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RESEARCH ARTICLE

Conductive grease synthesized using nanometer ATO as an additive

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Abstract: A new conductive grease was synthesized using a nanometer powder, i.e., Sb doped SnO_2 (ATO), as an additive. The typical properties of this new conductive grease were investigated in detail. The results indicate that ATO can dramatically improve the dropping point and reduce contact resistance. The tribological properties of the new conductive grease were investigated using the MFT-R4000 reciprocating friction and wear tester. The tribol-test results indicate that ATO can dramatically improve the tribological properties of the grease. When the ATO concentration is 0.1wt%, the grease demonstrates the best friction reduction properties; when the concentration is 0.5wt%, the grease demonstrates the best anti-wear properties. The worn surfaces were observed and analyzed by scanning electron microscopy and energy-dispersive X-ray spectroscopy, and the friction mechanisms for the new conductive grease are proposed. The excellent tribological properties of the new conductive grease are attributed to the mechanical effect of ATO, and the film formed by Sn and Sb elements or metallic oxide deposited on worn surfaces during the friction process.

Keywords: Sb doped SnO_2 (ATO); conductive grease; contact resistance; friction and wear; wear mechanism

1 Introduction

When lubricating grease is applied to the conductive parts of electrical equipment, such as electrical switches, integrated circuits, microelectronic mechanical systems, power machines, power transmission and transformation equipment [1–3], it not only reduces friction and wear in the mechanical systems but also plays a significant role in saving energy and reducing CO_2 emission by improving the lubrication efficiency, reducing the contact resistance, and prolonging service life; thus, the conductivity capacity and tribological properties of the grease become particularly important [4]. The conventional method of preparing conductive greases is by adding conductive additives to the base grease. However, existing conductive additives have many problems: While possessing good electrical conductivity, precious metal powders such as gold, silver, and nickel are too expensive to be suitable for large-scale employment; copper powder is cheap but is easily oxidized; carbon series materials have good electrical conductivity, but their color is too dark and hard to disperse.

Possessing good electrical conductive and optical properties, good weather resistance, chemical stability, anti-radiation, and infrared absorption [5, 6], Sb doped SnO_2 (ATO) is hailed as a promising multifunctional transparent conductive material [7] and has been widely used in solar cells [8], polymer light-emitting diodes (PLEDs) [9], photoelectrochemical water splitting [10], heat-insulating films [11], antistatic materials, and electrode materials [12]. However, few instances of ATO being employed in conductive greases have been reported.

In this paper, a conductive grease was synthesized using polyethylene oxide polypropylene oxide tin-butadiene styrene ether 50HB660 (PAG) as the base oil; polytetrafluoroethylene (PTFE) as the thickener; and Cu powder, Ag powder, and ATO as additives.

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The physicochemical and tribological properties of the synthesized conductive greases were investigated in detail, and the tribol-surfaces were examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) to explore the mechanisms of friction and wear.

2 Experimental details

2.1 Materials and preparation

The base oil, PAG, used in this study was purchased commercially from Dow Chemical (China) Investment Company. The grain size of the PTFE micro-powder (Dyneon™ TF9207) was about 4 μm and the density was 2.2 g/cm^3. The ethanol (Sinopharm) was analytical grade, and all the chemical reagents used were without further purification. The typical properties of Cu powder (Sinopharm), Ag powder (Sinopharm) and ATO (Beijing DK nano) are shown in Table 1, and the transmission electron microscope (TEM) image of ATO is shown in Fig. 1.

The lubricating greases were synthesized according to the following procedure. Firstly, the base oil (with a certain amount of the Cu, Ag, and ATO additives, initially dispersed in ethanol) was added to the corresponding vessel and stirred. Secondly, PTFE was slowly added and stirred vigorously. When the base oil and PTFE were uniformly mixed, a specific amount of the ethanol was injected and stirred for about 30 min to ensure that the PTFE was completely dispersed in the base oil. After that, the mixture was heated to about 90 °C and maintained at this temperature for about 30 min to remove the ethanol. Finally, the mixture was cooled to room temperature, and the PAG grease and the conductive greases (namely the PAG+additives grease) were obtained after three separate fine grinding/homogenization steps in a three-roller mill.

