with 1 V(room temperature, load:10 N, frequency: 2 Hz and stroke: 5 mm). It can be seen from Fig. 5(a) that the COFs of samples under dry sliding obviously indicates running-in (increasing) and steady state (stable and even decreasing) wear. During the stable wear, the ECR values of Ag coating are the most stable and lowest and its COFs are relatively low, which is due to low sliding shear force and antioxidation of the soft Ag film [29]. Although the mean COF and wear width of Ag/C coating under dry electrical sliding are the lowest because self-lubricating graphite phase lowers frictional shear and absorbs some load shortening running-in period, lubricating phase is the major reason for the highest and fluctuant ECR as the result of

Sample	Dropping point (°C)	Penetration (1/4 mm)	Copper corrosion (T2 copper, 100 °C, 24hrs)	Volume resistivity ( $\Omega$ cm)	Contact resistance ( $\mu\Omega$ )
Base grease	269	81.1	1a	$8.2 \times 10^{13}$	$32.1 \pm 0.1$
	271	81.5	1a	4 9 × 10 <sup>12</sup>	$30.1 \pm 0.1$
Graphite grease	273	87.7	la la	8.8×10 <sup>12</sup>	$30.5 \pm 0.1$
C1	280	78.3	la	$7.5 \times 10^{13}$	$31.6 \pm 0.1$
C2	284	82.2	1a	$6.2 \times 10^{12}$	$30.3 \pm 0.1$



Fig. 3. Surface and cross-section morphology of the coatings: (a) Ag topograph, (b) Ag cross-section, (c) treated Ag topograph, (d) treated Ag cross-section, (e) Ag/C topograph, (f) Ag/C cross-section and (g), (h) and (i) EDS elemental surface distribution corresponding to the composition of the red box in (f). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. (continued)

much lower conductivity of graphite [30]. The COFs of Cu substrate are much higher (mean COF of Cu is 0.619, about 2.2 times that of Ag and about 3.0 times that of Ag/C). And its ECR values are much fluctuant and high.

The COFs of samples lubricated by PAN grease are much lower than that under dry sliding, which is observed in Fig. 5(a) and (b). As revealed in Fig. 5(b), average COF and ECR value are ranked in the order of Ag < Cu < Ag/C. The lowest mean COF (0.056) is reached by Ag coating under boundary lubrication, which is about 50% that of Ag/ C and 75.0% that of Cu, and the wear width of Ag significantly reduces (wear width: 0.34 mm, about 61% that of Cu and Ag/C). The average ECR value of Ag under boundary lubrication (44.6m $\Omega$ ) is slightly higher than that under dry friction (just rising by 4.5%), but its mean COF greatly falls by 79.9%. The COF of Cu is quite low, but its ECR is very high (61.1m $\Omega$ ). The ECR values of Ag/C are also the highest, whose fluctuation is between 50m $\Omega$  and 70 m $\Omega$ , but its stable resistance value is a little lower than that in dry sliding.



Fig. 4. XRD patterns of silver coating and Ag-graphite composite coating.



Fig. 5. COFs, ECR values of samples Cu, Ag, Ag/C under (a) dry friction and lubricated by (b) PAN grease; (c) COFs, ECR values of Ag lubricated by three comparative conductive greases; the corresponding wear widths of (a) and (b). (voltage:1 V, room temperature:23–25 °C, load:10N, frequency: 2 Hz and stroke: 5 mm).



Fig. 6. Effects of load on (a)COF, ECR values and (b)wear width under PAN grease (voltage:1 V, load:10 N, frequency: 2 Hz and stroke: 5 mm).

In order to investigate the unique properties of the PAN grease, the comparative greases, two commercial greases C1 and C2 as well as the prepared Graphite grease, have been tested on Ag-steel tribo-pairs with 1 V (room temperature, load:10 N, frequency: 2 Hz and stroke: 5 mm).

