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Tribological synergistic effects between plasma nitrided 52100 steel and molybdenum dithiocarbamates additive in boundary lubrication regime

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ABSTRACT

The interactions and synergistic tribological effects between plasma nitrided 52100 steel and molybdenum dithiocarbamates (MoDTC) additive under boundary lubrication were studied in this work. The tribological behaviors of plasma nitrided and untreated steels under lubrication with different MoDTC concentrations were examined on a four-ball friction and wear tester. The results showed an obvious synergistic effect between plasma nitrided steel and MoDTC additive. The synergistic effect indicated a lower friction coefficient without an induction phase and a higher wear resistance, which was attributed to more amount of MoS_2 and absorbed carbon were formed in the tribofilm of the nitrided surface.

1. Introduction

Higher work efficiency and longer service life for modern equipments are urgently required, which mainly depend on the friction and wear characteristics of machine parts. The better tribological behaviors are obtained by optimized mechanical designs or appropriate lubrication strategies. The two contact surfaces of rubbing pairs already could not be separated by the lubricant oil film in the boundary (or mixed) lubrication regime, therefore, new materials or surface treatments are considered to be used [1,2]. Therefore, the research on the laws and mechanisms of synergistic effect between the modified solid surface and lubrication additives is very necessary for understanding how to achieve a lower friction coefficient and a higher wear resistance.

Plasma nitriding is an effective and widely used technique to improve the surface hardness and tribological and anti-corrosion properties of steels, cast irons, titanium and some alloys [3–7]. Nitrided steel parts are widely applied in engineering area in the boundary (or mixed) lubrication regime. The tribological behaviors of nitrided steel are effectively improved under lubrication with alkyl naphthalene, ionic liquid and liquid paraffin, which are attributed to the high hardness of nitrided layer and the adsorbed boundary lubricating film [8–10]. Our previous works presented the synergistic effects between nitrided steel and several anti-wear additives, such as zinc dialkylithiophosphate (ZDDP), phosphor and sulfur-free organotungsten and borate ester [11–13]. However, few works have been reported on the tribochemical interactions between nitrided steel surfaces and friction modifier additives.

As a friction modifier, molybdenum dithiocarbamates (MoDTC) is extensively used in the formulated oil. The effect of MoDTC compounds on friction reduction in most investigations had been attributed to the formation of tribofilms containing primarily MoS_2 and other molybdenum oxides [14–17]. However, the wear rates of DLC coatings lubricated with MoDTC were even higher than those under PAO lubrication [17]. Generally, a higher MoS_2/MoO_x ratio is recognized as a key factor providing a lower wear rate. Therefore, synergistic effects not only depend on MoDTC itself but also depend on the modified surfaces. It is supposed that the tribological system could achieve a much lower friction coefficient and wear rate through the high wear resistance of nitrided steel and the high friction reduction of MoDTC. Unfortunately, research on the synergistic effects between nitrided 52100 steel and MoDTC additive under boundary lubrication have not been reported so far.

In this paper, the friction and wear behaviors of plasma nitrided 52100 steel were compared with those of the untreated surface lubricated with MoDTC under boundary lubrication. It attempted

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Table 1
Typical physico-chemical properties of PAO.

Item	Value
Viscosity ($mm^2\,s^{-1}$, 40 °C)	16.68
Viscosity index	124
Flash point (°C)	213
Pour point (°C)	−72
Evaporation loss (%)	11.8

Table 2
Typical physico-chemical properties of MoDTC.

Item	Value
Appearance	Black-brown liquid
Density ($g\,cm^{-3}$)	1.01
Viscosity ($mm^2\,s^{-1}$, 40 °C)	700
Flash point (°C)	135
Mo content (%)	10.0
S content (%)	11.0

to reveal the synergistic effect between nitrided steel and MoDTC, as well as the composition of tribofilm formed on the nitrided steel surface.

2. Experimental details

2.1. Materials and lubrication

The samples used in this work were 52100 steel balls, with a diameter of 12.7 mm, hardness of 770 HV, and surface roughness Ra 0.025 μm. The samples were nitrided in a pulsed direct current plasma nitriding furnace (LDM2-25) at 550 °C with a voltage of 700 V and a pressure of 650 Pa, for a total duration of 5 h, using the ammonia as a source gas. After the nitriding process, the samples were cooled in vacuum to ambient temperature.