Table 1 Typical properties of the Cu, Ag and nano ATO.

Additives	Grain size	Dry basis content	Relative density	Melt point
Cu	75 μm	99%	10.49	1,083 °C
Ag	75 μm	99%	8.94	960 °C
ATO	20 nm	99.9%	9.5	1,100 °C

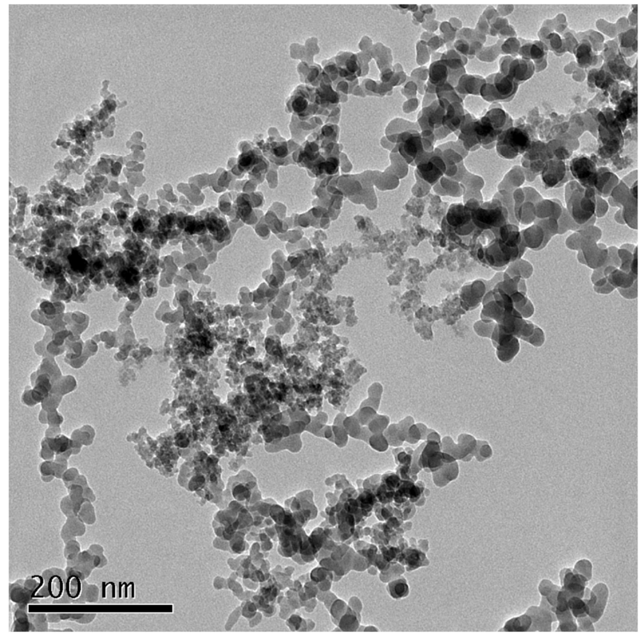

Fig. 1 The TEM image of nanometer ATO.

2.2 Characterization of the physical properties of the grease

The dropping point, the penetration, and the copper strip tests of the prepared lubricating greases were characterized under national standards GB/T 3498, GB/T 269, and GB/T 7326; the conductivity and volume resistivity were ascertained using a DDSJ-308A conductivity tester and a GEST-121 volume surface resistance tester, respectively. The initial and final contact resistances were measured by HLY-200A circuit resistance tester, and the testing current and time were 100 ampere and 10 seconds, respectively.

2.3 Friction and wear tests

A MFT-R4000 reciprocating friction and wear tester (Fig. 2) was employed to investigate the tribological performance of the conductive greases with a ball-on-disc configuration. Contact between the frictional pairs was achieved by pressing the upper ball (diameter 5 mm, AISI 52100 steel, hardness 710 Hv) against the lower stationary steel discs (ø 24 mm × 7.9 mm, AISI 52100 steel, hardness 340–350 Hv). The upper ball slid reciprocally at an amplitude of 5 mm against the stationary lower steel discs. All the tests were conducted at room temperature and each lasted for 30 min. All the disc specimens and steel balls were

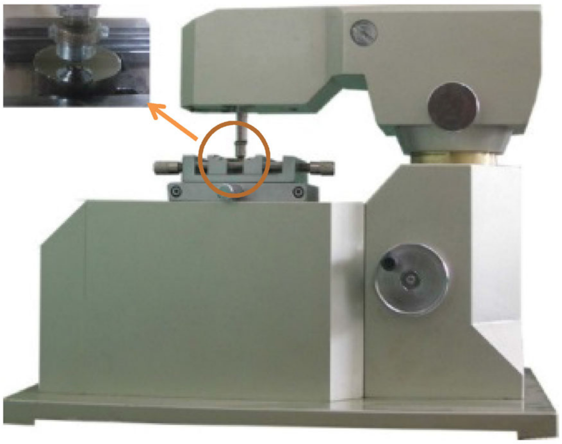

Fig. 2 The MFT-R4000 reciprocating friction and wear tester.