As shown in Fig. 5(c), it is clearly that the commercial grease C1 can't function at that state because the COF rises dramatically with loud noise. The test just runs five minutes with increasing COF and noise, which is enough to prove its worst tribological performance. However,



Fig. 7. Effects of current on (a) COF, ECR values and (b) wear width under PAN grease (voltage: 1 V, load: 10 N, frequency: 2 Hz and stroke: 5 mm).



Fig. 8. Effects of heat treatment on (a) COF, ECR values and (b) wear width under PAN grease (voltage:1 V, load:10 N, frequency: 2 Hz and stroke: 5 mm).

the C2 and graphite grease perform well and similarly. Compared with PAN grease (Fig. 5(b)), COF values of the two greases are about 1.43 times bigger than PAN grease. Besides the ECR values of the two greases (about 50 m $\Omega$ ) are higher than that of PAN grease. As shown in Fig. 5(c), the wear width of C2 grease is 1.5 times wider than that of PAN grease, and the wear width of graphite grease (0.37 mm) is slightly bigger than that of PAN grease.

# 3.2.2. Effects of load on friction and ECR of Ag under boundary lubrication

Fig. 6 shows the influence of load on tribological behavior and conductivity of Ag coating lubricated by PAN grease. It is seen that COFs of Ag basically increase with increasing load while the ECR values are relatively high except that at 10 N. In the meantime, the wear widths of Ag tend to increase as load increases. When the load is high (15 N), the COF and wear width soar while ECR value rises. However, while the load added to 20 N the COF reduces with wear width still increasing. When the load is lower (5 N), the ECR value becomes higher due to less real contact area [31], and the COF and wear width are almost as the same as 10 N.

# 3.2.3. Effects of current on friction and ECR of Ag under boundary lubrication

Fig. 7 shows the influence of current on tribological behavior and conductivity of Ag coating lubricated by PAN grease. When the current values are below 30 A, comparing the two cases, without and with current, there is no much difference of the COFs varying with time. Nonetheless when the current value is up to 30 A, compared to that without current, the COFs with current rises sharply and the wear under current is much severer (mean wear width is 1.7 times that without current).

3.2.4. Effects of heat treatment on friction and ECR of Ag under boundary lubrication

Fig. 8 shows the influence of heat treatment on tribological behavior and conductivity of Ag coating lubricated by PAN grease. The COF of heat treated Ag is higher than that of Ag as well as ERC. Nevertheless the wear width of treated Ag is slightly wider than that of Ag.

#### 3.3. Analysis of worn surface

Fig. 9 shows the SEM images of typical coated discs and Cu substrate within dry sliding and PAN grease. As shown in Fig. 9(a), the worn surface of Ag has plenty of transferred metal and furrows in sliding direction, and the edge of worn section in the insert picture is very sharp. These features prove Ag under dry friction has undergone severe adhesion and plastic deformation. It can be seen that some adhesive blocks and holes, micro-grooves and black spots on the worn surface of Ag/C under dry friction in Fig. 9(b). The black spots distributed along the furrows should be graphite grains extruded from Ag/C composite, to some extent which can prevent from direct contact of frictional pairs to reduce friction and wear (Fig. 5(a) and (c)). However, when the conductive grease has been applied, the all worn scars tested have become much smooth and small (Fig. 9(c), (d), (e) and (f)). The worn track of Cu lubricated by PAN grease has some visible furrows and many microholes, which are characters of abrasive and fatigue wear. The worn track of Ag/C indicates shear lips vulnerable to removal, exfoliation of flakes and furrows along with sliding direction (Fig. 9(d)). The exfoliation of surface (as depicted in Fig. 11(a)) results in the discontinuous lubricating film with microploughing and high and fluctuant COFs and ECR values. These are characteristics of fatigue wear and plastic deformation. The worn surface of treated Ag just contains some shallow furrows (Fig. 9(e)), which contributes to mild abrasive wear. However, the worn scar of Ag lubricated by PAN grease is the smoothest and smallest in these scars, even smoother than the original coating surface, which just contains some slight scratches originated from the rough surface (Fig. 9(e)). This result is the feature of plastic deformation.

