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Comparing tribological behaviors of plasma nitrided and untreated bearing steel under lubrication with phosphor and sulfur-free organotungsten additive

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ABSTRACT

The interactions and synergistic tribological effects between plasma nitrided bearing steel surface and phosphor and sulfur-free organotungsten lubricating additive compared with that of untreated steel were investigated in this paper. The tribological behaviors were examined on a four-ball friction and wear tester. The chemical characteristics of the tribofilms were analyzed by X-ray photoelectron spectroscopy (XPS). The results showed that the obvious synergistic effects of better tribological performance between nitrided surface and organotungsten additive were attributed to WN formed in the tribofilm and a stronger adsorption of organic carbon chains and higher contents of C and W element in the tribofilm.

1. Introduction

With the rapid development of modern industries and people's rising awareness about environment and health it was realized that some harmful elements like phosphor, sulfur and ash should be reduced in the lubrication additives along the direction of developing thermo-resistant, environment-friendly and high efficient additives [1–3]. Recently, the research on the new additives with compounds containing boron [4,5], nitrogen [6,7] and organometal [8–10] has been widely carried out. However, the newly developed additives still showed some shortages in friction-reduction, anti-wear, anti-oxidation, hydrolysis-resistance and dispersive ability, etc., they still cannot be used to take the place of the traditional phorsphor and sulfur-containing additives. The phosphor and sulfur-free organotungsten additive has shown its excellent anti-wear and anti-oxidation ability, however, research on the tribological mechanism of which has been rarely reported so far.

The friction and wear performance of a friction-pair is affected by a series of factors, in which the lubricating additives and surface modification are the main ones. Plasma nitriding is a widely used chemical heat treatments, it can produce a compact and high hardness nitrided layer on the surface of steel work-pieces to improve their fatigue, wear and corrosion resistance properties [11]. In modern equipment, severe wear usually occurs between the rubbing-pairs in the boundary or mixed lubrication condition [12]. So it is worthy and necessary to study the tribological properties of plasma nitrided surface under lubrication with special additives in order to meet the requirement of these rubbing-pairs. Investigations on the interaction between nitrided surface and phosphor and sulfur-containing additives by Yansheng Ma et al., suggested that cresyl phosphate ester and nitrided layer showed a noticeable synergistic effect [13–15]. Yanqiu Xia et al., studied the friction and wear properties of nitrided steel under the lubrication with paraffin oil, alkyl Kenai, ionic liquids and several other phosphor and sulfur-containing additives, indicated that the nitrided steel exhibited superior friction-reducing and anti-wear performance than the substrate [16–18]. However, researches on the interactions between nitrided surface and the phosphor and sulfur-free organotungsten additive have not been reported so far.

This paper examined systematically the tribological properties of substrate and plasma nitrided bearing steel lubricated with phosphor and sulfur-free organotungsten additive on a four-ball friction and wear tester. The composition and compound states of tribofilms on the worn surfaces were analyzed by modern surface analysis instruments. Based on the results the tribological mechanism of the synergistic effect between nitrided steel surface and organotungsten additive was discussed.

2. Experimental methods

2.1. Experimental materials and preparation

Specimens employed in current study were 52,100 steel balls with diameter of 12.7 mm and roughness of Ra 0.025 μm.

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The balls were nitrided in a LDM 2–25-type plasma nitriding furnace. The gas source was NH_3. The operation temperature was 520 °C, applied voltage was 700 V, and pressure in furnace was 670 Pa. The treatment time was 5 h with cooling in the furnace. The lubricating oil used was poly-α olefin (PAO) synthetic base oil, its kinematic viscosity was 16.68 mm^2/s at 40 °C with a VI of 124. The Phosphor and sulfur-free organotungsten additive (R.T. Vanderbilt Company) was an effective antioxidant and anti-wear agent used for a wide range of automotive and industrial lubricants containing 14% tungsten, 1.2% nitrogen (by mass), and its density was 1.06 g/cm^3 at room temperature [19–21].

2.2. Experimental methods

MS-10 JR four-ball friction and wear tester is the standard tester used to test the extreme pressure (EP) characteristics of greases and lubricating oils in sliding steel-on-steel applications, and it can also test the friction and wear properties of different lubricating oils [22,23], which was used to evaluate the friction and wear properties of the substrate and plasma nitrided surfaces of bearing steel under the lubrication with phosphor and sulfur-free organotungsten additive. The four balls used in each test were selected as the same material. In the test, a load of 400 N with the Hertz mean contact stress of 2.293 GPa and rotating speed of 1200 r/min were adopted; and the testing duration was 1 h. The lambda ratios for these tests were calculated as 0.812 and 0.13 for the substrate and nitrided surfaces, respectively. They are not same but both are less than 1. So the lubrication on substrate and nitrided surfaces are in the boundary regime. The organotungsten concentrations were selected as 0.0%, 0.25%, 0.5%, 1.0%, 1.5%, 2%, 2.5% (by mass). The maximum non-seizure loads (PB values) of these lubricating oils were also tested. The testing conditions were at a rotating speed of 1500 r/min, testing duration of 10 s at 25 °C. The friction coefficients were calculated by the ratio of friction force and pressure, the average wear scar diameters were measured using a 15 J-type microscope.