A synthetic oil poly-alpha-olefin (PAO) with viscosity grade 4 was used as the base oil, and a friction modifier MoDTC was used as the additive. The typical physico-chemical properties of PAO and MoDTC are listed in Tables 1 and 2. The MoDTC concentrations (mass fraction) in the base oil were 0.0%, 0.5%, 1.0%, and 1.5%, respectively.

2.2. Friction and wear test

The friction and wear tests were carried out on a MS-10JR four-ball friction and wear tester. In the present work, the tribotest was conducted under four balls of a same material at the condition of bath lubrication, a load of 392 N (corresponds to the initial Hertz mean contact stress of 2.293 GPa), linear speed of 0.461 m/s, and test duration of 60 min. Before the wear test, for evaluating the Extreme-Pressure (load-carrying) capacity of lubricants, the maximum non-seizure load (PB value) was tested. The applied normal load, 392 N, is much lower than 470 N that of the PB value of PAO [12]. It means that no seizure happened on the rubbing surfaces during the wear test. There is a temperature probe at the bottom of the oil bath. The oil was heated by the friction heat. The temperatures continued increasing and the final temperatures were mainly within the limit of 60–70 °C. The friction force and friction coefficient were measured by a piezoelectric force transducer connected to the computer. The worn scars were measured by a microscope. The tests were replicated at least three times. A good repeatability for the friction coefficient and worn scars in the whole process of the test was recorded and the results were averaged.

The minimum film thickness was determined using the Dowson and Hamrock minimum film thickness equation for an elastohydrodynamic point contact [18]. The lambda is a ratio of minimum lubricant film thickness to starting composite root mean square surface roughness. The film thickness and lambda ratio were calculated using Eqs. (1) and (2), respectively. The minimum film thickness,

$$h_{\min} = 3.63 R_x \frac{G^{*0.49} U^{*0.68}}{W^{*0.073}} \left(1 - e^{-0.68k}\right) \tag{1}$$

where $G^* = \alpha E'$; $U^* = \eta_0 U / E' R_x$; $W^* = W / E' R_x^2$ and η_0 is dynamic viscosity; α is the viscosity-pressure coefficient; R_x is equivalent curvature radius of ball; W is the normal pressure; E' is the effective modulus of elasticity and k is elliptical parameter.

$$\Lambda = \frac{h_{\min}}{\sqrt{2R_q^2}} \tag{2}$$

where R_q is the roughness of the balls.

The lambda ratio value is 0.81 and 0.13 for the untreated surface and the nitrided surface, respectively, and both are below 1 which means that the lubrication occurred in the boundary lubrication regime.

2.3. Surface analysis

The cross-sectional hardness of the sample was measured on MH-6 Vickers′ microhardness tester at an applied load of 1.96 N for 5 s. Measurements were conducted for three times on each sample and the results were averaged. The JSM-6460LV scanning electron microscope (SEM) equipped with Oxford 7573 energy dispersive spectrometer (EDS) was utilized to observe the surface morphologies of the balls and the worn scar of the balls. The EDS was used to measure the elemental distribution of the worn surface. The chemical analysis of tribofilms was performed by a PHI Quantera SXM X-ray photo-emission spectroscopy (XPS). The instrument was employed a high-power rotating anode and monochromatised X-ray of Al $K\alpha$ ($h\nu = 1486.6$ eV) source. The diameter of the analyzed area was 100 μm. The residual pressure in the spectrometer was always below 6.7×10^{-8} Pa. The system was calibrated according to ISO 15472:2001 with an accuracy of ±0.1 eV. The analyzer was operated in the fixed-analyser-transmission mode with a pass energy of 55 eV and a step size of 0.2 eV (full-width-at-half-maximum (FWHM) of the peak height for Ag 3d5/2=0.5 eV). The position of C1s peak (284.8 eV) was considered as the reference for charge correction. The samples for XPS analysis were cleaned in the mixed solution of petroleum ether and absolute ethanol to remove residual oil and contaminants. Casa XPS software was used to analyze the XPS curves obtained from long scans, and the quantitative analyses of the peaks were performed using peak area sensitively factors. XPS handbook [19] was used to find the chemical species corresponding to the binding energies of the peaks.

3. Results and discussions

3.1. Characterization

The typical surface SEM morphologies of the balls are shown in Fig. 1. It can be clearly seen that the spherical particles were piled up closely with a lot of fine micro-porosities. The micro pores are distributed on the nitrided surface, which resulted in a higher roughness Ra 0.16 μm. However nothing was found on the untreated