Conductive and tribological properties of TiN–Ag composite coatings under grease lubrication

Feihu LIN, Yanqiu XIA*, Xin FENG

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

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Abstract: TiN–Ag composite coatings were prepared by pulsed bias arc ion plating. X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) were applied to analyze the compositions of the coatings. Tribological properties of the coatings were studied using an MFT-R4000 ball-on-disk friction tester in the presence of lubricating greases containing multilayer graphene. Scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were used to analyze the worn surface compositions of the lubricating films. The results show that with the decrease in Ag in the film, hardness increased but electrical conductivity decreased. The coating with 10 at% Ag content shows the best friction-reducing and anti-wear properties, which can be attributed to the moderate content of Ag embedded in the TiN crystal gap that enhanced the grain bonding force to improve the anti-wear and self-lubricating ability. Graphene can be adsorbed on the coating as a solid lubricant.

Keywords: silver; tribology; contact resistance; lubricating grease

1 Introduction

Owing to the rapid development of technology, electrical contacts are ubiquitous in various devices [1]. In a power and signal transmission system, the reliability, stability, accuracy, and service life of the system depend on the electrical contact materials [2, 3]. Most of the electrical contacts are permanent connections, however, the relative motion of the contacts still occur owing to changing vibrations and temperatures because of the different thermal expansion coefficients of the electrical contacts [4–6]. Researchers have focused on the electrical conductivity and wear resistance of sliding contact components. However, the wear process between electric contacts is much more complicated when current-carrying occurs because it is not only affected by mechanical factors, such as hardness and roughness, but also

by current-thermal effects and operating conditions. In terms of tribology, the lubrication and wear resistance of electrical contact materials are two important factors that determine the long-term stable operation of sliding connections [7, 8]. When current carrying occurs, the heat caused by the combination of current-thermal effects and friction can significantly damage the contact pair, resulting in increased friction coefficient (COF) and wear rate [9].

Ag-based materials exhibit high conductivity, self-lubricating, anti-oxidation, anti-sulfuration, and anti-fusion welding properties. However, owing to high temperature and its low hardness, the Ag layer suffers from severe wear, plastic deformation, and surface oxidation during the current-carrying friction process, resulting in increased contact resistance [10]. Poor performances cannot justify high costs; hence, Ag-based materials are not widely used as electrical

* Corresponding author: Yanqiu XIA, E-mail: xiayq@ncepu.edu.cn

contact materials. Meanwhile, Cu-based materials are more advantageous compared with Ag-based materials in terms of cost [11], however, they oxidize easily in air under thermal conditions, resulting in high contact resistances.

In recent years, many new materials with superior mechanical properties have been synthesized and utilized for tribological applications. These materials have been effectively incorporated in the fabrication of functional coatings to reduce friction and wear [12]. The development of cermet coatings used as an electrical contact material is an attractive research area. André et al. [13] prepared Ti–Ni–C ceramic composite coatings by unbalanced magnetron sputtering. The results showed that composite coatings with high C content and certain Ni content exhibited excellent current-carrying tribological properties and the lowest dynamic contact resistance. Wang et al. [14] used magnetron sputtering to deposit Ti/MoS₂, Pb/MoS₂, and MoS₂ coatings to obtain a sliding electrical contact material with high electrical conductivity and good wear resistance. The results showed that the COF of the coating with a current of 0.5 A decreased, and the wear rate of the coating was higher than that without current. Lewin et al. [15] prepared a nanocrystalline TiC/ α -C nanocomposite coating by magnetron sputtering under different deposition conditions. They discovered that a coating containing a small portion of the α -C matrix phase demonstrated good electrical and tribological properties. Compared with Ag-based composites, some cermet composites have better mechanical properties and similar electrical conductivities [16].

Various conductive additives can affect electrical properties. Ge et al. [17] prepared conductive greases with carbon nanotubes, carbon black [18], ionic liquids [19–23], and Sb-doped SnO₂ [24]. They discovered that all these conductive additives improved the conductivity and tribological performances of conductive greases. Jia et al. [25, 26] discovered that graphene can significantly enhance the tribological and electrical properties of electrical contact materials. Cao et al. [27] used three types of nano-montmorillonite additives to afford lubricating greases. The results showed that the inorganic modification montmorillonite can increase the number of electron traps in the

base grease, thereby achieving excellent insulating performances. In addition, the additive (1.5 wt%) significantly enhances the anti-friction and anti-wear abilities.

Synergistic lubricants offer many advantages, such as better lubrication efficiency and service life, as well as reduced contact resistance and energy. Chen et al. [28] investigated the friction and wear properties of Ag, heat-treated Ag, and Ag–C coatings on Cu substrates with and without grease lubrication. They discovered that the electrical, friction-reducing, and anti-wear properties of Ag coatings were better than those of the remaining layers, which was crucial to satisfy the requirements of stability, safety, and efficient operation of power equipment.

The first objective of this study is to investigate the mechanical properties of TiN–Ag coatings on a Cu substrate; the second objective is to prepare a highly conductive grease by adding graphene particles; and the third objective is to study the tribological and electrical properties of TiN–Ag coatings in the presence of boundary lubrication and current carrying.