Fig. 10 shows the corresponding EDS spectrums of worn tracks in Fig. 9. Besides, Table 4 shows the corresponding contents of elements. As revealed in Table 4, the worn tracks of Ag and Ag/C contain Cu element when the friction pairs are under dry sliding. Therefore it can be inferred that the both coatings are worn out, which is exactly consistent with the adhesive wear (Fig. 9(a) and (b)). In addition, the

content of O element on wear track of Ag/C is much lower than that of Ag under dry friction and the distribution of C element on Ag/C worn area covers the wear region tested by EDS (Fig. 11). It indicates that during the friction process, because of the covering of graphite on the worn surface, the self-lubricating film of the graphite lowers the friction force and prevents the oxidation of the Ag/C coating but raises the ECR values [32,33], which is proved in Fig. 5(c). However, when PAN grease is applied in the friction process, the content of Cu element on all worn tracks of coatings is not tested and the content of O element reduces greatly. Thus it can be referred that the tribofilms formed by PAN grease can protect friction pairs from direct contact resulting in good tribological properties and antioxidation.



Fig. 9. SEM morphologies of worn surfaces of (a) Ag and (b) Ag/C under dry sliding, and (c) Cu, (d) Ag/C, (e) treated Ag and (f) Ag under boundary or mixed lubrication (voltage:1 V, room temperature:23–25 °C, load:10 N, frequency: 2 Hz and stroke: 5 mm).



Fig. 9. (continued)

#### 4. Discussion

#### 4.1. Tribological behaviors and conductive performances

As described above, it is different for the tribological behavior under different electrical sliding states lubricated by the conductive PAN grease. As reported, pure copper is easily oxidized to generate a protective film by oxygen atoms of polar molecules from lubricants, thereby which can reduce friction [34]. But influenced by the alternative shear force, the hard oxide debris peeled off from friction progress as the third body can cause abrasive damage (which can be seen in Fig. 9(c)). As depicted in Fig. 5(b), the tendency of COFs is against the variation of ECR values under Ag and Ag/C coatings. It is reasonable to assume this tribofilm is non-conductive [18,19]. As reported, the carbon from Ag/C can react with O to form gases under current [32,33]. Given the nonconductive tribofilm and relatively low conductivity of graphite phase, joule heat accumulated quickly, and then it accelerate the reaction of C. The escaped gases destroy the tribofilm, and this causes poor lubrication, even exfoliation of surface, which results in high COFs and ECR values. However, the lubricating film is relatively solid on Ag surface. As reported, soft Ag film can reduce friction well [35] and nanoparticles can induce micro-bearing effect [36]. In addition, combined with conductivity of PAN grease, Ag coating exhibits friction and wear reducing and low ECR.

#### 4.2. Conductive and electrical wear mechanisms

Based on the previous description and analysis about the friction behavior and conductivity, the conductive and electrical wear mechanisms can be proposed. Fig. 12 shows the conductive mechanism of Ag



Fig. 10. EDS spectrums of the worn surfaces.

coating with conductive addictives under boundary regime. In the runin period, the boundary-lubricated film is very thin and cannot totally cover the asperities between Ag coating and upper ball, so the asperities with direct contact play a key role in direct movement of electron (Fig. 12a), which corresponds to the low ECR values and high COFs of Ag in run-in period (Fig. 5(b)). With the time passing, surface asperities have been ground and the tribofilm has become thick enough to cover the wear area. Besides, the PAN micro-particles tend to aggregate and deposit on the wear surface. In such situation, the grease layer and tribofilm can act as barriers for conductivity. The conductive mechanism under boundary lubrication with PAN powder (Fig. 12b) can be attributed to "tunnel effect" (as shown in Fig. 12c) and "percolation theory" [37–41]. As descript in Fig. 12(b), the electrons activated by the thermal vibration or strong internal electric field can easily cross the barrier and jump to the adjacent grains to generate tunnel current, thereby significantly lower and stabilize the ECR values, which accords with steady wear period of Ag in Fig. 5(b). With heat accumulation by joule and friction heat, the tribofilm has grown thicker and thicker, and thereby the nonconductive tribofilm lead to larger ECR values and smaller COFs (corresponding to that in Fig. 5(b)). The



