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Advanced silicate-based lubricant additive induced diamond-like carbon structured restoration layer

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ABSTRACT

An advanced silicate based lubricant additive has been employed in long-term pin-on-disk tribological experiments. The worn steel/steel surfaces were characterized using nano-indentation, SEM, XPS, and Raman spectroscopy for their physical, mechanical, and chemical properties. The average nano-hardness of the repaired layers on the disk and the pin is 10.2 GPa and 16.7 GPa respectively, which is substantially higher than that of the disk (HV 221, or 0.71 GPa) and the pin (HRC55, or 1.8 GPa) before tribological tests, forming super hard surfaces on the contact pair surfaces. Combined Raman spectroscopy and XPS studies suggest the formation of diamond-like carbon based restoration layers. A new formation mechanism of the restoration DLC layer contributing to hard and smooth contact surfaces is proposed.

1. Introduction

Modern machining process conditions have become increasingly demanding, which typically involve elevated temperature, high pressure, and high velocity. Lubrication has a long history as an effective means to improve wear resistance and reduce friction [1–5]. An advanced silicate-based lubricant additive $Al_4[Si_4O_{10}](OH)_4$ [6,7] has been developed recently. The most noteworthy feature of the additive is that only a small amount (<1 wt%) can significantly reduce friction, and even restore the friction pair surface. Several studies have shown that the additive substantially improved the anti-wear and friction-reducing properties of steel–steel friction pairs [8–10]. Yu [11] investigated the restoration layer formed on the worn surface using the lubricant additive composed of flaky aluminum–magnesium silicate and catalysts. It was reported that a diamond-like carbon (DLC) film with Si or Si–O elements and high hardness formed on the worn surface [11]. Apart from the above studies, there is no study under *long-term* operating conditions. In addition, most published research mainly focused on the friction performance of restoration layer, but confirmation of DLC layer using Raman analysis and the role of lubricant additives on the formation of DLC layer have not yet been reported.

The purpose of this study is to understand the effect of the silicate-based additive in long-term 300-h tribological tests. The worn surfaces with the application of lubricant additive will be characterized. The formation of DLC layer on the repaired contact layer will be examined by Raman spectroscopy. The DLC formation mechanism will also be proposed. It should be noted that the diamond-like carbon structure in the work is different from conventional DLC film which is widely accepted as a kind of amorphous carbon film material prepared by CVD/PVD and liquid phase methods.

2. Experimental details

2.1. Tribological tests

Tests were performed using a pin-on-disk tribo-tester. It has 45 steel pins and disks with a chemical composition of 0.42–0.50 wt% C, 0.17–0.37 wt% Si, 0.50–0.80 wt% Mn, ≤ 0.2 wt% Cr, ≤ 0.30 wt% Ni and ≤ 0.25 wt% Cu with Fe as the balance. The dimension of 45 steel pin was 8 mm in thickness and diameter 12.7 mm, and the disk was 70 mm in diameter and 3 mm in thickness. The pins and the disks were controlled to be HRC55 and HV 221 hardness by heat treatment respectively. Each specimen was finished to a constant surface roughness of 0.8 μm R_a.

Continuous 300-h test with a variational loading profile 98 N (0–72 h), 147 N (72–156 h) and 245 N (156–300 h) was carried out to discover the properties of the worn surface.

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2.2. Lubricant and additive

The lubricant used in this experiment was SAE 30 engine oil as a baseline. We did not use additive-free base oil because we try to study the tribological properties in a simulated realistic condition. Silicate-based lubricant $Al_4[Si_4O_{10}](OH)_4$ was used as a additional additive. The additive is composed of silicate powders prepared from natural minerals and some dispersants with an average particle size of 0.3–3 μm [6,12]. The additive was added to the SAE 30 engine oil at a concentration of 0.8 wt%. During the tests, the lubricant oil was fed into the contact point between the pin and the disk by a circulating drip-feeding pipe. The average feeding rate of the flow was about 10 ml/min.

2.3. Worn surface analysis

After the tribological tests, atomic force microscope (AFM, SPM-9500J2; Shimadzu, Tokyo, Japan) was used to measure the roughness. A nano-indenter (ENT-1100, Elionix Co., Tokyo, Japan) was used to measure the nano-hardness of the worn surface, in which the samples were indented with maximum applied loads in the range of 0.5–500 mN. For each sample, the hardness was calculated using five tests.

To characterize the microstructure and wear mechanism of the coated samples, SEM (JSM-6460LV; JEOL Co. Ltd., Japan) was used to observe the cross-sectional morphology of the repaired pin in 300-h test.

The samples were irradiated with Raman spectroscopy (RS; RM2000, Renishaw, England) to study the DLC structure of the samples. The measurements were carried out with a laser wavelength of 514.532 nm. A low input power of 3.5 mW was used in order to minimize possible beam-heating effects. The structural characterization of DLC film formed on the worn surfaces was performed using X-ray photoelectron spectroscopy (XPS, AEM PHI5300, PE Co.).