Graphene has been widely used as a solid lubricant or lubricant additive. It is a semi-metal because of the metallic bonding in the in-plane direction; hence, its conductivity is high. Therefore, graphene is added to polyurea grease to improve its conductive and tribological properties. To investigate the relationship between electrical properties and tribological behaviors, friction and wear tests are performed, which include the presence of both boundary lubrication and current carrying.

2 Experimental

2.1 Materials

Polyurea grease was obtained from Changsha Zhongcheng Petrochemical Co., Ltd. (China) and the base oil was poly alpha-olefins (PAO) (The parameters are shown in Table 1 and 2). Multilayer graphene (MLG) was obtained from State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences and was added to the grease. Acetone was purchased

Table 1 Typical data of PAO.

Item	Typical date	Experiment method
Appearance	Clean and transparent	Visualization
Viscosity 40 °C	396	American Society of Testing
Viscosity 100 °C	39	Materials ASTM, D445-2018
Viscosity index	147	ASTM D2270-2010
Pour point	−36	ASTM D97-2016
Flashpoint (°C)	281	ASTM D2893-2003

Table 2 Typical data of polyurea grease.

Item	Typical data	Experiment method
Appearance	Smooth grease	Visualization
Dropping point (°C)	> 300	GB/T 3498-2008
Non-working cone penetration/0.1 mm	278	GB/T 269-1991
Corrosion (copper sheet, aluminum sheet, 100 °C, 3 h)	Up to stand	SH/T 0331-1992
Evaporation (99 °C, 22 h) (%)	0.65	GB/T 7325-1987
Contact resistance stability factor, <i>K</i>	0.57	Enterprise method
pH	7	Enterprise method
Salt spray test	A	GB/T 2423.17-2008
Low-temperature performance (−40 °C, 2 h)	No crack	GB/T 2423.1-2008

from Sinopharm Chemical Reagent Co., Ltd., China. Ag and Ti targets were purchased from Oukai Sputtering Target Technology Co., Ltd., China.

MLG (0.2 wt%) was added to the ethanol solution as an additive, and the polyurea grease was added and mixed uniformly. Subsequently, ethanol was evaporated to yield polyurea grease containing MLG. Finally, the mixture was cooled to room temperature and homogenized using a three-roll mill to obtain multilayer graphene grease (MGLG).

2.2 Coating deposition

TiN–Ag composite coatings were deposited on Cu bases (25 mm × 25 mm × 5 mm) by a DG-2-Z Y arc ion plating system. The Cu bases were polished using sandpapers and a diamond polishing agent to the required roughness of approximately 0.02 μm. Polished Cu sheets were ultrasonically cleaned in

acetone for 15 min. In this system, two vertically arranged identical Ag and Ti circular targets were used, i.e., 99.9% purity, diameter of 6 cm, and separated by 10 cm in the chamber. The substrates were clamped to a stainless steel holder in a vacuum chamber with different angles between the two targets to control the Ag content of the coatings. The distance between the bases of the bracket and the target was approximately 20 cm (Fig. 1).

When the chamber had been pumped down to a base pressure less than 6.0×10^{-3} Pa using a mechanical pump and molecular pump, Ar gas was introduced into the chamber to 0.3 Pa. Before the deposition, the substrate temperature and duty cycle were adjusted to 150 °C and 20%, respectively, and the substrates were sputtered by Ar ions with a pulsed bias voltage of −800 V in 5 min. With the preparatory steps completed, the substrate temperature and duty cycle were adjusted to 300 °C and 40%, respectively; the bias voltage was decreased to 200 V and the Ag and Ti targets were maintained at 60 and 80 A, respectively. The Ti–Ag interface layer was deposited onto two types of substrates to enhance the bonding property in 5 min. Subsequently, the substrate temperature and duty cycle were increased to 500 °C and 80%; the nitrogen gas flow rate was 56 sccm after the Ar gas was discontinued, and the operating pressure was approximately 0.4 Pa. Subsequently, TiN–Ag coatings were deposited onto the interface layer, and the coating thickness was maintained at 10 μm. Finally, annealing was performed *in situ* to form silver nanoparticles in the coating.

Fig. 1 Sketch of the vacuum chamber.

2.3 Characterization

The surface morphology and Ag content of the TiN–Ag coatings were analyzed through scanning electron microscope (SEM; EVO-18, Zeiss) and energy dispersive spectroscopy (EDS; Bruker), respectively. The Vickers hardness of these coatings was measured using a microhardness meter (AE TTX, Anton Paar). The bonding strength of the samples was qualitatively tested using a bending tester (RST³, Anton Paar). The phase structure was analyzed by X-ray diffraction (XRD; D/Max-2400, Rigaku). The binding energies of the chemical composition and the carbon allotrope on wear scars were analyzed through X-ray photoelectron spectroscopy (XPS; PHI-5702, American Institute of Physics Electronics Company) and Raman microscopy (inVia, Renishaw), respectively.