Fig. 11. (a) Worn surface and (b) EDS surface distribution of C element with Ag/C under dry sliding.

 Table 4

 Contents of the typical elements on the worn surfaces.

Worn surface	Element (wt%)					
	Ag	0	Cu	С	Ν	Si
Ag-dry sliding	87.58 62.89	2.45	9.07 34 29	0.69	-	0.21
Cu-PAN	-	2.91	92.81	4.28	-	-
Ag/C-PAN	97.33	0.41	-	1.67	0.59	-
Treated Ag-PAN	98.67	1.33	-	-	-	-
Ag-PAN	96.15	0.92	-	1.36	0.62	0.95



Fig. 12. Conductive sketch of Ag coating under boundary lubrication regime.



Fig. 13. Schematic diagram of electrical wear mechanism.

larger ECR, in turn, generates much more heat (proved by 'melting edges' in Fig. 9(f)) to damage somewhat the tribofilm not break it down totally (proved by the smooth wear track), thereby which lowers ECR values and raises COFs. Conversely, the lowered ECR can lead to the tribofilm thickening again with appropriate heat, which results in larger ECR values and smaller COFs again. This process occurs again and again, resulting in the fluctuant COFs and ECR values of Ag which can be seen in Fig. 5(b).

Fig. 13 shows electrical wear mechanism of Ag coating with conductive addictives under boundary regime. The balance and saturated tribofilm has been formed and prevented the direct contact of rubbing surface, which can be deduced from the smoothest wear track of Ag (Fig. 9(f)). As explained above, regardless of fluctuation of the ECR values, they tend to rise with time. Therefore the joule heat rises and accumulates, eventually resulting in local softening of Ag coating and the thin adsorption film. However, as shown in Fig. 13, the thin tribofilm is capable of isolating the rubbing surfaces. Besides, the PAN grains can turn sliding friction into rolling friction. All these factors reduce friction and prevent direct contact between hard steel ball and heat-softened surface of Ag. The heat-softened surface is prone to plastic deformation. Meanwhile the heat-softened area is squeezed out by hard ball pressed into soft area though the thin film. As the ball reciprocates along the wear track, the extruded material is deposited along the wear edges and heated up further by friction and extrusion force. Consequently, it shows melting features, which can be proved by the 'hill' areas after squeezed soft materials have cooled. Meanwhile, the alternating stress acts on the heat-softened wear tracks through the tribofilm, and the softened worn surface is repeatedly rolled and ground, which contributes to polishing effect of the worn surface (Fig. 9(f)).

#### 5. Conclusion

Coatings fine Ag, heat treated Ag and Ag/C were prepared by electrodeposition. Compared with Ag/C composite coating under boundary lubrication and dry sliding, the Ag coating with PAN grease exhibits excellent boundary-lubricated tribological characteristics and conductive capacity. Compared with the Ag coating under dry friction, the boundary tribofilm protects the worn surface from severely adhesive wear and oxidation, even induces the worn surface polished and stabilizes ECR values in run-in period except a slight high mean ECR value. Compared with under no current, the Ag coating under boundary lubrication can function under a current rage, 0–20 A. All in all, combined with PAN grease, Ag coating under boundary lubrication can hold huge promise for the sliding electrical application with simple design, excellent tribological performance and relatively low ECR.

#### Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant. 51575181).

