Tribology International 55 (2012) 1–6

Contents lists available at SciVerse ScienceDirect

Tribology International

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

The anti-seizure effect of Ag nanoparticles additive in multialkylated cyclopentanes oil under vacuum condition

Songwei Zhang [a,b], Litian Hu [a,*], Haizhong Wang [a], Dapeng Feng [a]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 25 February 2012
Received in revised form
18 May 2012
Accepted 22 May 2012
Available online 1 June 2012

Keywords:
Vacuum
Multialkylated cyclopentanes
Ag nanoparticles
Seizure-like high friction

ABSTRACT

The effect of surface-modified Ag nanoparticles as additives of multialkylated cyclopentanes (MACs) was investigated in air and vacuum by a vacuum four-ball tribometer. The results showed that both the MACs and MACs containing Ag nanoparticles exhibited steady and low friction coefficients and slight wear in air. However, under vacuum conditions, MACs showed the initial seizure-like high friction, while introducing Ag nanoparticles could effectively eliminate it. Confirmed by the surface analysis, the improved tribological performances caused by Ag nanoparticles could be ascribed to the metal Ag boundary film formed on the friction pair surfaces during tests.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Liquid lubricants are frequently used in space mechanisms due to their low mechanical noise, no wear in the elastohydrodynamic (EHL) regime, ease of replenishment, ability to remove wear debris, and insensitivity to environmental factors [1]. However, the application for liquid lubrication under high vacuum conditions has been a technical challenge for many years [2–5]. The high vacuum environment induces rapid evaporation of the liquid lubricants employed, and undoubtedly, the loss of the liquid lubricants could result in failure of the mechanism. For metal mechanisms, oxide films usually act as protective films and, in some cases, contribute to the final surface films through either chemical reaction or chemical adsorption. However under high vacuum condition, the absence of oxide films may cause severe friction and wear [1].

In recent years, multialkylated cyclopentanes (MACs) has received increasing attention as a kind of space lubricants. MACs, in which two to five alkyl groups are attached to a single five-member carbon ring, is readily available from the reaction of dicyclopentadiene and commercially available alcohols [6]. Therefore, the wide availability of a number of commercial alcohols allows for the preparation of MACs with vast combinations of properties. MACs exhibits many excellent properties, such as, extremely low volatility, high viscosity index, wide running temperature, low pour point and good solubility with many commercial additives [6]. So some researches concerning the evaluation of MACs have been reported [5,7]. Under vacuum conditions, it was found that MACs and PFPE might show initial seizure-like high friction under the boundary lubrication condition, and correspondingly they would also suffer the initial high wear volume [8–10]. Masuko et al. [9] suspected that since the occurrence of this high friction was a delicate phenomenon, some unknown uncontrollable variables might affect the results. This is so adverse for MACs used as a kind of lubricant for space application. Therefore, additives, which have good solubility with MACs and simultaneously can be used for space application, are in great request.

Extensive researches about the preparation of surface-modified nanoparticles have been conducted [11–13]. Up to now, the study on the tribological properties of nanoparticles used as oil additives have been received intensive attention, and results showed that nanoparticles can improve the tribological performances of the base oil [14–17].

In this paper, based on sliding friction experiments, friction and wear characteristics of MACs base oil and MACs with Ag nanoparticles under different atmospheric conditions are compared. The severe initial seizure-like high friction observed with MACs base oil is reported, and the effects of Ag nanoparticles on preventing such initial seizure-like high friction are reported.

2. Experimental details

2.1. Characterization of MACs

MACs was synthesized in the laboratory according to the literature [6] and the structure was characterized by the

* Corresponding author.
E-mail address: lthu@licp.cas.cn (L. Hu).

0301-679X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.triboint.2012.05.021

IFS 66v/s Fourier transformation infrared spectroscopy (FTIR), and the thermal properties were measured by the Perkin–Elmer TGA-7 thermogravimetric analysis (TGA) which was conducted in nitrogen atmosphere from 20 °C to 600 °C. The other typical properties are listed in Table 1.