2.4 Tribological and electrical conductivity tests

The tribological properties and contact resistance of the samples were investigated using a current-carrying friction and wear tester (MFT-R4000) with a ball-on-disk configuration (Fig. 2). The upper tribological pair was a Cu ball (ϕ 5 mm). Grease was coated onto the contact area of the sliding pair. The upper pair was driven to yield a reciprocating motion against the lower coatings under grease lubrication. The surrounding humidity and temperature were maintained at approximately 40% and 20 °C for all tests, respectively. Constant static loads were applied to the upper pair (5, 10, and 15 N). Constant voltages were applied (0.5 and 1.5 V) under the sliding pair during every 30 min. The length of the sliding track was 4 mm, and the sliding frequency was 2 Hz. The COF and instantaneous current was recorded by a computer attached to this instrument.

The electrical contact resistance (ECR) can be calculated using Ohm's law, and its stability is expressed by the standard deviation (SD). The mean value of the COF was calculated, and the wear rate was calculated using Eq. (1):

$$W = \frac{V}{S \times L} = \frac{H \times A}{S \times L} \quad (1)$$

where W is the substrate wear rate, V is the wear scar volume, S is the total sliding distance, L is the

Fig. 2 Schematic diagram of electrical conductivity.

applied load, H is the grinding crack length, and A is the cross-sectional area of the wear scar.

3 Results and analysis

3.1 Surface morphology of coatings

Figures 3(a), 3(e), and 3(i) show that many droplets and pits appeared on the coating surfaces, which were likely caused by bias arc-ion plating [29]. Many Ag nanoparticles embedded in TiN crystal can be observed [30, 31]. Figure 3(i) shows that when the Ag content increased to a sufficiently high amount, the surface became coarser with plenty of sputtered grains on the surface.

As shown in Fig. 3, all related elements were distributed uniformly in the TiN–Ag coatings, implying that the coatings were prepared successfully. A small amount of Ag can be observed in Fig. 3(d), whereas a large amount in Fig. 3(l). These are consistent with the EDS analysis.

3.2 Phase structure and chemical composition

Figure 4 shows the XRD patterns of the coatings with 2 at%, 10 at%, and 30 at% Ag contents. The phase compositions were determined based on the Bragg angle and the intensity of diffraction peaks. The face-centered cubic (fcc) TiN and fcc-Ag phase were generated through the deposition of the coatings. With the increase in Ag content, the Ag phase position exhibited stronger diffraction peaks. The TiN diffraction peaks were weaker than the Ag peaks with increased Ag content, because the

Fig. 3 Surface morphologies of the coatings: (a) TiN–Ag coating with 2 at% Ag content, (e) TiN–Ag coating with 10 at% Ag content, (i) TiN–Ag coating with 30 at% Ag content, and (b–d, f–h, j–l) the surface elements distribution in green frames by EDS corresponding to (a, e, and i).

Fig. 4 XRD pattern of coatings with 2 at%, 10 at%, and 30 at% Ag contents.

increase in Ag content resulted in difficult fcc-TiN crystallization.

3.3 Physical property of the coatings

Table 3 shows that the bonding strength of the coatings did not change significantly with Ag content, whereas the Vickers hardness of the samples increased rapidly with the decrease in Ag content. When the Ag content decreased to 2 at%, the hardness reached the highest value of 25.7 GPa. If the Ag content continues to decrease, the hardness

Table 3 Critical load (LC1), Vickers hardness (HV), and module of elasticity (EIT) of TiN–Ag coatings with different Ag contents.

Ag content (at%)	LC1 (N)	HV (GPa)	EIT (GPa)
2	13.2	25.7	392.5
10	12	20.7	379.7
30	No crack	13.7	227.9

will decrease as well [31]. Furthermore, the elastic modulus increases rapidly with the decrease in Ag content. As the Ag content decreases to a certain extent, the elastic modulus of the coating increases, which indicates that the coating has a higher resistance to plastic deformation.

3.4 Conductive and tribological properties

In general, the high temperature generated in the electrical contact zone can be changed by different current densities, which may significantly affect the tribological and electrical performances. To analyze the conductive and tribological properties of the TiN–Ag coatings under current-carrying, current densities were adjusted in the experiment by changing the loop voltage.

Figures 5(a) and 5(c) compare the coatings with

2 at%, 10 at%, and 30 at% Ag contents and a Cu base under 0.5 V. When the Ag content was 30 at%, the COF was the lowest compared with those of others. With the decrease in Ag content, the COFs of the coatings increased, and the COF of the 2 at% Ag content was much higher than that of the Cu base, indicating that the self-lubricating ability weakened with decreasing Ag content. The COF of the coating with 2 at% Ag content increased significantly to approximately 0.4. This implies that the lower the Ag content, the lower is the loading capacity. Figure 5(b) shows the ECR versus time, which can be used to characterize the electro-tribological properties. As shown in Figs. 5(b) and 5(c), the Ag content did not significantly affect the ECR at a certain range, e.g., the electrical conductivity increased only slightly as the Ag content reached 30 at%, whereas the current stabilities of the Cu base and 10 at% Ag coating were relatively higher

than those of others. As shown in Fig. 5(d), the wear rate of the coating with 10 at% Ag was minimal compared with that of the coatings with other Ag contents, and its wear rate was slightly less than that of the Cu base. However, although the reduction in Ag content increased the hardness of the coating, the wear rate of the coating with 2 at% Ag content increased significantly.