#### References

- Slade PG. Electrical contacts: principles and applications. New York: Marcel Dekker; 1999. p. 155–270.
- [2] Shea JJ. Electrical contacts principles and applications. Electr Insul Mag 2000;16(2):37–8.
- [3] Yasar I, Canakci A, Arslan F. The effect of brush spring pressure on the wear behaviour of copper-graphite brushes with electrical current. Tribol Int 2007;40(9):1381-6.
- [4] He DH, Manory R. A novel electrical contact material with improved selflubrication for railway current collectors. Wear 2001;249(7):626–36.
- [5] Fouvry S, Jedrzejczyk P, Chalandon P. Introduction of an exponential formulation to quantify the electrical endurance of micro-contacts enduring fretting wear: application to Sn, Ag and Au coatings. Wear 2011;271(9–10):1524–34.
- [6] Mann D, Javey A, Kong J, Wang Q, Dai HJ. Ballistic transport in metallic nanotubes with reliable Pd ohmic contacts. Nano Lett 2003;3(11):1541–4.
- [7] Ma XC, He GQ, He DH, Chen CS, Hu ZF. Sliding wear behavior of copper–graphite composite material for use in maglev transportation system. Wear 2008;265(7– 8):1087–92.
- [8] Leung CH. Contact materials, silver graphite, silver-refractory-graphite. US: Springer; 2013. p. 468–70.
- [9] Rigou VI, Marginean G, Frunzăverde D, Câmpian CV. Silver based composite coatings with improved sliding wear behaviour. Wear 2012;s290-291(4):61-5.
- [10] Chen L, Chen X, Mu C, Qi G. Method of Preparing silver-based electrical contact materials with directionally arranged reinforcing particles. US Pat Appl 13/578378 2010
- [11] Rehani B, Joshi PB, Khanna PK. Fabrication of silver-graphite contact materials using silver nanopowders. J Mater Eng Perform 2010;19(1):64–9.
- [12] Azhar SM, Es-saheb M. Homogenous silver-tungsten composite production for electrical contacts. Res J Appl Sci Eng Tech 2015;9(8):549-60.
- [13] Ghorbani M, Mazaheri M, Khangholi K, Kharazi Y. Electrodeposition of graphitebrass composite coatings and characterization of the tribological properties. Surf Coat Tech 2001;148(1):71–6.
- [14] Ray N, Kempf B, Mützel T, Froyen L, Vanmeensela K, Vleugels J. Effect of WC particle size and Ag volume fraction on electrical contact resistance and thermal conductivity of Ag–WC contact materials. Mater Des 2015;85:412–22.
- [15] Li WS, Li YM, Zhang J, Liu Y, Dong HF. Progress in the research and application of silver-based electrical contact materials. Mate Rev 2011;25(11):34–9.
- [16] Slade PG. High Current Contacts: A review and tutorial. Zurich In: Proceedings of the 21st international conference on electrical contacts; 2002, pp. 413-424.
- [17] Braunovic M, Myshkin NK, Konchits VV. Electrical contacts: fundamentals, applications and technology. Florida: CRC press; 2006. p. 121–89.
- [18] Fan XQ, Xia YQ, Wang LP. Tribological properties of conductive lubricating greases. Friction 2014;2(4):343-53.
- [19] Fan XQ, Xia YQ, Wang LP, Pu JB, Chen TD, Zhang HB. Study of the conductivity and tribological performance of ionic liquid and lithium greases. Tribol Lett 2014;53(1):281–91.