The microhardness of the samples was measured by MH-6 micro-hardness tester, and the applied load was 1.96 N with loading time of 5 s. D/max-2550 model X-ray diffraction spectrometer (XRD) was utilized to analyses the phase structure of the nitrided surface with Cu-K_α radiation as the excitation source. JSM-6460 LV model low vacuum scanning electron microscope (SEM) with energy dispersive spectroscope (EDS) was used to observe the surface morphologies and analyze the elements of the surface. PHI Quantera X-ray photoelectron spectroscope (XPS) was utilized to identify the chemical state of the compounds formed on the worn surface with Al-K_α ($h\nu$=1486.6 eV) radiation as the excitation source and the binding energy of contaminated carbon (C1s, 284.6 eV) as reference. The samples for XPS analysis were thoroughly cleaned using a mixed solution of petroleum ether and absolute ethanol in an ultrasonic bath to remove residual oil and contaminants.

3. Results and discussion

3.1. Microstructure and hardness

Fig. 1 shows the surface morphologies of the substrate and nitrided samples. It can be seen that the substrate surface was smoother, while the nitrided surface showed more gray particles. Its roughness was increased to Ra 0.16 μm due to the cathode sputtering in the plasma nitriding process. The electron spectroscopy analysis indicated that the nitrided surface contained higher concentration of nitrogen (14.27 at%).

The cross-sectional morphology of the nitrided layer is shown in Fig. 2. It can be seen that a gray nitrided layer was formed on the surface of the sample, the thickness of which is about 12 μm. Fig. 3 shows the variation of the hardness of nitrided layer with the depth of the layer. The hardness value reached 900 to 1000 HV in the 0–40 μm depth range from the surface. Then it decreased linearly in the range of 40 to 140 μm. When the distance from the surface is larger than 140 μm, the hardness remained at a lower value.

Fig. 4 exhibits the XRD analysis results of substrate and nitrided samples, it can be found that the substrate surface was mainly composed of martensite and austenite, while the nitrided surface was mainly composed of γ′-Fe_4N and ε-$Fe_{2-3}N$.

3.2. Tribological behaviors

Fig. 5 shows the variation of friction coefficients of the substrate and nitrided surfaces with testing time under lubrication with different concentrations of organotungsten additive. It can be seen

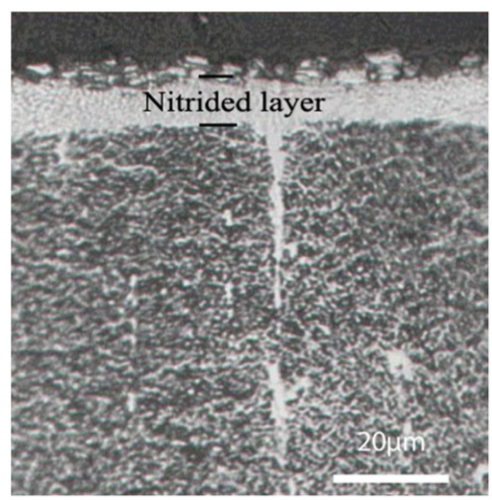

Fig. 2. Morphologies of cross-section.

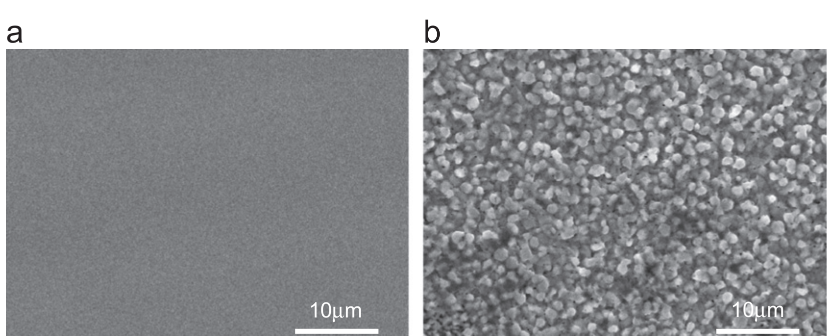

Fig. 1. SEM images of (a) substrate surface and (b) nitrided surface.