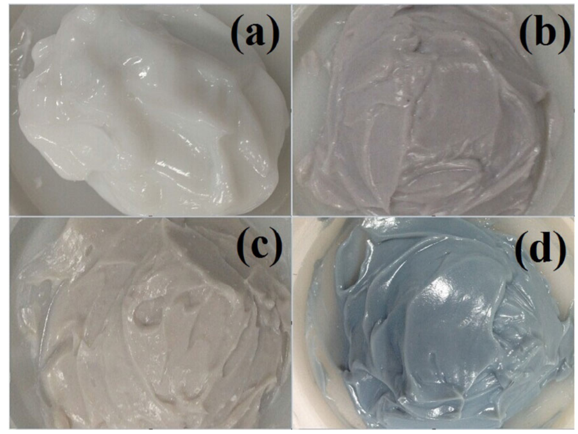

Fig. 3 The photo images of (a) PAG grease, (b) PAG+Cu grease, (c) PAG+Ag grease and (d) PAG+ATO grease.

cleaned in petroleum ether using an ultrasonic cleaner for 10 min, before and after each tribol-test. Prior to the friction and wear test, about 1 g grease was introduced to the ball–disc contact area and the coefficient of friction (COF) was recorded automatically by a computer connected to the MFT-R4000 tester. The wear widths of the lower discs were determined using an optical microscope. Three repeated measurements were performed, and the average values with error bars are reported in this article. The morphologies of the worn surfaces were analyzed using a JSM-5600LV SEM (JEOL, Tokyo, Japan), and the elements in the tribofilm were investigated using EDS.

3 Results

3.1 Physical properties of the greases

Photo images of the prepared lubricating greases are shown in Fig. 3. Table 2 lists the typical properties of the lubricating greases. The PAG grease has a relatively low dropping point (281 ℃) and all lubricating greases have good corrosion resistance (copper corrosion 1a). ATO can dramatically improve the dropping point of the grease as ATO nanoparticles have a relatively high specific surface area (SSA) [13]; this presents an obstacle to the movement of the liquid molecules, attributed to surface force (similar to intermolecular force). Thus, ATO nanoparticles have relatively high adsorption [14], responsible for the improvement in the dropping point of the grease.

Table 3 lists the conductive capacity of the lubricating greases. The stabilizing coefficient is the ratio of final

Table 2 Physical properties of the greases.

Sample	Dropping point (℃)	Penetration (0.1 mm)	Corrosion grade
PAG grease	281	316	1a
PAG + 0.1wt% Cu grease	329	312	1a
PAG + 0.2wt% Cu grease	328	310	1a
PAG + 0.3wt% Cu grease	328	301	1a
PAG + 0.4wt% Cu grease	327	299	1a
PAG + 0.5wt% Cu grease	325	298	1a
PAG + 0.1wt% Ag grease	328	309	1a
PAG + 0.2wt% Ag grease	328	306	1a
PAG + 0.3wt% Ag grease	330	305	1a
PAG + 0.4wt% Ag grease	329	303	1a
PAG + 0.5wt% Ag grease	327	299	1a
PAG + 0.1wt% ATO grease	331	303	1a
PAG + 0.2wt% ATO grease	332	302	1a
PAG + 0.3wt% ATO grease	329	302	1a
PAG + 0.4wt% ATO grease	330	301	1a
PAG + 0.5wt% ATO grease	329	297	1a
PAG + 0.75wt% ATO grease	331	295	1a
PAG + 1.0wt% ATO grease	331	293	1a

contact resistance and initial contact resistance. The mechanism of ATO increasing the conductivity is in accordance with percolation theory [15–19]. The ATO conductive greases have lower contact resistance than other prepared greases. The ATO can reduce the contact resistance, thus can decrease heat generation by resistance, reduce energy consumption, and make the current more stable.

Table 3 Conductive properties of the greases.