Fig. 1 is the FTIR spectrum of MACs. As indicated in Fig. 1, MACs is similar with other saturated hydrocarbons with alkyl components. It can be found that C–H stretching vibration bands at 2955 and 2853 cm^{-1}, C–H band modes at 1466 and 1378 cm^{-1}, and band at 721 cm^{-1} is the $-(CH_2)_x-$ rocking vibration, where $x>4$. Fig. 2 shows the TGA curve of MACs. It can be seen that MACs has high thermal stability and it loses little weight at <300 °C.

2.2. Synthesis and characterization of Ag nanoparticles

The Ag nanoparticles were prepared according to the literature [18] and their structure was characterized by the JEM-1200EX/S transmission electron microscopy (TEM), TGA and the ESCALAB 210 X-ray photoelectron spectrometer (XPS).

The main preparation process was as follows: 5 g silver oleate was placed in a 250 mL flask, which was equipped with a magnetic stirrer. 60 mL triethylamine was added by a funnel, and then the reaction solution was stirred at 80 °C for 2 h. After cooling to room temperature, the addition of acetone (20 mL) to the solution would produce precipitate, which was collected by filtration, washed with a small amount of acetone, and dried under vacuum. The Ag nanoparticles disperse well in nonpolar and weak polar organic solvents, such as benzene, toluene, petroleum ether, chloroform and MACs.

Fig. 3 presents the TEM micrograph of Ag nanoparticles. It can be seen that the diameter of the Ag nanoparticles are about 4–6 nm. Fig. 4 shows XPS spectrum of Ag nanoparticles. In the XPS spectrum, the binding energies for the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks are 367.93 eV and 373.93 eV, respectively, which are in good agreement with the values of zerovalent silver (Ag $3d_{5/2}$: 367.93 eV and Ag $3d_{3/2}$: 373.93 eV) [19]. Fig. 5 presents the TGA curves of oleic acid and Ag nanoparticles. It can be found that the weight loss for oleic acid starts at 190 °C, while the surface-modified Ag nanoparticles do not lose weight until 240 °C, indicating that the thermal stability of oleic acid is raised after coated on the surface of Ag nanoparticles. It could be also found that the mass fraction of metal Ag in the Ag nanoparticles is more than 80%.

2.3. Vacuum four-ball tribometer

A vacuum four-ball tribometer was designed and developed for the experiments based on the configuration of a traditional

Table 1
Typical properties of the lubricant.

Lubricant	Average molecular weight	Kinematic viscosity (cSt)		Viscosity index	Surface tension ($mN\ m^{-1}$)	Vapor pressure at 20 °C (Pa)
		40 °C	100 °C			
MACs	630	56	9.3	148	24.5	5.6×10^{-6}

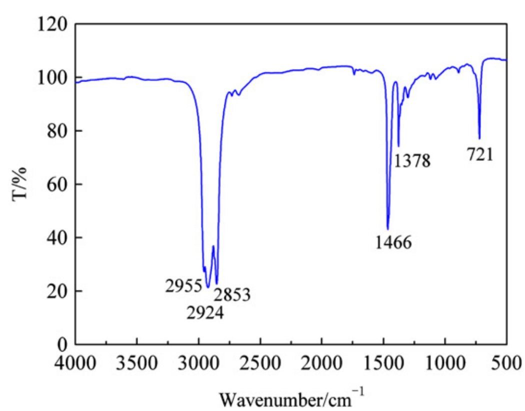

Fig. 1. IR-spectrum of multialkylated cyclopentanes (MACs) oil.

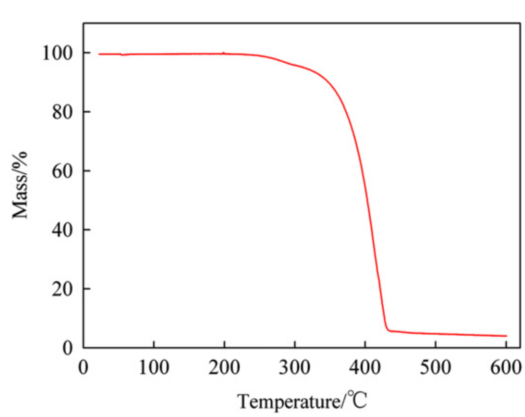

Fig. 2. TGA curve of MACs oil.