As the load voltage increased to 1.5 V, compared with Figs. 5(a), 5(c) and Figs. 6(a), 6(c), the COF of the coatings decreased slightly. As shown in Fig. 6(b), as the load voltage increased to 1.5 V, the contact resistance of different materials increased significantly, which might be attributed to the higher temperature at the surrounding of the friction pair contact area. However, as shown in Fig. 6(d), as the voltage increased from 0.5 to 1.5 V, the coatings with 10 at% Ag content exhibited better anti-wear properties, especially at high currents. This might because the

Fig. 5 Evolution of (a) COF, (b) ECR for Cu base and TiN-Ag coating samples, (c) average of COF and SD of ECR, and (d) wear rate under grease (voltage: 0.5 V; load: 15 N).

moderate Ag content yielded good effects on the lubricating coatings at high temperatures. However, this contributed negatively to the Cu base and the coatings with 2 at% and 30 at% Ag contents because the wear rate was more severe as the voltage increased. In summary, it was discovered that when the Ag content was 10 at%, the coating exhibited excellent anti-wear and electrical properties.

3.5 Wear scars of TiN–Ag coating surface

Figures 7 and 8 show the surface morphologies of worn scars. As shown in Figs. 7(b) and 8(b), at the Ag content of 2 at% and loading of 15 N, the adhesive wear damaged the surface and further deteriorated the surface when the voltage increased to 1.5 V. Widespread pulling-out, avulsion, and some furrows were observed on the worn surfaces. The phenomenon was attributed to the failure of the boundary lubricating film. Figures 7(c) and 7(d) show slight sliding cracks on the surface under 0.5 V. As the voltage increased to 1.5 V, many particles,

microprotrusions, and slight polishing appeared on the worn surface, as shown in Figs. 8(c) and 8(d). The particles might be mounts of Ag grains precipitated at a relatively high temperature [30], and arc erosion was produced in pairs. Figures 7(f) and 8(f) show that not only many severe furrows and pits, but also some microcutting and microfraction appeared on the surface; this could be attributed to the embedded Ag nanocrystals in TiN crystal, which resulted in constitutional defects and hence yielded an unstable coating structure, thereby reducing the anti-wear property of the coating. If the current is sufficiently large and the conductive medium has high conductivity, then arc erosion can be generated at a low voltage.

3.6 Raman spectra and XPS analyses of worn surfaces

Table 3 shows the Raman shift list. To investigate the absorption films and the partial carbonization of the grease on the wear scar under current-carrying

Fig. 6 Evolution of (a) COF, (b) ECR for the Cu base and TiN–Ag coating samples, (c) average of COF and SD of ECR values; (d) wear rate under grease (voltage: 1.5 V; load: 15 N).

Fig. 7 SEM morphologies of (a) worn surfaces and (b) TiN-Ag coatings with 2 at% Ag content; (c, d) TiN-Ag coatings with 10 at% Ag content; (e, f) TiN-Ag coatings with 30 at% Ag content under MGLG (voltage: 0.5 V; load: 15 N; frequency: 2 Hz; stroke: 4 mm).

Fig. 8 SEM morphologies of (a) worn surfaces and (b) TiN-Ag coatings with 2 at% Ag content; (c, d) TiN-Ag coatings with 10 at% Ag content; (e, f) TiN-Ag coatings with 30 at% Ag content under MGLG (voltage: 1.5 V; load: 15 N; frequency: 2 Hz; stroke: 4 mm).

conditions, a Raman spectrum is shown (Fig. 9). Figure 9(a) shows the Raman spectrum of the wear scar with 2 at% Ag coating. The Raman spectrum peaks only at approximately 230 and 530 cm^{-1} , and almost no adsorption films were detected on the wear scar. Figure 9(b) shows the Raman spectrum of the surface with 10 at% Ag coating, where a weak absorption peak appeared near 1,111 cm^{-1} , which can form adsorption films through additives in grease. Several other absorption peaks appeared in dark and bright spots. The broad asymmetric

Fig. 9 Raman spectrum of wear scar of (a) TiN–Ag of 2 at% Ag, (b) TiN–Ag of 10 at% Ag, and (c) TiN–Ag of 30 at% Ag (voltage: 1.5 V; load: 15 N).

absorption peak between 1,230 and 1,580 cm^{-1} , and the obvious peaks indicate the formation of physical adsorption films of amorphous carbon or graphene. The amorphous carbon was likely owing to the partial coking of PAO and carbonaceous additives at high temperatures and current-carrying conditions. The D peak generated at approximately 1,350 cm^{-1} was derived from the breathing pattern of the disordered sp^2 carbon atom, and the G peak at approximately 1,580 cm^{-1} from the in-plane bond extension of all sp^2 atom pairs [32, 33]. The absorption peak at 2,874–2,903 cm^{-1} was owing to the amount of PAO adsorbed on the surface of the wear scar during the tribological process [34]. It is apparent from Fig. 9(c) that a broad asymmetric peak appeared in the range of 1,100–1,700 cm^{-1} , and strong D and G peaks were identified by fitting Raman spectroscopy. Stronger adsorption film layers, which can be produced by amorphous carbon and graphene, were formed.