Sample	Conductivity (μs/cm)	Initial contact resistance (μΩ)	Final contact resistance (μΩ)	Stabilizing coefficient
PAG grease	0	111.7	110.2	1.014
PAG + 0.1wt% Cu grease	0.0103	98.3	97.8	1.005
PAG + 0.2wt% Cu grease	0.0105	94.5	94.1	1.004
PAG + 0.3wt% Cu grease	0.0112	81.2	80.6	1.007
PAG + 0.4wt% Cu grease	0.0124	77.3	76.9	1.005
PAG + 0.5wt% Cu grease	0.0145	59.6	59.1	1.008
PAG + 0.1wt% Ag grease	0.0101	70.4	70.1	1.004
PAG + 0.2wt% Ag grease	0.0101	65.6	65.2	1.006
PAG + 0.3wt% Ag grease	0.0106	63.2	62.8	1.006
PAG + 0.4wt% Ag grease	0.0106	57.3	57.0	1.005
PAG + 0.5wt% Ag grease	0.0111	49.6	49.2	1.008
PAG + 0.1wt% ATO grease	0.0115	50.8	50.6	1.004
PAG + 0.2wt% ATO grease	0.0123	45.8	45.6	1.004
PAG + 0.3wt% ATO grease	0.0127	44.6	44.3	1.007
PAG + 0.4wt% ATO grease	0.0168	41.4	41.1	1.007
PAG + 0.5wt% ATO grease	0.0229	39.2	38.9	1.008
PAG + 0.75wt% ATO grease	0.0281	38.3	38.1	1.005
PAG + 1.0wt% ATO grease	0.0302	38.2	38.1	1.003

3.2 Tribological test results

To investigate the tribological properties of ATO, three influence factors (additive concentration, load, and frequency) were investigated in this paper.

3.2.1 *Effect of additive concentration*

Figure 4 demonstrates the evolution of COF with time and wear widths of the prepared lubricating greases at room temperature at 20 N and 5 Hz. The ATO greases exhibit better friction-reducing behavior than other greases. The COFs show little change between 0.108 and 0.115 with an increase in ATO concentration; slightly increased COFs might result from the slight degradation of mechanical properties occurring in the PAG+ATO grease [20]. When the ATO concentration is 0.1wt%, it exhibits the lowest COF (about 0.108) of the prepared greases. Moreover, the COF of ATO grease is much more stable than PAG grease. The wear widths are dramatically reduced as the ATO concentration increases, and a 0.5wt% concentration of ATO can generally improve the anti-wear property of the PAG grease by about 30%. When the additive concentration is higher than 0.5wt%, the wear width of all greases increases substantially, resulting from the surplus particles acting as abrasive particles during the sliding friction process.

3.2.2 *Effect of load*

Figure 5 shows the average COFs and average wear widths of PAG grease containing 0.1wt% ATO and 0.5wt% ATO at different loads, at 5 Hz at room temperature. It is shown that the average COFs of PAG+ATO greases (about 0.108–0.113) are much lower than those of other greases (all above 0.115), and rise with increases in the load, to some extent. It is shown that ATO is capable of superior friction-reducing behavior at all loads. The PAG+ATO greases have relatively narrower wear widths than other greases, and the wear width of PAG+0.5wt% ATO grease remains considerably less than with other greases under test conditions, indicating the best anti-wear capability.