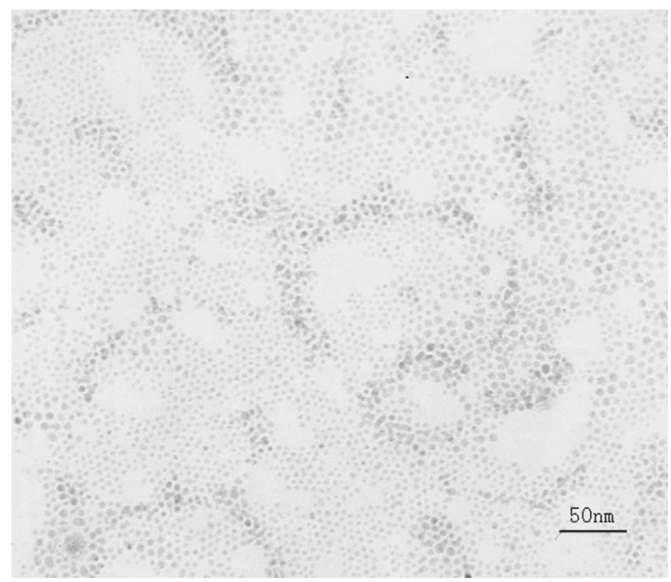

Fig. 3. TEM micrograph of Ag nanoparticles.

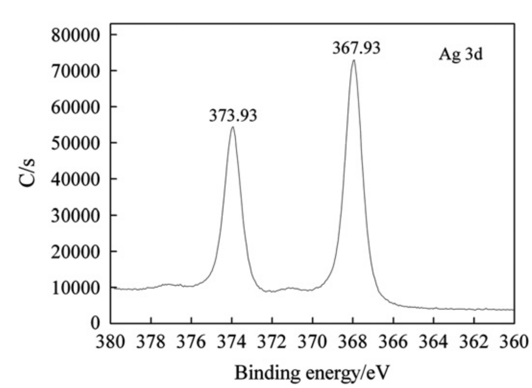

Fig. 4. XPS spectrum of Ag nanoparticles.

four-ball tribometer by the State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Moreover, the schematic of the vacuum four-ball tribometer is shown in Fig. 6. The vacuum chamber was evacuated by using a series of a turbo molecular pump and a mechanical pump. The tribological characteristics of liquid lubricants for space applications were evaluated by this tribometer under the pressure of 2.0×10^{-4} Pa. The tribometer could also be operated at low vacuum (about 10 Pa) and at atmospheric pressure with air or nitrogen.

The tribological properties of MACs containing different concentrations (mass fraction) of Ag nanoparticles under high vacuum ($\sim10^{-4}$ Pa) were investigated using the vacuum four-ball tribometer. These tests were performed under the load of 392 N with a rotating speed of 1450 rpm at 25 °C and 75 °C for 30 min. The tribological properties of MACs base oil and MACs with 1% Ag nanoparticles were also investigated in air and low vacuum ($\sim$10 Pa) at 25 °C. The 12.7 mm (1/2 in) diameter balls were used as test specimen which were made of AISI 52100 bearing steel (0.95–1.05%C, 0.25–0.45%Mn, 0.15–0.35%Si, 1.40–1.65%Cr, ~0.30%Ni, ~0.25%Cu, ~0.025%S, ~0.025%P) with a hardness of 60–63 HRC. Before and after each test, the test specimen were ultrasonically cleaned in petroleum ether (normal alkane with a boiling point of 60–90 °C). For each sample, three parallel tests were performed to minimize data scattering. At the end of each test, the wear scar diameters of the three lower balls were measured with an optical microscope to an accuracy of 0.01 mm, and then the average values of wear scar diameter for the three identical tests was calculated as the wear scar diameter (WSD) in this paper.

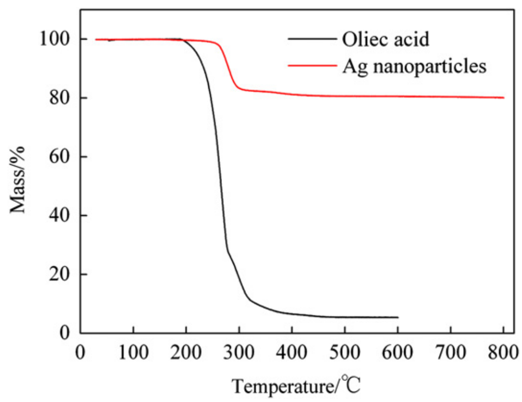

Fig. 5. TGA curves of oleic acid and Ag nanoparticles.

