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Synergistic effects between sulfurized-nanocrystallized 316L steel and MoDTC lubricating oil additive for improvement of tribological performances

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ABSTRACT

The synergistic effects between sulfurized-nanocrystallized 316L stainless steel and molybdenum dithiocarbamates (MoDTC) additive under boundary lubrication were investigated in this paper. The tribological behaviors of the treated steel were investigated on a ball-on-disc SRV tribometer. The chemical analysis of tribofilms was performed by X-ray photoelectron spectroscopy (XPS). The results showed that the sulfurized-nanocrystallized sample exhibited the lowest coefficient of friction (0.060) and the lowest wear rate under MoDTC lubrication. The sulfurized ultrasonic cold forging technology (UCFT) composite treatment provided a strong support to the soft FeS layer and prolonged its service time. The MoS_2 decomposed by MoDTC can achieve the lowest coefficient of friction.

1. Introduction

Friction and wear are the major failure forms of mechanical parts, which often play important roles in the higher work efficiency and longer service life of modern equipments [1]. 316L stainless steel (316LSS) is a widely used material for piston ring due to its excellent properties in corrosion and oxidation resistance. The piston ring works in the condition of high temperature, high pressure, high speed and lack of enough lubricant, leading to the severe wear at the sliding interface with the cylinder wall. Nevertheless, the high coefficient of friction and low hardness of 316LSS restrict its tribological behaviors.

Surface modification techniques have been widely applied to improve the tribological behaviors and lengthen the service life of machine parts. Surface nanocrystallization [2] and low temperature ion sulfuration are becoming effective and widely used surface modification techniques in industrial field. The hardened layer induced by surface nanocrystallization improves the wear resistance and anti-scuffing behaviors of steel [3–7], but the high hardness can intensify the wear of its counterparts. The sulfurized layer is a good solid lubrication film that shows significant friction-reducing and anti-scuffing properties, but the thin solid lubrication film can be quickly worn away if the substrate is not hard enough to support it well [8–10]. However, the nanocrystallized layer can give a great support to the sulfurized layer, decreasing the temperature and the treated time of ion sulfurization treatment. Wang et al. [11] reported that the supersonic fine particles bombarding (SFPB) plus low temperature ion sulfurization can decrease the coefficient of friction and increase the wear resistance property notably under dry sliding condition. Therefore, the composite treatment of surface nanocrystallization and low temperature ion sulfuration would have positive effects on the tribological performances.

The selection of appropriate lubrication is another critical solution for improving tribological properties of the piston ring. Molybdenum dithiocarbamates (MoDTC) is the most commonly used friction modifier, which is widely used in the engine oil [10,12–17]. MoDTC can reduce friction by forming a MoS_2-containing film and molybdenum oxides on the tribological contact surfaces to improve friction reducing properties [18,19]. An important factor for improved friction performance is the ratio of MoS_2 with the high-friction species such as MoO_3 [15]. Yue et al. [10] proposed that the sulfur-nitrided surface exhibited the best synergistic effects with MoDTC displaying the lowest coefficient of friction and wear volume. Wang et al. [7] reported that the sample treated by ultrasonic cold forging technology (UCFT) exhibited the lower coefficient of friction and wear rate than the untreated sample under MoDTC lubrication. However, researches on the

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synergistic effects between sulfurized UCFT 316LSS and MoDTC have not been reported so far.

In this paper, the synergistic effects between sulfurized UCFT treatment and MoDTC were investigated. The chemical analysis of tribofilms was performed by X-ray photoelectron spectroscopy (XPS). It can be helpful to further provide the basic theory of the composite surface modification technology between the surface nanocrystallization and low temperature ion sulfuration, promoting a wide application of the composite surface modification technology in engineering fields.

2. Experimental details

2.1. Materials

The experimental material used in this work was 316LSS disc with a thickness of 3 mm, and the surface average roughness R_a was 4 nm. Table 1 shows its chemical composition [20]. The disc was machined into the size of 60 × 60 mm^2 for UCFT treatment.

UCFT treatment used ultrasonic vibratory energy as a source, and several tens of thousands of strikes per second to the material surface as constant pressure were applied. These strikes caused severe plastic deformation on the surface layer, which induced a nanocrystallized structure. The schematic diagram was demonstrated in the literature [3,7]. A tungsten carbide ball was fixed on an ultrasonic device and it struck the surface of a workpiece at a frequency of 20 kHz. The parameters used in this work are shown in Table 2. The samples were ultrasonically cleaned for 10 min by immersing in acetone after the treatment.

