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Tribological assessment of coated piston ring-cylinder liner contacts under bio-oil lubricated conditions

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A B S T R A C T

To alleviate high friction and corrosive wear in piston ring and cylinder liner friction pairs lubricated with bio-oil, four kinds of coatings: Ni-P, Ni-P-MoS_2, Ni-P-GO and Ni-P-MoS_2-GO have been prepared via chemical nickel plating technology. A multi-functional engine piston ring-cylinder liner tribometer was employed to evaluate their tribological behaviors. Furthermore, the changes of the bio-oil under different frictional conditions were analyzed by Fourier transform infrared spectroscopy. The results show that adhesive wear, scratching, spalling and mild wear took place respectively on the worn surfaces of piston rings with Ni-P, Ni-P-MoS_2, Ni-P-GO, and Ni-P-MoS_2-GO coatings. Ni-P-MoS_2-GO coated piston rings showed excellent friction-reducing and anti-wear performance and subsequently have great potential for accelerating the application of bio-oil in IC engines.

1. Introduction

Piston ring and cylinder liner friction pairs are almost the most important parts in the internal combustion (IC) engines because more than 30% of the energy consumption in an IC engine is caused by the piston ring-cylinder liner system [1]. To cope with the energy shortage and enhance the fuel efficiency, decrease of the friction and wear of the piston ring-cylinder liner contacts has attracted lots of researchers. Etsion et al. [2] used laser surface textured piston rings to improve the fuel efficiency. They found that the laser texturing did not alter the exhaust gas components, but the laser-textured piston rings could reduce the fuel consumption by 4%, comparing with those without texture. However, under corrosive conditions, surface texture might not play a protective role for piston ring – cylinder liner contacts, while coatings on friction pairs have been considered as an effective method to decrease the corrosive wear.

Many efforts have been exerted on surface coating technologies for more than fifty years. Skopp et al. [3] analyzed the tribological behavior of titanium suboxide coatings for piston ring/cylinder liners under different conditions. It was found that thermally sprayed titanium suboxide coatings for piston ring exhibits a similar friction and wear performance to commercial Mo-based coatings on piston ring. Cylinder liner-piston ring material with diamond like carbon (DLC) coatings exhibited better friction and wear performance than uncoated stainless [4]. Two kinds of coatings including thermal-sprayed CrN and physical vapor deposited DLC on the nitrided stainless steel and chrome plated stainless steel piston rings have been studied by Tung et al. [5] under fully-formulated engine oils. Results showed that DLC coating had the lowest wear on cylinder liner. Unfortunately, DLC coating has a high internal stress [6], which leads to an abrupt spalling for coating. Chemical plating coating has become popular in recent decades, because of its lower internal stress, excellent mechanical properties, good anti-corrosion and anti-wear performances [7].

On the other hand, recently, bio-oil has become one of the most promising alternatives to fossil fuel, which has many advantages including reproducible, carbon-neutral, and environmental friendly [8]. However, high contents of acidic components makes bio-oil easy to corrode the metal, which results in it cannot be used in IC engines directly [9]. Coating is an effective method to prevent metals from the corrosion of bio-oil. Developing a novel coating to relieve the corrosion of bio-oil and to improve the tribological properties of cylinder liner/piston ring contacts will be helpful in accelerating the application of bio-oil in IC engines. In our previous work, electroless Ni-P and Ni-Cu-P coating was prepared on engine cylinder liner and their tribological behavior lubricated by bio-oil has been investigated [7]. The Ni–Cu–P coating on cylinder liner has demonstrated a very potential to accelerate the application of bio-oil in IC engines. Nevertheless, to the best of our knowledge, few reports have covered the friction and wear behavior of coated piston rings lubricated by bio-oil [7,10]. Samples with Ni-P coatings have been proved with much better tribological

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properties than those without coatings. Therefore, the samples without coatings have not been investigated in this work, while four kinds of coatings: Ni-P, Ni-P-MoS_2, Ni-P-GO, and Ni-P-MoS_2-GO have been deposited on piston rings and their tribological properties have been compared. Finally, the corresponding mechanisms were revealed.

2. Experimental

2.1. Materials

The cylinder liner samples were made from boron cast iron (Chemical components: 3.22% C, 2.33% Si, 0.25% P, 0.81% Mn, 0.05% B, 0.36% Cr and others are Fe) and supplied by the Kaishan Cylinder Co. Ltd (China). Samples were cut to 122 mm in length, 15.6 mm in width and 6.3 mm in height. The top piston ring specimens were ductile iron (Chemical components: 3.55% C, 2.72% Si, < 0.08% P, < 0.5% Mn, 0.03% Mg and others are Fe) and purchased from the Nanjing Feiyan Piston Ring Co., Ltd (China). The test rings were cut to 8 mm in length, 2 mm in width and 4 mm in height. The Anhui Province Key Laboratory of Biomass & Clean Energy at the University of Science and Technology of China supplied the bio-oil used in this research with the pH value between 2 and 3, and its kinematic viscosity at 40 °C is 13.2 cSt, and the composition and main physiochemical properties can be can be found in previous work [11]. The main components of the bio-oil are composed of acids, alcohols, ketones, aldehydes, phenols, esters, sugars, furans, guaiacols and multifunctional compounds.