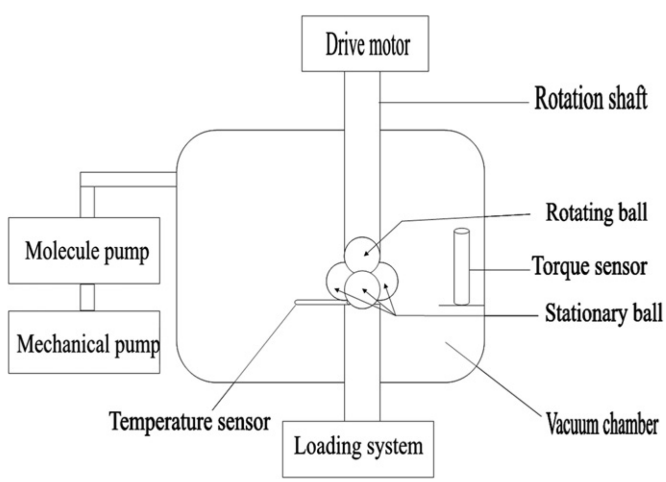

Fig. 6. Schematic of the vacuum four-ball tribometer.

3. Results and discussion

3.1. Tribological properties of the Ag nanoparticles

Fig. 7 shows the mean friction coefficient and the WSD values as a function of additive concentration of Ag nanoparticles at 25 °C and 75 °C under high vacuum. It can be seen that the friction coefficient and the WSD values decrease greatly when Ag nanoparticles were added into MACs. The addition of Ag nanoparticles could reduce the friction coefficient and the WSD values effectively of base stock even at very low concentration, and the optimal additive concentration is 1%. As seen from Fig. 7a and b, Ag nanoparticles could reduce the friction coefficient and the WSD values more effectively at higher temperature (75 °C).

Fig. 8 shows the friction coefficient as a function of rotating time lubricated by MACs with different concentrations of Ag nanoparticles. As shown in Fig. 8, all nanoparticle concentrations in MACs exhibit the anti-seizure effect, but the level is different. With the increase in the nanoparticle concentration, the seizure-like high friction appears lower and more short-lived. However, when the nanoparticle concentration increases to 1.5%, it exhibits sharply fluctuant friction coefficient during the friction process. At lower nanoparticle concentrations, such as 0.25% and 0.5%, the stable and strong boundary film could not be formed. So the transient high friction coefficients were higher than 0.27. At higher nanoparticle concentration (1.5%), more Ag nanoparticles deposited on the rubbing surface to form strong metal film, so the lowest transient high friction coefficient among the all

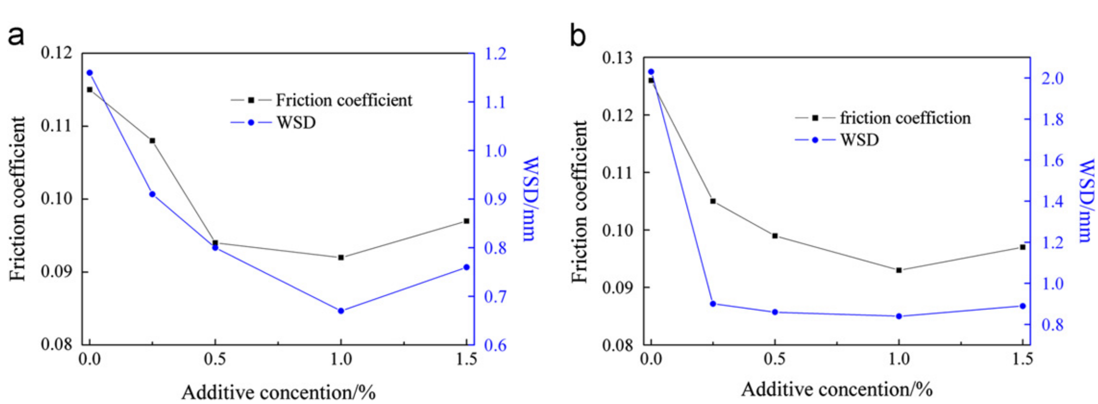

Fig. 7. Average friction coefficient and the WSD values as a function of additive concentration of Ag nanoparticles at (a) 25 °C and (b) 75 °C under high vacuum.