3. Results

3.1. The roughness and nano-hardness of the worn surface

Surface roughness of the disk and the pin was measured using an AFM with two scan areas. The original surface roughness R_a of the samples was about 0.8 μm, whereas that of two different scan areas of the worn surface became $R_a = 60.318$ nm on the disk and 8.053 nm on the pin. It can be considered that the surface roughness was significantly reduced in the friction and wear process.

The average results of nano-hardness at five different locations on the worn surfaces are shown in Fig. 1. The depth of indentation in the nano-hardness test was 150 nm, indicating the hardness of the repaired layer. The average nano-hardness of the repaired layers on the disk and the pin is 10.2 GPa (Fig. 1a) and 16.7 GPa (Fig. 1b) respectively. The hardness values are substantially higher than the hardness of the disk (HV 221, or 0.71 GPa) and the pin (HRC55, or 1.8 GPa) before the tribological tests, suggesting forming super hard surfaces on the contact pair surfaces. It should also be mentioned that the nano-hardness of the worn surface on the pin was 50% greater than that on the disk, suggesting the running time influenced the mechanical properties of the repaired layer significantly. It was also noted that the nano-hardness data of the worn disk was more scattered than that of the worn pin, which indicated, the effect of the silicate additive possessed certain selectivity at different locations of the worn surface [13].

3.2. SEM and EDX examination

Fig. 2 shows the cross-sectional SEM images of the worn pin and line scan of several elements. Low-magnification SEM image of the cross section of the worn pin can be seen in Fig. 2a, a clear white and transparent repaired layer can be estimated to from 1 μm to 5 μm, the bottom of this cross section showed the smallest value of 1 μm. It is also noted that there is no obvious interface with the substrate, and crack was inhibited. The repaired layer of the worn pin is not even and the thickness is also different at the different worn areas, which demonstrated the repairing process is selective.

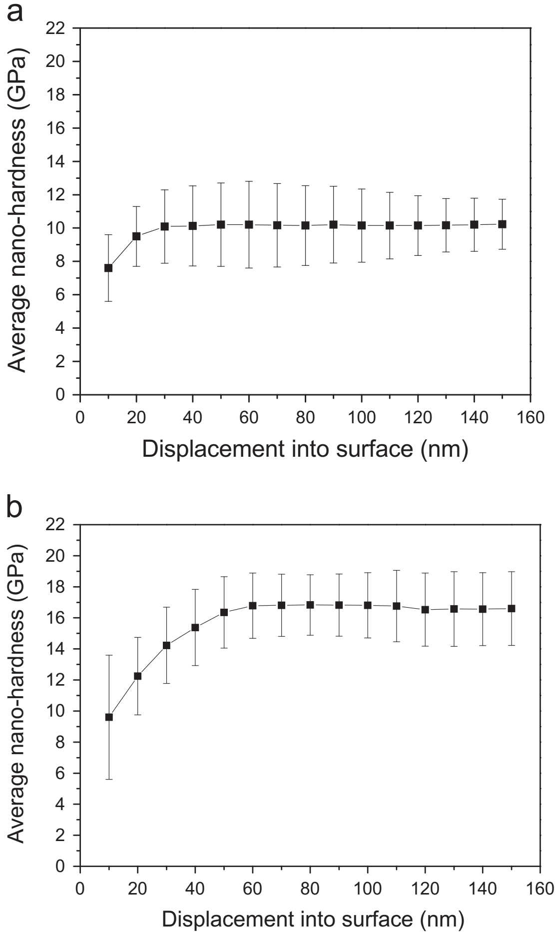

Fig. 1. Nano-hardness of (a) worn disk surface and (b) worn pin surface.

After it was amplified as shown in Fig. 2b, line SEM/EDX scan was conducted along from the substrate to the repaired layer on the cross section of the pin. Fig. 2c–f shows the EDX data of concentration of the element of carbon, oxygen, iron and calcium respectively. It can be seen that carbon concentration increased significantly on the area of the repaired layer, while iron concentration decreased with the distance from the substrate. High carbon content on the top surface would probably be diamond like carbon film. The DLC films are well known for their amorphous carbon microstructure, high hardness, low friction, and they show excellent wear resistance in oil-lubricated conditions. The hardness of the synthetic DLC films ranged from 10 to 60 GPa [14,15], which is consistent to the hardness measured using nanoindentation as discussed in Section 3.1. The low friction coefficient and wear resistance had been verified in previous studies [10]. The detailed structural characterization of DLC films is carried out by using Raman spectroscopy as discussed in Section 3.3.

3.3. Raman spectroscopy study

Diamond-like carbon films have been widely studied for their excellent properties, such as high hardness [16], high wear resistance [16], low friction coefficient [17], chemical inertness, high electrical resistance and optical transparency in the visible and infrared lights