3.2.3 *Effect of frequency*

The COFs and wear widths of the lubricating greases

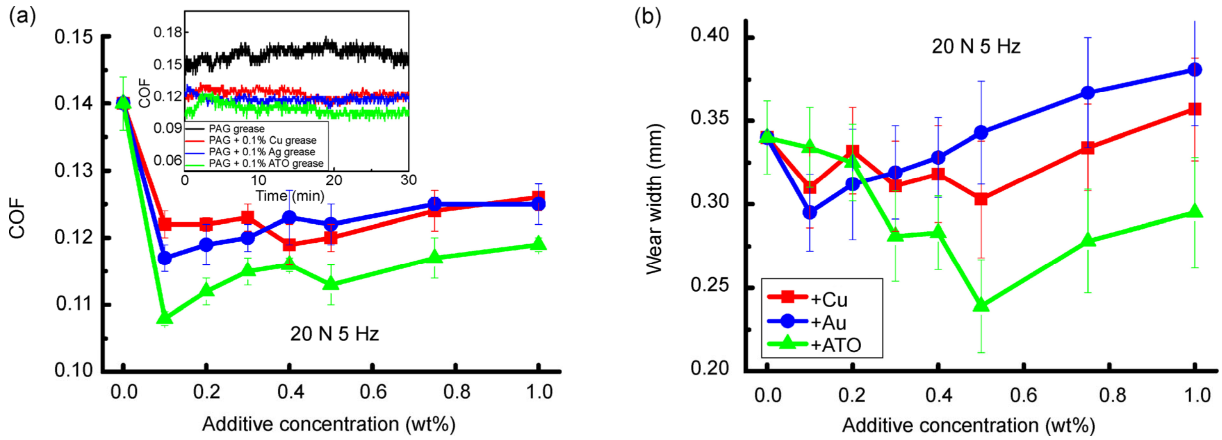

Fig. 4 (a) Coefficient of friction (COF) for PAG grease with additives at different concentrations at room temperature; (b) average wear width of the discs lubricated by PAG grease with additives at different concentrations at room temperature (load = 20 N; frequency = 5 Hz; stroke = 5 mm; duration = 30 min).

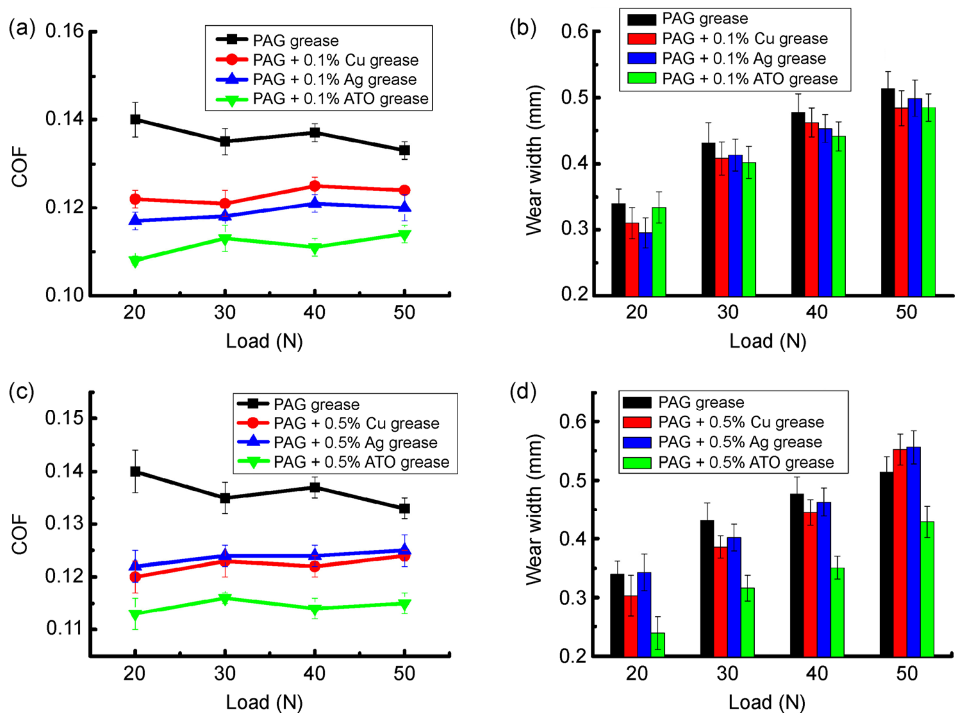

Fig. 5 (a) and (c) Average COFs, and (b) and (d) average wear widths at 20, 30, 40 and 50 N for PAG grease with Cu, Ag and ATO additives at 0.1wt% and 0.5wt% concentrations at room temperature (frequency = 5 Hz; stroke = 5 mm; duration = 30 min).

at various frequencies are shown in Fig. 6. The COFs of the PAG+ATO greases decrease with frequency increases, to some extent, and are lower than those of other greases at concentrations of both 0.1wt% and 0.5wt%. The COF can be reduced by nearly 10% (plus 0.5wt% ATO at 50 N and 5 Hz), thus ATO has better friction-reducing properties. The results of the wear widths clearly demonstrate that the PAG+0.5wt% ATO grease has far better anti-wear performance than other greases during the 30 min test time at whole frequencies.