nanoparticle concentration was obtained. However, the stability and continuity of the oil film was destroyed by the larger particles formed by the colliding and sticking of nanoparticles. Therefore, a sharply fluctuant friction coefficient during the friction process was also obtained. At the optimal nanoparticle concentration of 1%, the lowest and most stable friction coefficient was obtained. Because accompanying the continuous oil film, the strong and stable metal Ag boundary film was formed on the surfaces of steel friction pairs.

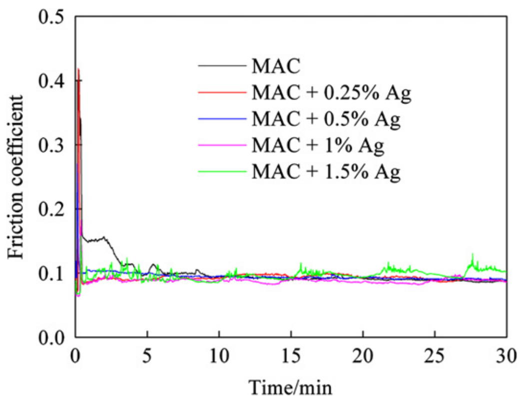

Fig. 8. Friction coefficient as a function of rotating time lubricated by MACs containing different Ag nanoparticle concentrations under high vacuum at 25 °C.

Fig. 9 shows the friction coefficient as a function of rotating time lubricated by MACs and MACs with 1% Ag nanoparticles in air, low vacuum and high vacuum, respectively. It can be seen from Fig. 9a that MACs exhibits initial seizure-like high friction under either low vacuum or high vacuum. However, their magnitudes are different (i.e., higher in high vacuum (0.42) than in low vacuum (0.38)), and the durations are longer in high vacuum. Nevertheless, such phenomenon of transient initial high friction could be eliminated when 1% Ag nanoparticles were added into MACs as shown in Fig. 9b. The anti-seizure mechanisms of Ag nanoparticles could be that the adsorption and deposition of Ag nanoparticles on the friction pair surfaces formed the boundary film, which separated the steel friction pairs from each other to decrease the shearing stress and inhibited the initial high friction effectively under vacuum.

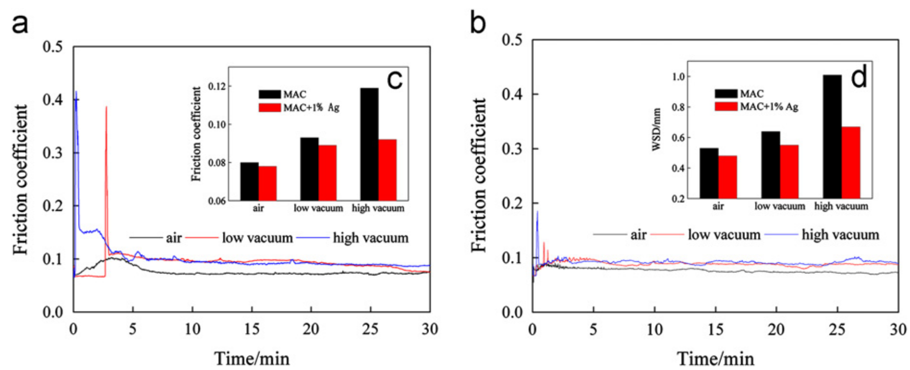

Fig. 9. Friction coefficient as a function of rotating time lubricated by (a) MACs and (b) MACs with 1% Ag nanoparticles in air, low vacuum and high vacuum. The inset indicates (c) the mean friction coefficient and (d) the WSD values lubricated by MACs and MACs with 1% Ag nanoparticles in air, low vacuum and high vacuum.