The composition of the adsorbed films on the worn surface was further analyzed through XPS-peak-differentiating analysis. As shown in Figs. 10(a), 10(b), and 10 (c), the wear scar on sample B exhibited better absorbing films compared with the others. Furthermore, Fig. 10(d) shows that Cu barely appeared in sample B, which was attributed to the excellent synergistic lubrication, indicating complex chemicals with different-level reactions during the current-carrying friction. The strong Cu peak in sample C was owing to the rupture of the TiN–Ag coating to expose the substrate, and the weak peak of sample A was attributed to the physical adsorption of abrasive Cu chips on the surface of the coating. Figure 11(a) shows the XPS spectra of C 1s on the wear scars of the samples to clarify the composition of absorbing films containing C. The strong peak at 284.9 eV of C 1s can be

Table 3 Raman shift list.

Index	Raman shift (cm^{-1})
Olefin	1,655–1,677; 2,920–2,937
Titanium nitride	210–320; 500–680
Poly- α -olefin	2,800–3,000
Graphite	1,580–2,700

Fig. 10 XPS spectra of several elements on the worn surface of (A) TiN-Ag of 30 at% Ag content, (B) TiN-Ag of 10 at% Ag content, and (C) TiN-Ag of 2 at% Ag content lubricated with MGLG (voltage: 1.5 V; load: 15 N).

Fig. 11 XPS spectra of the worn surface of TiN-Ag (10 at%) with fitting peaks (voltage: 1.5 V; load: 15 N).

assigned to the C–H chemical bond of organic C on the surface scar, and the peak at binding energy 285.5 eV was associated with the C–C hydrocarbon. The two peaks were derived from the physically adsorbed films of PAO or other organic chemical absorbing films [35]. In addition, the weak peak at 288.5 eV belonged to the C–O chemical bond [36]. As shown in Fig. 10(b), the peak of N 1s centered at 399.9 eV, corresponding to the C–N bond in

organic nitrogen compounds [35–38]. This was owing to the high-temperature chemical reaction during the friction process on the coating surface. The peaks of O 1s located at 530 and 531.8 eV, as shown in Figs. 10(c) and 11(c), were those of the C=O organic compound [36] and TiO₂ [38], respectively. This illustrates that the surface of the coatings with moderate Ag content under grease lubrication forms ideal adsorption or reaction films.

4 Discussion

Most electrical contact materials are Cu or Cu-based Ag-plated sheets, which offer better conductivities and current stability compared with other materials; however, their anti-wear property is poor owing to their low hardness. Therefore, they cannot satisfy cases that require high wear resistance, system stability, and long life circles. Ceramic metal composites are expected to solve this problem. However, it is difficult to lubricate ceramic composites, and their self-lubricating ability and conductivity are not sufficient to satisfy the requirements of reciprocating friction situations in the presence of current-carrying [39].

In this study, when the Ag content was 2 at%, the COF of the TiN–Ag composite coating was 0.4–0.5 and the fluctuation was significant. The main wear form was severe adhesive wear, indicating that a stable boundary lubrication was difficult to form, and its tribological property was much lower than that of coatings under the same conditions. When the Ag content of the coating was 10 at% and 30 at%, respectively, the COF was maintained in the range of 0.05–0.15. The main wear forms were slight adhesive wear and abrasive wear, and distinct adsorption films were detected on the surface of the wear scars. These are the general case in boundary lubrication.

When the Ag content (2 at%) was low, the contact area of the coating exhibited severe wear. One of the reasons was that the surface of the coating could not easily produce an Ag-rich layer under current-carrying friction, and microbumps and pits could not easily deform plastically to form a smooth surface, resulting in poor solid lubrication performance. Because the true contact area of the friction pairs was reduced and the contact resistance of the coating was relatively high, a large amount of heat was generated to cause a significant increase in the temperature of the contact region, which might cause the grease to fail. Furthermore, an extremely low Ag content resulted in failed adsorption films. The polar group in the grease and the long-chain structure of the hydrocarbon could not be adsorbed on the surface by weak van der Waals force, and extreme pressure additives could not react with the surface coating and form chemical adsorption films. In addition, the significantly different hardness between the two friction pairs

produced a large amount of worn debris serving as three-body wear under boundary lubrication. This was because the small contact area between the wear debris and the coatings tended to produce great stress. Even if the soft material is plastically deformed, the stress applied to the hard material will far exceed the yield limit, resulting in serious wear. In addition, the residual particles generated between the two friction pairs can cause further wear. Therefore, the worse synergistic lubrication effect results in severe adhesive wear in the contact area.