3.2.4 Surface analysis

To study the lubrication mechanism, SEM and EDS were used to analyze the worn surfaces. Figure 7 displays the SEM morphologies of the worn surfaces on steel discs lubricated by the prepared greases at room temperature. It can be clearly seen that the worn

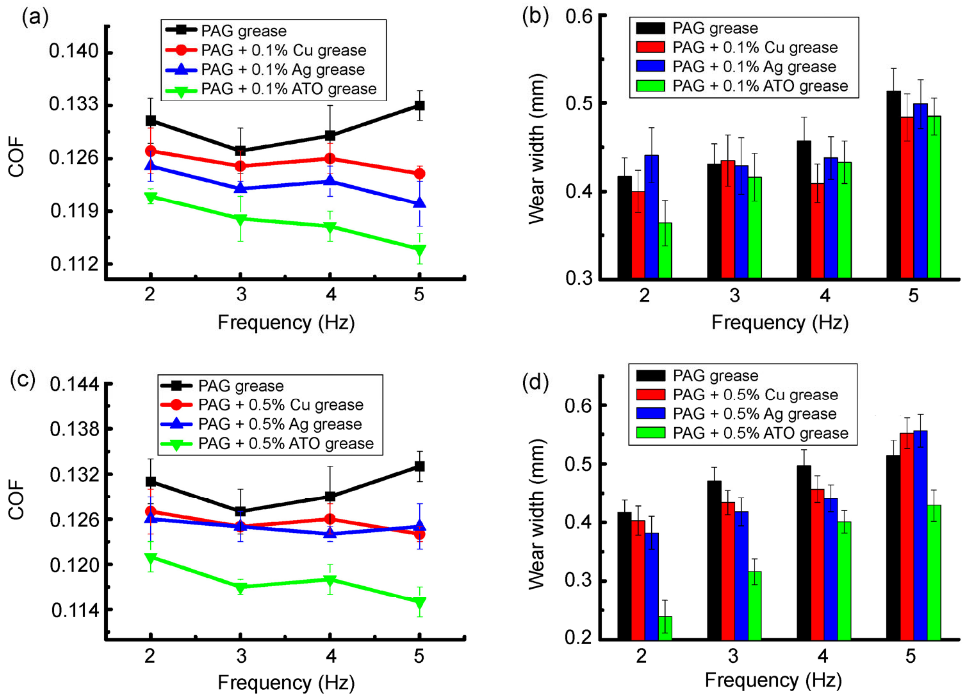

Fig. 6 (a) and (c) Average COFs and (b) and (d) average wear widths at 2, 3, 4 and 5 Hz for PAG grease with Cu, Ag and ATO additives at 0.1wt% and 0.5wt% concentrations at room temperature (load = 50 N; stroke = 5 mm; duration = 30 min).