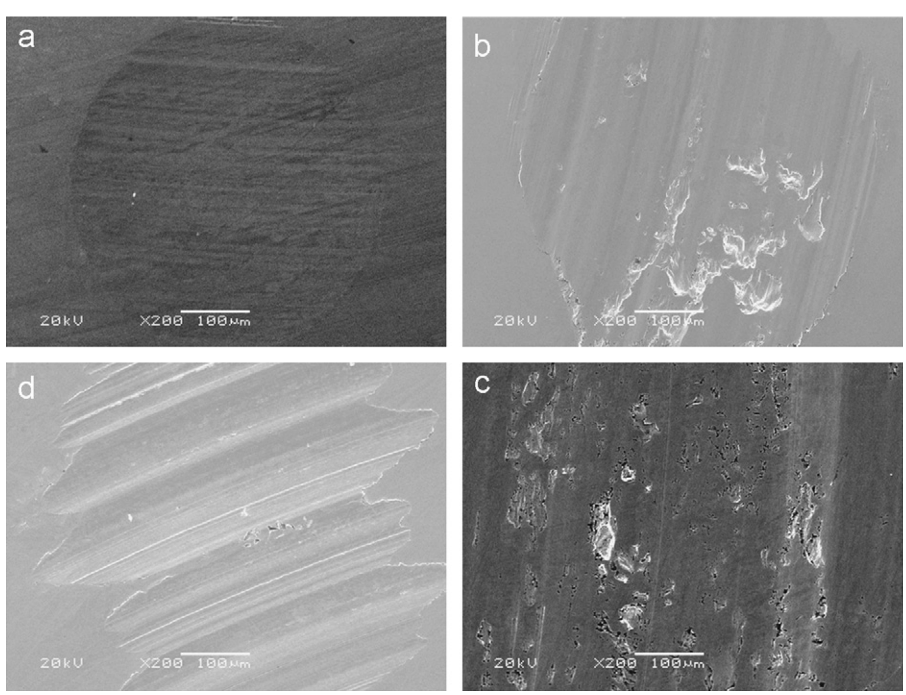

Fig. 10. SEM images of the wear scar surfaces lubricated by MACs base oil in (a) air, (b) low vacuum and (c) high vacuum and (d) by MACs with 1% Ag nanoparticles under high vacuum at 25 °C.

Fig. 9c and d presents the comparisons of the mean friction coefficient and the WSD values lubricated by MACs base oil and MACs with 1% Ag nanoparticles in air, and under low and high vacuum. It can be seen that the average friction coefficient and the WSD values increase observably from air to low vacuum then to high vacuum when lubricated by MACs base oil. The average friction coefficients and WSD values decrease more remarkably in high vacuum than that in air and low vacuum when Ag nanoparticles were added into MACs base oil.

3.2. Analysis of the worn surfaces

Fig. 10 shows the SEM images of the wear scar surfaces lubricated by MACs base oil and MACs with 1% Ag nanoparticles. It could be observed that MACs exhibited very smooth wear surface in air and relatively rough surfaces under vacuum, and the difference should be contributed to the forming of continuous boundary oxide film in air. Severe plastic deformation and adhesive wear could be found on the rough worn surface lubricated by MACs base oil under high vacuum. However, the worn surface is smooth without such plastic deformation or adhesive wear when lubricated by MACs with 1% Ag nanoparticles. Furthermore, the WSD value of the steel ball lubricated by MACs base oil is remarkably larger than that of the steel ball lubricated by MACs with 1% Ag nanoparticles. Therefore, the results further show that the antiwear ability was markedly improved when 1% Ag nanoparticles were added into MACs. The initial high wear volume is thought to be related to the initial seizure-like high friction [9]. A reasonable explanation for the antiwear mechanism of Ag nanoparticles is possibly that the boundary film of metal Ag formed due to the adsorption and deposition of Ag nanoparticles on the steel ball, which effectively eliminates the initial high wear, and the Ag nanoparticles can repair the worn surface to some extent during the steady friction state.

More analysis of the wear scar surfaces by EDX was done in order to detect the formation of the metallic boundary film. Fig. 11 gives the EDX spectrum of the marked area of the wear scar surfaces lubricated by MACs with 1% Ag nanoparticles under high vacuum at 25 °C. The result shows that about 32.31 wt% Ag element was found on the worn surface. It can be concluded that Ag nanoparticles were deposited on the friction pair surface to form Ag boundary film, which contributed to excellent lubricity. That is also the reason why MACs with 1% Ag nanoparticles give the low and stable friction coefficient.