As the Ag content increased to an appropriate range, the tribological property of the coating was improved significantly, especially at high voltages. This occurred because when the applied voltage increased, the temperature around the contact point of the friction pairs increased, and the high specific surface area of the Ag nanoparticles rendered them highly chemically active. Under the action of cyclic stress and high temperature, it is easy to form a Ag-rich layer on the friction interface [29, 39–41]. In addition, the high temperature of the contact area softened the coatings; furthermore, with a certain polishing effect, the direct contact area of the friction pair increased, and thereby reducing the peak pressure. These factors facilitated the formation of stable lubricating and adsorption films on the surface. The moderate Ag content-enabled most of the Ag grains to be intercalated between the TiN crystal gap and increased the bonding force between the grains, which reduced the generation of internal stress, ensuring a more stable structure in the coatings to reduce avulsion [40]. In addition, when the hardness of the coating approached that of the upper Cu ball, the wear debris decreased, and thereby reducing the three-body wear.

As the Ag content continued to increase, a thick Ag-rich film was formed on the coating surface during friction in the presence of current-carrying. The tribological properties of the TiN–Ag coatings improved owing to the use of grease. However, the materials existed primarily in the form of grains inside the coatings, which decreased the stability of the crystal structure and weakened the anti-wear property.

The contact resistance of the coatings changed

slightly according to the Ag content, and a moderate Ag content improved the electrical property. The conductive mechanism under boundary lubrication can be attributed to the quantum tunnel effect. When the Ag content was 2 at%, the conductivity of the coating was relatively poor, because the discontinuous Ag-rich layer and low Ag content increased the electrical resistance, and significant adhesive wear occurred on the contact surface, causing the surface Ag-rich layer to fail and the current stability to decline. This caused the contact face of the friction pairs to be unstable and the contact resistance to fluctuate significantly. When the Ag content was approximately 10 at%, the sample indicated a lower ECR and SD of the ECR compared with those with 2 at% Ag content. This occurred because of the relatively thick Ag-rich layer and the low resistance of the coatings, as well as the more stable coating conductivity by the Ag-rich layer. In addition, the SD of the ECR caused the moderate content of Ag embedded in the TiN crystal gap to enhance the grain bonding force to reduce wear. As the Ag content increased to a high percentage (30 at%), the coatings showed a comparative higher ECR. This was because the coating surface was smoothed by deformation and microshear effect, and thereby thickening the lubricating film layer and causing a high electrical resistance. In addition, the high contact resistance produced a significant amount of heat and enabled an oxidation layer, which had a high resistivity, to form on the wear surface, and thereby increasing the contact resistance.

As reported in previous studies, TiN coatings possess excellent anti-wear properties and lower resistance values, however, the wear volume can reach $1.401 \times 10^{-4} \text{ mm}^3$ under non-current-carrying conditions, which is much higher than the wear rate obtained in this experiment [42]. Adding Ag to TiN can yield better tribological properties, and the lowest wear rate was $1 \times 10^{-7} \text{ mm}^3/(\text{N} \cdot \text{mm})$ with 0.8 at% Ag content under room temperature and non-current-carrying conditions, which was close to the optimal value obtained in this experiment [31]. The experimental rule of TiN–Ag at high temperatures was reflected in the results of this experiment, but the wear was more severe compared with the wear

morphology [43], indicating that the local high temperature caused by the current–thermal effect was one of the main influencing factors of wear, and that the grease exerted a good lubrication effect. In our previous studies, excellent current-carrying tribological properties were obtained by preparing Ag coatings and PAN grease [28]. Subsequently, using TiN–Ag coatings and MGLG, wear resistance was further improved while ensuring electrical performance.

5 Conclusions

In this study, a synergetic strategy based on conductive grease and TiN–Ag coatings of different Ag contents was developed to enhance tribological and electrical properties for sliding electrical contact applications. The conclusions are as follows:

1) Both fcc-TiN and fcc-Ag phases were generated in the coatings, as shown by XRD. With increasing Ag content, the main diffraction peaks of the Ag phase became stronger, but the main diffraction peaks of the TiN phase became weaker. This deteriorated the stable coating structure, resulting in lower hardness and elastic modulus.

2) At 10 at% Ag content, the coating demonstrated excellent anti-wear performance, and its electrical and tribological properties were excellent under high voltages. This was because a large amount of Ag precipitated during the current-carrying friction experiment, which improved the self-lubricating performance. In addition, the addition of Ag improved the electrical properties of the coating.

3) MGLG and TiN–Ag (10 at%) coating demonstrated a good synergistic lubrication effect. This was because the graphene and adsorption films formed on the friction surface demonstrated anti-wear and conductive properties. Furthermore, MLG formed conductive paths in the grease to enhance the electrical performance.