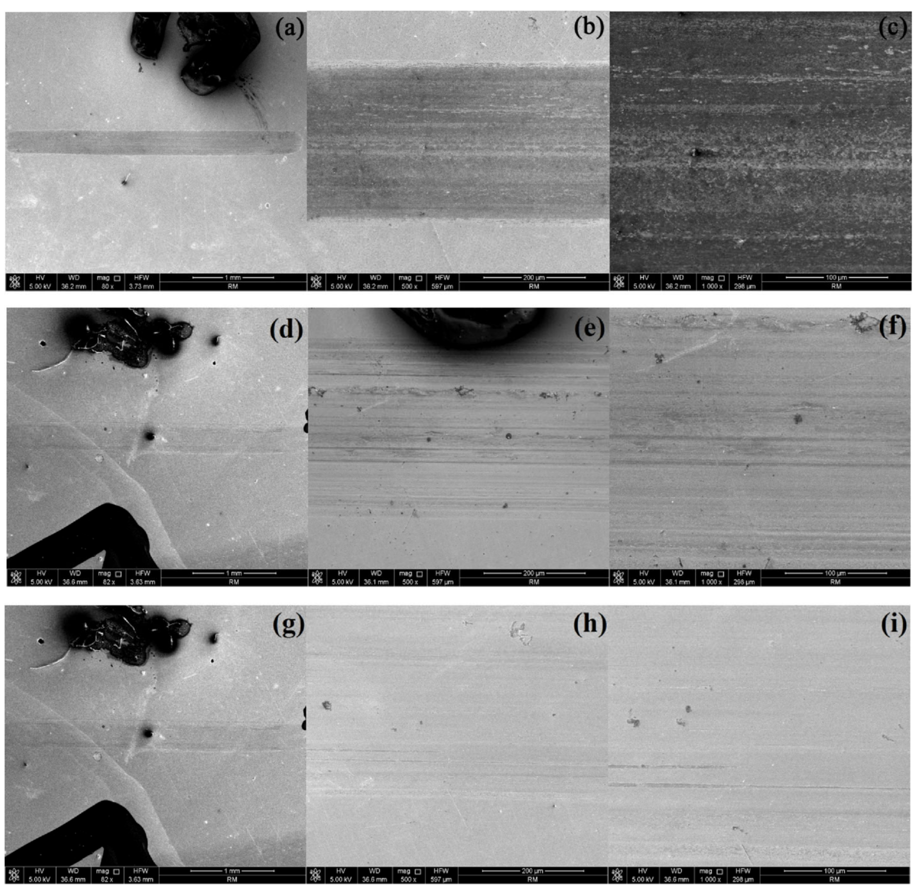

Fig. 7 SEM morphologies of the worn surfaces lubricated by different lubricant at 50 N and 5 Hz: (a)–(c) PAG grease; (d)–(f) PAG+ 0.1wt% ATO grease and (g)−(i) PAG+ 0.5wt%ATO grease.

surface of the steel disc lubricated by PAG grease (Figs. 7(a)–7(c)) shows much wider and deeper wear scars, with some deep and narrow grooves demonstrating that severe scuffing occurred in this instance.

In marked contrast, the worn steel surfaces lubricated by PAG grease with 0.1wt%ATO and 0.5wt%ATO (Figs. 7(d)–7(i)) show much smoother and smaller wear scars; only a little adhesive wear could be observed. Scuffing is greatly alleviated, as proof of the excellent tribological properties of ATO additives. Moreover, the worn surface of 0.5wt% is even smoother than that of 0.1wt% ATO, in agreement with wear width results. The results are also consistent with the aforementioned tribol-test data, again proving that ATO additives demonstrate better tribological performance.

EDS analysis was employed to clarify further the chemical component of several typical elements on the worn surfaces. Figure 8 gives the EDS of the typical elements on the worn surfaces lubricated by the PAG grease and PAG+0.5wt% ATO grease at 50 N and 5 Hz.

The low peaks of Sn and Sb elements [21, 22] shown in Fig. 8(b) are attributed to the low ATO concentration in grease (only 0.5wt%). However, the element concentration confirms the existence of Sn and Sb at 0.79wt% and 0.43wt% on the worn surfaces, respectively. It is concluded that the Sn and Sb deposited metallic oxide during the sliding process, and the protecting film significantly contributed to the friction-reducing and anti-wear properties of the lubricating grease [23]. Thus, the ATO additives exhibited excellent tribological properties.