- Tribology International 110 (2017) 161–172
- [20] Ge XY, Xia YQ, Feng X. Influence of carbon nanotubes on conductive capacity and tribological characteristics of poly(ethylene glycol-ran-propylene glycol) monobutyl ether as base oil of grease. J Hyg Epidemiol Microbiol Immunol 2016;8(66):396-7.
- [21] Ge XY, Xia XY, Shu ZY, Zhao XP. Erratum to: conductive grease synthesized using nanometer ATO as an additive. Friction 2015;3(1):56–64.
- [22] Cao ZF, Xia XY, Ge XY. Conductive capacity and tribological properties of several carbon materials in conductive greases. Ind Lub Tribol 2016;68(5):577–85.
- [23] Heeger AJ, Smith P, Fizazi A, Moulton J, Pakbaz K, Rughooputh S. Recent progress in conducting polymers: opportunities for science and Opportunities for technology. Synth Met 1991;41(3):1027–32.
- [24] Syed AA, Dinesan MK. Review: polyaniline-a novel polymeric material. Talanta 1991;38(8):815–37.
- [25] Yeh JM, Liou SJ, Lai CY, Wu PC, Tsai TY. Enhancement of corrosion protection effect in polyaniline via the formation of polyaniline-clay nanocomposite materials. Chem Mater 2001;13(3):1131-6.
- [26] Alam J, Riaz U, Ashraf SM, Ahmad S. Corrosion-protective performance of nano polyaniline/ferrite dispersed alkyd coatings. Coat Technol Res 2008;5(1):123–8.
- [27] Sun W, Chen G, Zheng L. Electroless deposition of silver particles on graphite nanosheets. Scr Mater 2008;59(10):1031–4.
- [28] Liu N, Qi S, Li S, Wu X, Wu L. Preparation and characterization of phenol formaldehyde/Ag/graphite nanosheet composites. Polym Test 2011;30(4):390–6.
- [29] Hu JJ, Muratore C, Voevodin AA. Silver diffusion and high-temperature lubrication mechanisms of YSZ-Ag-Mo based nanocomposite coatings. Compos Sci Technol 2007;67(3-4):336-47.
- [30] Wingert PC, Allen SE, Bevington R. The effects of graphite particle size and processing on the performance of silver-graphite contacts. IEEE Trans Compon hybrids Manuf Technol 1992;15(2):154–9.
- [31] Xie XL, Zhang L, Xiao JK, Qian ZY, Zhang T, Zhou KC. Sliding electrical contact behavior of AuAgCu brush on Au plating. Trans Nonferrous Met Soc China 2015;25(9):3029–36.
- [32] Wang J, Feng Y, Li S, Lin S. Influence of graphite content on sliding wear characteristics of CNTs-Ag-G electrical contact materials. Trans Nonferrous Met Soc China 2009;19(1):113–8.
- [33] Rabinowicz E, Ping C. Wear of silver-graphite brushes against various ring materials at high-current densities. Compon hybrids Manuf Technol IEEE Trans 1980;3(2):288–91.
- [34] Mo YH, Tao DH. Tribological performance of nano-tin as lubrication additives used in steel-copper tribo-pair. Ind Lub Tribol 2011;63(2):72–7, [6].
- [35] Roberts EW, Todd MJ. Space and vacuum tribology. Wear 1990;136(1):157–67.[36] Tomala A, Vengudusamy B, Ripoll MR, Suarez AN. Interaction between selected
- MoS2 nanoparticles and ZDDP tribofilms. Tribol Lett 2015;59(1):1–18. [37] Ruschau GR, Yoshikawa S, Newnham RE. Resistivities of conductive composites. J
- Appl Phys 1992;72(3):953–9.[38] Paria MK, Maiti HS. Electrical conductivity and defect structure of polycrystalline
- tin dioxide doped with antimony oxide. J Mater Sci 1982;17(11):3275–80. [39] Simmons JG. Generalized formula for the electric tunnel effect between similar
- electrodes separated by a thin insulating film. J Appl Phys 1963;34(6):1793–803.
  [40] Li L, Morris JE. Electrical conduction models for isotropically conductive adhesive joints. IEEE Trans Compon Packag Manuf Technol Part A 1997;20(1):3–8.
- [41] Marshall DW. Copper-based conductive polymers: a new concept in conductive resins. J Adhes 2000;74(1-4):301-15.