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References

- [1] Slade P G. *Electrical Contacts: Principles and Applications*. New York (USA): CRC Press, 1999.
- [2] Cho K H, Hong U S, Lee K S, Jang H. Tribological properties and electrical signal transmission of copper-graphite composites. *Tribol Lett* **27**(3): 301–306 (2007)
- [3] Senouci A, Zaidi H, Frene J, Bouchoucha A, Paulmier D. Damage of surfaces in sliding electrical contact copper/steel. *Appl Surf Sci* **144–145**: 287–291 (1999)
- [4] Liu X L, Cai Z B, He J F, Peng J F, Zhu M H. Effect of elevated temperature on fretting wear under electric contact. *Wear* **376–377**: 643–655 (2017)
- [5] Yang H J, Hu Y, Chen G X, Zhang W H, Wu G N. Correlation between the wear and vibration of the contact strip in a contact wire rubbing against a contact strip with electrical current. *Tribol Trans* **57**(1): 86–93 (2014)
- [6] Noël S, Correia S, Alamarguy D, Gendre P. Fretting behaviour of various intermetallic compounds in electrical contacts: Influence on reliability. *Wear* **271**(9–10): 1515–1523 (2011)
- [7] Antler M. Electrical effects of fretting connector contact materials: A review. *Wear* **106**(1–3): 5–33 (1985)
- [8] Myshkin N K. Tribological problems in electrical contacts. *Tribol Int* **24**(1): 45–49 (1991)
- [9] Babu S S, Santella M L, Feng Z, Riemer B W, Cohron J W. Empirical model of effects of pressure and temperature on electrical contact resistance of metals. *Sci Technol Weld Join* **6**(3): 126–132 (2001)
- [10] Rudolphi Å K, Jacobson S. Gross plastic fretting mechanical deterioration of silver coated electrical contacts. *Wear* **201**(1–2): 244–254 (1996)
- [11] Hasegawa M, Imai K, Makimoto J, Sawa K. An experimental study on operating characteristics of Ag, Pd and Cu contacts in argon atmosphere. In *Proceedings of the Forty-ninth IEEE Holm Conference on Electrical Contacts*, Washington, DC, USA, 2003: 190–197.
- [12] Khadem M, Penkov O V, Yang H, Kim D. Tribology of multilayer coatings for wear reduction: A review. *Friction* **5**(3): 248–262 (2017)
- [13] André B, Lewin E, Jansson U, Wiklund U. Friction and contact resistance of nanocomposite Ti–Ni–C coatings. *Wear* **270**(9–10): 555–566 (2011)
- [14] Wang P, Yue W, Lu Z B, Zhang G G, Zhu L N. Friction and wear properties of MoS₂-based coatings sliding against Cu and Al under electric current. *Tribol Int* **127**: 379–388 (2018)
- [15] Lewin E, Olsson E, André B, Joelsson T, Öberg Å, Wiklund U, Ljungcrantz H, Jansson U. Industrialisation study of nanocomposite Nc-TiC/a-C coatings for electrical contact applications. *Plasma Processes Polym* **6**(S1): S928–S934 (2009)
- [16] Öberg Å, Kassman Å, André B, Wiklund U, Lindquist M, Lewin E, Jansson U, Högborg H, Joelsson T, Ljungcrantz H. Conductive nanocomposite ceramics as tribological and electrical contact materials. *Eur Phys J Appl Phys* **49**(2): 22902 (2010)
- [17] Ge X Y, Xia Y Q, 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 Tribol* **138**(1): 011801 (2016)
- [18] Cao Z F, Xia Y Q, Ge X Y. Conductive capacity and tribological properties of several carbon materials in conductive greases. *Ind Lubricat Tribol* **68**(5): 577–585 (2016)
- [19] Fan X Q, Xia Y Q, Wang L P. Tribological properties of conductive lubricating greases. *Friction* **2**(4): 343–353 (2014)
- [20] Wang Z Y, Xia Y Q, Liu Z L, Wen Z Z. Conductive lubricating grease synthesized using the ionic liquid. *Tribol Lett* **46**(1): 33–42 (2012)
- [21] Fan X Q, Wang L P, Xia Y Q. Oil-soluble lithium salts as novel lubricant additives towards improving conductivity and tribological performance of bentone grease. *Lubricat Sci* **27**(6): 359–368 (2015)
- [22] Fan X Q, Xia Y Q, Wang L P, Pu J B, Chen T D, Zhang H B. Study of the conductivity and tribological performance