Schematic diagrams of friction mechanisms and the distribution of ATO particles in the grease are shown in Fig. 9. The improvement of the tribological properties of ATO can be explained by the following three aspects. First, with the lubricating greases stably and uniformly located between the two contact surfaces, the nanoparticles (ATO) served as spacers during sliding, preventing direct contact between them [24]. Second, the nanoparticles also had a rolling effect that changed sliding friction into rolling friction and had a protective effect [25]. Third, due to their small size, nanoparticles may serve as nuclear centers for developing continuous polymer regions, then connect with each other to form a tightly-structured network; and this may contribute to the improved anti-wear ability of the grease [26]. Moreover, Sn and Sb ions were deposited as a film on the protecting surface during the sliding process, serving to enhance it. Therefore, the COFs and wear widths were stable and narrow at room temperature, and the worn surfaces lubricated by ATO grease were relatively smooth.

Conductive grease containing ATO can be used in power transmission and transformation equipment such as cable clips for transmission lines (Fig. 10).

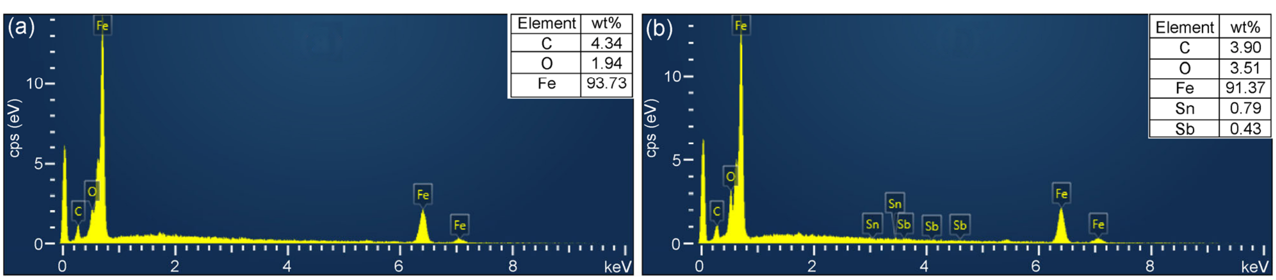

Fig. 8 The EDS of the elements on the worn surface lubricated by (a) PAG grease; and (b) PAG+0.5wt%ATO grease at 50 N and 5 Hz.

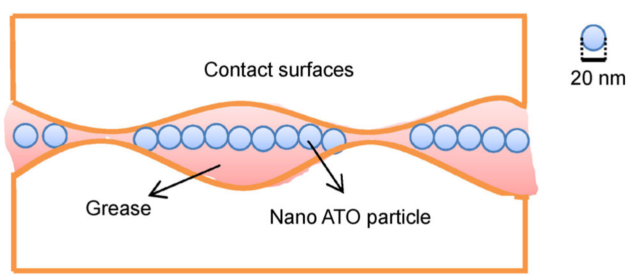

Fig. 9 Schematic of friction mechanism of the nano ATO particles in grease.

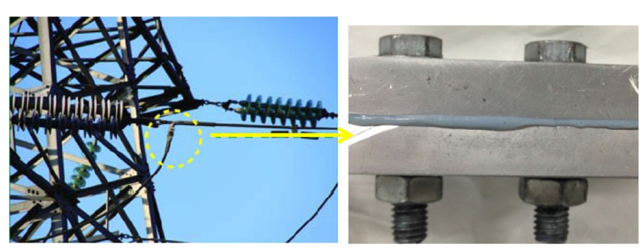

Fig. 10 Cable clip coated by nano ATO conductive grease.

4 Conclusions

Nanometer ATO, a new kind of conductive additive, possesses a superior conductive capacity and a lower contact resistance in grease. It can be used in the conductive parts of electrical equipment. ATO conductive grease shows better friction-reducing and anti-wear properties. EDS analysis indicates that the Sn and Sb form a film or metallic oxide deposit on worn surfaces during the sliding process. The protecting film significantly contributes to the friction-reducing and anti-wear properties of the ATO conductive greases.

Acknowledgments

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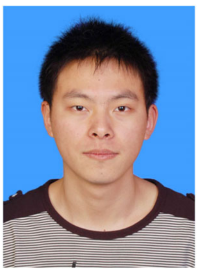

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