For the preparation of the coatings, nickel sulfate ($NiSO_4·6H_2O$) was purchased from the Shanghai Liangren Chemical Co., Ltd (China). Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), Sodium hypophosphite ($NaH_2PO_2·H_2O$) and sodium acetate (CH_3COONa) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium citrate ($Na_3C_6H_5O_7·2H_2O$) was supplied by the Guangdong Shantou Xilong Chemical Company. The lactic Acid ($C_3H_6O_3$), thiourea (NH_2CSNH_2) and molybdenum disulfide (MoS_2) with an average diameter of ~30 µm microsheets were all received from the Shanghai Chemical Reagent Co., Ltd. Finally, the propionic acid ($C_3H_6O_2$) was purchased from the Tianjin Guangfu Fine Chemical Research Institute. All of the chemicals were of analytical grade, and used as received without further processing. The graphene oxide (GO) with most of the sheets larger than 5 µm used in the coatings was prepared according to previous work [12].

2.2. Coating preparation

The piston ring samples were put into an alkaline solution (NaOH 50g/L; Na_2CO_3 25g/L) at 80 °C to degrease, and then washed by deionized water. The samples were then immersed in 50% dilute hydrochloric acid until uniform minute bubbles occurred on their surfaces, and they were then washed with deionized water. After that, the test specimens were placed in a plating bath solution for 60 min with a stirring speed of 300 rpm. A list of detailed process parameters is given in Table 1. MoS_2 and GO particles were well dispersed by stirring with the help of sodium dodecyl sulfate (SDS) as surfactant and the particles were diffused and retained on the surface of the substrate [7,13]. Then they were embedded with Ni-P matrix and deposited on the substrate as shown in Fig. 1. After plating, the specimens were washed with deionized water and dried at 40 °C in a vacuum drying oven. For labeling, the coating without solid particles, with MoS_2 only, with GO only and with MoS_2 plus GO were named Ni-P, Ni-P-MoS_2, Ni-P-GO and Ni-P-MoS_2-GO, respectively.

2.3. Coating characterization

The specimens were cleaned again with acetone before characterization. A JEOL JSM-5600LV Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray spectrometer (EDX) was used to observe the micro-morphologies and detect the elemental compositions of the coating surfaces using accelerating voltage of 20 kV. The crystal structures of the coatings were analyzed using a Rigaku D/MAX2500 V X-ray Diffraction (XRD) instrument with Cu Kα radiation, 2θ varying from 5° to 90° and a scanning velocity of 10° min^{-1}. The microhardness of the coatings on the plated surfaces without polishing was measured using an MH-3 micro-vickers hardness tester at a load of 0.98 N for 10 s. Each sample was tested ten times, and the hardness value of each coating was calculated from the average of these values.

Table 1
Composition and operating conditions for electroless coatings.

Composition and operating conditions	Values			
	Ni-P	Ni-P-GO	Ni-P-MoS_2	Ni-P-MoS_2-GO
GO (g/L)	/	0.1	/	0.1
MoS_2 (g/L)	/	/	1	1
$NiSO_4·6H_2O$ (g/L)	26	26	26	26
$NaH_2PO_2·H_2O$ (g/L)	30	30	30	30
$Na_3C_6H_5O_7·2H_2O$ (g/L)	15	15	15	15
$C_3H_6O_3$ (mL/L)	17	17	17	17
CH_3COONa (g/L)	10	10	10	10
NH_2CSNH_2 (mg/L)	1	1	1	1
$C_3H_6O_2$ (mL /L)	2	2	2	2
pH	4.5 ± 0.1	4.5 ± 0.1	4.5 ± 0.1	4.5 ± 0.1
Temperature (°C)	88 ± 2	88 ± 2	88 ± 2	88 ± 2
Time (min)	60	60	60	60

2.4. Tribological tests

The friction and wear tests were carried out on a multi-functional piston ring- cylinder liner tribometer. The schematic diagram of the friction pairs are shown in Fig. 2. As can be seen, the piston ring slides on the cylinder liner via a reciprocating friction mode during the frictional process, with oil supplied through a drip feed. A more detailed test specification is given in Table 2. The test conditions were chosen to simulate the real applications. The coefficient of friction was recorded automatically via the ratio of friction force to normal load. The wear loss of the friction pairs was calculated by the weight of the samples before and after sliding, to an accuracy of 0.1 mg. Each sliding test was repeated three times to obtain a standard deviation.

After friction, the bio-oil was collected from each testing condition. The samples were washed by acetone and ultrasonically clean for 30 min. The worn surfaces of the piston ring were then observed by SEM, and the bonding energy of the typical active elements including C, O, Ni, P, Mo and S on the worn surfaces were characterized by a Thermo Scientific ESCALAB250Xi X-ray photoelectron spectroscopy (XPS) with a monochromatized Al Kα x-ray source. The chemical shifts of XPS peaks were standardized by the C 1s peak at 284.6 eV.

3. Results and discussion

3.1. Coating components and structures

Fig. 3 shows the SEM images of the four coatings, with insets showing a magnified area. The Ni–P coating displayed a relatively smooth surface with a typical cauliflower-like micro-morphology (Fig. 3a), which is similar to literature results [14]. Fig. 3b shows the effect of the introduction of MoS_2, with grains and ‘debris’ observed on surfaces, indicating that the MoS_2 was embedded in the Ni–P matrix via the co-deposition process [15]. Some porous structures can be seen on the surfaces of Ni-P-GO coating in Fig. 3c, in contrast to Wu et al. observed nodular structures [16]. This may be because the graphene oxide interfered with the deposition of the Ni-P coating, as a result of