XPS analysis was used to further clarify the chemical state of typical Ag element on the worn surface. Fig. 12 gives the XPS spectrum of Ag on the worn surface lubricated by MACs with 1% Ag nanoparticles at 25 °C for 30 min under high vacuum. It can be seen that the binding energy of Ag appears at 367.93 eV and 373.93 eV, which are in good agreement with metal Ag [19]. Thus, it can be concluded that there was no tribochemical reaction that took place between Ag nanoparticles and steel surfaces, but Ag nanoparticles were deposited on the friction pair surface to form metal Ag boundary film, which contributed to low shearing stress and excellent lubricity.

4. Conclusions

Sliding friction experiments were carried out under vacuum and in air lubricated by MACs and MACs containing Ag nanoparticles. Based on the above experimental results, the following conclusions are drawn:

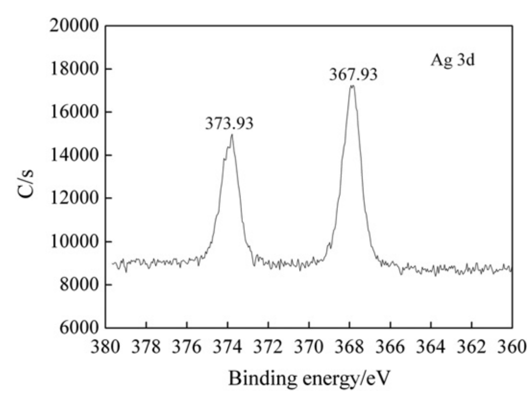

Fig. 12. XPS spectrum of Ag on the wear scar surface lubricated by MACs with 1% Ag nanoparticles under high vacuum at 25 °C.

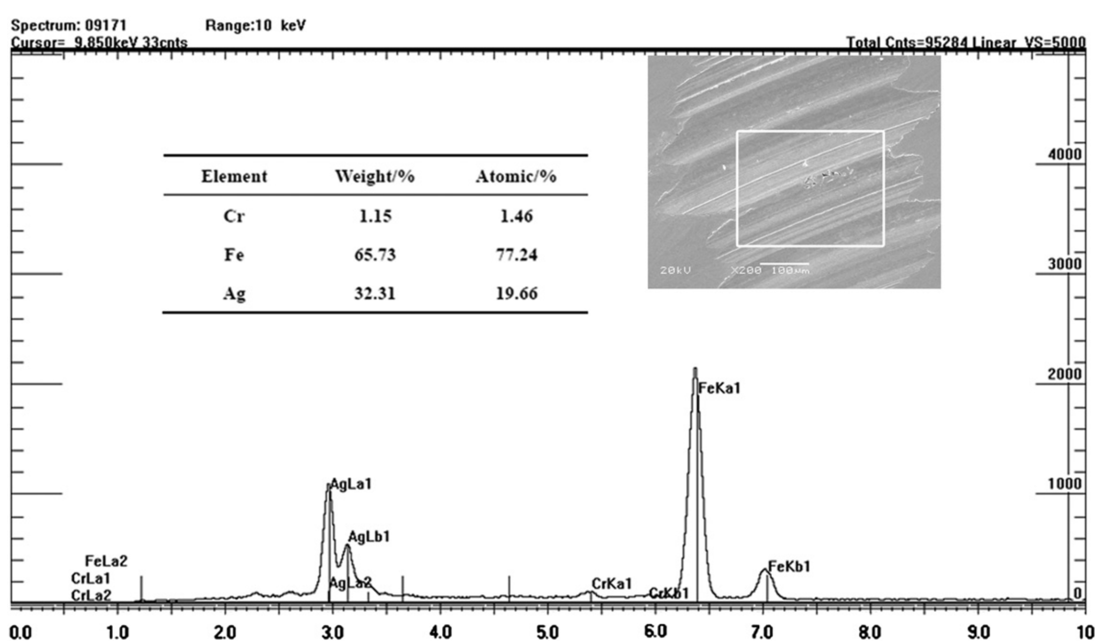

Fig. 11. EDX spectrum of the marked area of the wear scar surfaces lubricated by MACs with 1% Ag nanoparticles under high vacuum at 25 °C.