- of ionic liquid and lithium greases. *Tribol Lett* **53**(1): 281–291 (2014)
- [23] Ge X Y, Xia Y Q, Shu Z Y. Conductive and tribological properties of lithium-based ionic liquids as grease base oil. *Tribol Trans* **58**(4): 686–690 (2015)
- [24] Ge X Y, Xia Y Q, Shu Z Y, Zhao X P. Erratum to: Conductive grease synthesized using nanometer ATO as an additive. *Friction* **3**(4): 352 (2015)
- [25] Jia Z F, Li H Q, Yao Z, Frazer L, Qian B S, Borguet E, Ren F, Dikin D A. Electrical and mechanical properties of poly(dopamine)-modified copper/reduced graphene oxide composites. *J Mater Sci* **52**(19): 11620–11629 (2017)
- [26] Jia Z F, Zhao P P, Ni J J, Shao X, Zhao L M, Huang B X, Ge B, Ban C L. The electrical conductivities and tribological properties of vacuum hot-pressed Cu/reduced graphene oxide composite. *J Mater Eng Perform* **26**(9): 4434–4441 (2017)
- [27] Cao Z F, Xia Y Q, Xi X. Nano-montmorillonite-doped lubricating grease exhibiting excellent insulating and tribological properties. *Friction* **5**(2): 219–230 (2017)
- [28] Chen J H, Xia Y Q, Hu Y C, Hou B Y. Tribological performance and conductive capacity of Ag coating under boundary lubrication. *Tribol Int* **110**: 161–172 (2017)
- [29] Zhang M. Honeycomb-like nanocomposite Ti–Ag–N films prepared by pulsed bias arc ion plating on titanium as bipolar plates for unitized regenerative fuel cells. *J Power Sources* **198**: 196–202 (2012)
- [30] Kelly P J, Li H, Benson P S, Whitehead K A, Verran J, Arnell R D, Iordanova I. Comparison of the tribological and antimicrobial properties of CrN/Ag, ZrN/Ag, TiN/Ag, and TiN/Cu nanocomposite coatings. *Surf Coat Technol* **205**(5): 1606–1610 (2010)
- [31] Ju H B, Yu L H, Yu D, Asempah I, Xu J H. Microstructure, mechanical and tribological properties of TiN–Ag films deposited by reactive magnetron sputtering. *Vacuum* **141**: 82–88 (2017)
- [32] Wang J, Guo X C, He Y, Jiang M J, Gu K C. Tribological characteristics of graphene as grease additive under different contact forms. *Tribol Int* **127**: 457–469 (2018)
- [33] Fan X Q, Xia Y Q, Wang L P, Li W. Multilayer graphene as a lubricating additive in bentone grease. *Tribol Lett* **55**(3): 455–464 (2014)
- [34] Praveena M, Guha K, Ravishankar A, Biswas S K, Bain C D, Jayaram V. Total internal reflection Raman spectroscopy of poly(alpha-olefin) oils in a lubricated contact. *RSC Adv* **4**(42): 22205–22213 (2014)
- [35] Yang G B, Zhang J F, Zhang S M, Yu L G, Zhang P Y, Zhu B L. Preparation of triazine derivatives and evaluation of their tribological properties as lubricant additives in poly-alpha olefin. *Tribol Int* **62**: 163–170 (2013)
- [36] Zhang M, Wang X B, Fu X S, Xia Y Q. Performance and anti-wear mechanism of CaCO₃ nanoparticles as a green additive in poly-alpha-olefin. *Tribol Int* **42**(7): 1029–1039 (2009)
- [37] Jia Z F, Xia Y Q, Pang X J, Hao J Y. Tribological behaviors of different diamond-like carbon coatings on nitrided mild steel lubricated with benzotriazole-containing borate esters. *Tribol Lett* **41**(1): 247–256 (2011)
- [38] Mandrino D, Podgornik B. XPS investigations of tribofilms formed on CrN coatings. *Appl Surf Sci* **396**: 554–559 (2017)
- [39] Ray N, Kempf B, Mützel T, Froyen L, Vanmeensel 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* **85**: 412–422 (2015)
- [40] Mulligan C P, Gall D. CrN-Ag self-lubricating hard coatings. *Surf Coat Technol* **200**(5–6): 1495–1500 (2005)
- [41] Endrino J L, Nainaparampil J J, Krzanowski J E. Microstructure and vacuum tribology of TiC–Ag composite coatings deposited by magnetron sputtering-pulsed laser deposition. *Surf Coat Technol* **157**(1): 95–101 (2002)
- [42] Liu L, Shen H H, Liu X Z, Guo Q, Meng T X, Wang Z X, Yang H J, Liu X P. Wear resistance of TiN(Ti₂N)/Ti composite layer formed on C17200 alloy by plasma surface Ti-alloying and nitriding. *Appl Surf Sci* **388**: 103–108 (2016)
- [43] Köstenbauer, H, Fontalvo G A, Mitterer C, Keckes J. Tribological properties of TiN/Ag nanocomposite coatings. *Tribol Lett* **30**(1): 53–60 (2008)

Feihu LIN. He received his bachelor degree from Shaanxi University of Science & Technology University in 2015, China. He is currently a master student at North China

Electric Power University. His research interests focus on preparation and tribological property investigation of coatings and lubricating greases.

Yanqiu XIA. He received his Ph.D. degree in mechanical engineering from Northeastern University, China, in 1999, and was selected as a professor (Hundreds Talent Program of Chinese Academy of

Science) in 2007. He joined the School of Energy Power and Mechanical Engineer, North China Electric Power University in 2010. His current position is as a professor. His research areas cover the tribology of mechanical and electrical equipment, oil monitoring, and artificial intelligence.

Xin FENG. She received her Ph.D. degree in systems engineering from Northeastern University, in 2007, China. She joined the School of Energy Power and Mechanical

Engineer, North China Electric Power University in 2010. Her current position is as an associate professor. Her research areas cover tribology and artificial intelligence.