The UCFT samples were sulfurized in a LDM2-25 pulsed direct current plasma nitriding furnace. The samples were ultrasonically cleaned in acetone for 10 min. The principle of low temperature ion sulfuration is similar to that of ion nitriding [8,21]. 316L steel was put on the cathode plate with DC voltage applied between the components and the container wall. The solid sulfur became sulfur gas when the temperature was up to 230 °C, and the sulfur plasma permeated into the steel with the crystals and defects to form the compound FeS. Table 3 shows the technology parameters of ion sulfuration.

2.2. Surface analysis

The hardness variation along the depth was measured on a cross-sectional sample by a SHANGHAI EVERONE PRECISION MH-6 microhardness tester, and the load (50 g) lasted for 5 s. The JSM-7001F scanning electron microscope (SEM) was utilized to observe the surface morphologies of the test samples. The roughness and the wear volume were measured by an Aep Technology Nano-Map-D 3D profiler. The morphologies of the counter ball wear surfaces were investigated by a BX51M Olympus optical microscope (OM). X-ray diffraction (XRD) analysis was carried out on a D/max-2500 X-ray diffractometer with Cu-Ka radiation source to obtain the phase identification in the modified layer. Each sample was carried with a 2θ range of 30–90° and the scanning speed was 5°/min.

A PHI Quantera X-ray photoelectron spectroscopy (XPS) was used to determine the chemical states of typical elements on the wear tracks of the tested samples. The instrument utilized a high-power rotating anode and monochromatised X-ray of Al Ka ($h\nu$ = 1486.6 eV) source. The wear surfaces were sputtered for about 5 nm in depth by Ar ion in order to remove the adsorption of the contaminated carbon and possibly oxygen on the top surface. The binding energy of 284.8 eV for C 1s was considered as a reference for charge correction. The measured area is 100 × 100 μm^2. The take out angle is 45°. The beam power is 25 W. The beam energy is 15 KV. XPSpeak software was used for performing the curve fitting procedures on XPS peaks obtained. X-ray photoelectron spectroscopy (XPS) spectrum of standard chemicals was accumulated in order to obtain reference peak positions and curve fitting parameters for analysis of pure additives, adsorbed films formed on steel surface, and boundary lubrication film formed on steel surfaces [22]. The curve fitting algorithm used in this work was the Gaussian–Lorentzian sum formula and asymmetric Gaussian–Lorentzian sum formula. The asymmetric one was used only for curve fitting of Fe 2p3/2, while the symmetric one was used for all the other regions. O 1s spectrum is fitted with Gaussian–Lorentzian with FWHM of 1.55 eV and Gaussian ratio of 80%. Fe 2p3/2 spectrum is fitted with Asymmetric Gaussian–Lorentzian with FWHM of 1.38 eV and Gaussian ratio of 40% for metal peak, FWHM of 2.8 eV and Gaussian ratio of 60% for oxide peak. In the case of an asymmetric spectrum like Fe 2p3/2, not only curve fitting parameters but also type of background affect curve fitting result as peak positions or number of peaks [22]. Peak area ratio, difference between binding energies of full-width at half-maximum (FWHM) were constrained in order to obtain information with the most appropriate chemical meaning [23]. The value of FWHM of XPS peaks obtained in this work was a convolution of analyser resolution [23] and of natural FWHM of the peak [15,24].

Before XPS analysis, the samples were immersed in the mixed solution of acetone and absolute ethanol to eliminate the residual lubricant and contaminants.

2.3. Characterization

The typical SEM morphologies of the sulfurized surface and the sulfurized UCFT surface are shown in Fig. 1. It can be clearly seen that the two surfaces are covered by a lot of particles. The sulfurized layer is stacked with fine spherical particles embedded in each other randomly in a stacked constitution. The sulfide particles distributed on the sulfurized UCFT samples are obviously more than that of the sulfurized sample. The porosities distributed on the surfaces, result in a higher roughness. The surface roughness R_a of the untreated surface

Table 1
Nominal composition of 316LSS.

Element	C	Cr	Mo	Mn	Ni	Cu	Si	S	Fe
Contents (wt%)	0.019	17.07	2.04	1.68	11.95	1.14	0.35	0.007	Balance

Table 3
Technology parameters of ion sulfuration.

Samples	Gases source	Sample bias (V)	Pressure (Pa)	Temp (°C)	Duration (h)
Untreated and UCFT samples	Sulfur powder	1000	160	230	2

Table 2
The parameters of the UCFT treatment.

Vibration frequency (kHz)	Amplitude (μm)	Load (N)	Spindle speed (rpm)	Feed rate (mm rev^{-1})	Tip diameter (mm)	Number of shots per mm^2
20	20	300	200	0.025	10	96,000