1. Both the friction coefficients and the WSD values increased remarkably from air to low vacuum then to high vacuum lubricated by MACs base oil.
2. Ag nanoparticles were effective in improving the tribological properties of MACs base oil, especially in eliminating the initial seizure-like high friction under vacuum condition.
3. The tribological mechanism of Ag nanoparticles was the adsorption and deposition of Ag nanoparticles on the friction pair surfaces to form the boundary film, which decreased the shearing stress and effectively inhibited initial high friction under vacuum condition.
4. Ag nanoparticles could be considered as a potential candidate of lubricating oil additives for space application.

Acknowledgment

The authors acknowledge financial support from the China National Science and Technology Program of 973 (2011CB706603).

References

[1] Zaretsky EV. Liquid lubrication in space. Tribology International 1990;23:75–93.
[2] Murray S, Lewis P, Babecki A. Lubricant life tests on ball bearings for space applications. ASLE Transactions 1966;9:348–60.
[3] Fusaro RL, Khonsari MM. Liquid lubrication in space. NASA/TM-1992-105198.
[4] Jones Jr WR, Shogrin BA, Jansen MJ. Research on liquid lubricants for space mechanisms. Journal of Synthetic Lubrication 2000;17:109–22.
[5] Jones Jr WR, Jansen MJ. Lubrication for space applications. NASA/CR-2005-213424.
[6] Venier C, Casserly E. Multiply-alkylated cyclopentanes (MACs): a new class of synthesized hydrocarbon fluids. Lubrication Engineering 1991;47:586–91.
[7] Jones WR, Poslowski AK, Shogrin BA, Herrera-Fierro P, Jansen MJ. Evaluation of several space lubricants using a vacuum four-ball tribometer. Tribology Transactions 1999;42:317–23.
[8] Masuko M, Jones Jr WR, Helmick LS. Tribological characteristics of perfluoropolyether liquid lubricants under sliding conditions in high vacuum. Journal of Synthetic Lubrication 1994;11:111–9.
[9] Masuko M, Mizuno H, Suzuki A, Obara S, Sasaki A. Lubrication performance of multialkylatedcyclopentane oils for sliding friction of steel under vacuum condition. Journal of Synthetic Lubrication 2007;24:217–26.
[10] Masuko M, Fujinami I, Okabe H. Lubrication performance of perfluoropolyalkylethers under high vacuum. Wear 1992;159:249–56.
[11] Johnson S, Evans S, Mahon S, Ulman A. Alkanethiol molecules containing an aromatic moiety self-assembled onto gold clusters. Langmuir 1997;13:51–7.
[12] Zhang H-X, Siegert U, Liu R, Cai W-B. Facile fabrication of ultrafine copper nanoparticles in organic solvent. Nanoscale Research Letters 2009;4:705–8.
[13] Wang Y, Asefa T. Poly(allylamine)-stabilized colloidal copper nanoparticles: synthesis, morphology, and their surface-enhanced Raman scattering properties. Langmuir 2010;26:7469–74.
[14] Xue Q, Liu W, Zhang Z. Friction and wear properties of a surface-modified TiO2 nanoparticle as an additive in liquid paraffin. Wear 1997;213:29–32.
[15] Chen S, Liu WM. Preparation and characterization of surface-coated ZnS nanoparticles. Langmuir 1999;15:8100–4.
[16] Zhang M, Wang X, Fu X, Liu W. Investigation of electrical contact resistance of Ag nanoparticles as additives added to PEG 300. Tribology Transactions 2009;52:157–64.
[17] Zhang M, Wang X, Fu X, Xia Y. Performance and anti-wear mechanism of $CaCO_3$ nanoparticles as a green additive in poly-alpha-olefin. Tribology International 2009;42:1029–39.
[18] Yamamoto M, Kashiwagi Y, Nakamoto M. Size-controlled synthesis of monodispersed silver nanoparticles capped by long-chain alkyl carboxylates from silver carboxylate and tertiary amine. Langmuir 2006;22:8581–6.
[19] Wagner CD, Riggs WM, Davis LE, Moulder JF. Handbook of X-ray photoeletron spectroscopy. Norwalk: Perkin-Elmer Corporation; 1979.