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Study of the Regenerated Layer on the Worn Surface of a Cylinder Liner Lubricated by a Novel Silicate Additive in Lubricating Oil

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Some special silicate particles as additives in lubricating oil have shown a certain self-repairing function for the rubbing pairs of industrial equipment in recent R&D of extreme pressure antiwear additives. This article introduces an investigation on the regenerated layer on the worn surface of a practical cylinder liner lubricated by lubricating oil with a silicate additive using some advanced techniques like transmission electron microscopy (TEM), atomic force microscopy (AFM), nano-hardness tester, scanning electron microscopy (SEM), auger electron spectroscopy (AES), and Raman spectroscopy. The basic formula of the mineral in the silicate additive is $Al_4[Si_4O_{10}](OH)_4$. *Through some macro- and microanalyses, it was found that the silicate additive showed an obvious improving effect on their friction surface and self-repairing function. The roughness of the worn surface could be decreased greatly to several tens of nanometers, and its hardness was still above 10 GPa. The worn surface with some pits and cracks had been covered by a transparent regenerated layer, and the wear of cylinder liners was maintained at almost zero-wear level on average. The mechanism of the self-repairing function was approached. It was revealed that the silicate additive was acting as a catalyst to promote a series of complex tribochemical reactions to form a regenerated layer with amorphous carbon structure on the worn surface under high-friction temperature and pressure in the friction and wear process.*

KEY WORDS

AES (Auger); Antiwear Additives; Diesel Engines; Friction Modifiers; Railroad; Self-Lubrication Friction

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INTRODUCTION

Modern lubricating oils always contain a variety of extreme pressure antiwear additives to meet many severe working conditions of equipment. Nowadays, more researchers are focusing on the environmentally friendly lubricating oil additives and nanoparticle additives, which possess fascinating antiwear and friction-reducing properties and present a new trend of development in the area of additives (Liu *(1)*; Spikes *(2)*; Hsu *(3)*; Chen and Liu *(4)*). The layered silicate minerals have been applied in lubrication field for several years. These include bentonite, sepiolite, and smectite as thickening agents in the high-temperature greases (Chtourou, et al. *(5)*). In recent years, some silicate minerals have been used as additives in lubricating oil, and the results have showed an incredible effect of forming an autorepaired layer on the worn surface and displaying lower roughness, higher hardness, and improved tribological performance during the wear process (Liu and Guo *(6)*). Jin and Wang *(7), (8)* studied the application of serpentinite particles with formula $Mg_6[Si_4O_{10}](OH)_8$ in lubricating oil for the internal combustion locomotive. They found that the autorepaired layer was composed of only Fe, C, and O elements. Wang *(9)* thought the microstructure of the autorepaired layer was composed of Fe_2C, Fe_3O_4, and carbide. Yu *(10)* investigated the autorepaired layer formed on the worn surface, using a lubricating additive composed of some flaky aluminum-magnesium silicate and other catalysts; he reported that a sort of diamond-like carbon film with Si or Si-O elements and high hardness formed on the worn surface. Tian and Yue *(11), (12)* studied the tribological performance of a flaky aluminum-magnesium silicate, analyzed the microstructure and composition of autorepaired layer, and pointed out that after a long time of running, an autorepaired layer with high-carbon content was formed, which was very beneficial for improving the tribological performance. However, the mechanism of silicate particles as a lubricating oil additive is still unclear. The silicate additive $Al_4[Si_4O_{10}](OH)_4$ is one such new additive, which has been widely used and has shown an excellent effect in

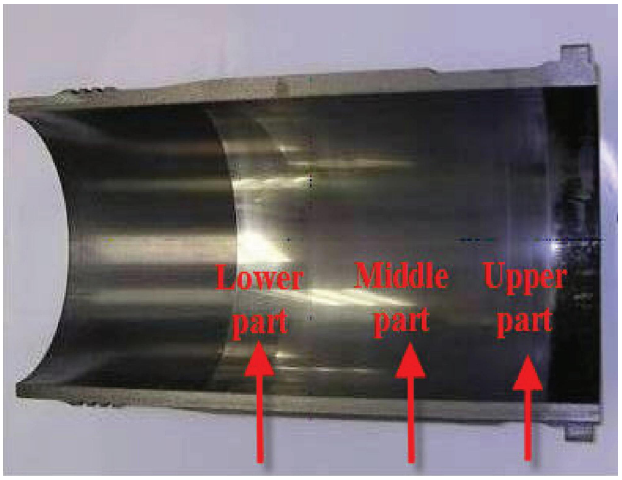

Fig. 1—Photo of the practical worn chrome-plated cylinder liner.

applications in recent years. In order to explore its effect and mechanism, the practical worn surface of a chromium-plated cylinder liner was analyzed, and on this basis, a tentative mechanism was developed.

EXPERIMENTAL DETAILS

A chromium-plated cast iron cylinder liner from the internal-combustion engine of a locomotive after running 260,000 km under the lubrication with the silicate additive was analyzed. The picture of its outward appearance is shown in Fig. 1. It can be clearly seen that the surface of the cylinder liner has become very smooth, like a mirror, and it seems to be coated by a thin and transparent film, while the original wear tracks, especially at the upper and lower dead positions, are still visible but cannot be felt by touching.

The silicate additive is composed of silicate powders prepared from natural minerals and some dispersants (Nikolaevich, et al. *(13)*). The granularity of the silicate powder ranges from 1 to 5 μm. The silicate particles exhibit a thin layer of hexagonal structure, the plane size is less than 1 μm, and the longitudinal size ranges from 20 to 40 nm. It contains Al, Si, and O elements, as shown in Fig. 2. The crystal structure was determined by its diffraction pattern, and then the formula of the mineral was determined to be $Al_4[Si_4O_{10}](OH)_4$. The additive was added to the engine lubricating oil of the locomotive at a concentration of 6 wt%.

The transmission electron microscope (TEM) and energy dispersive X-ray spectroscope (EDS) were used to analyze the microstructure and composition of the silicate particles. The atomic force microscope (AFM) and nonohardness tester were used to measure the roughness, nanohardness, and modulus of the worn surface. The scanning electron microscope (SEM), with energy dispersive X-ray spectroscopy (EDS), was used to characterize the composition and microstructure. Auger electron spectroscopy (AES) was used to determine the element distribution as a function of depth of the worn surface. Raman spectroscopy was used to measure the carbon structure of the worn surface.

RESULTS

The Wear Loss Diameter Measurements

The diameter at three different locations of 12 cylinder liners on the engine was measured with an inside micrometer before and after the test of lubricating oil containing silicate additive. The results are shown in Fig. 3. It can be found that, in general, the wear of cylinder liners was maintained at almost zero-wear level on average; some data were even negative, which indicates that a repaired layer (or regenerated layer) was probably formed on the worn surface. These phenomena were quite apparent at the upper position, which indicates that the effects of the silicate additive are uneven on different locations of the cylinder liner.

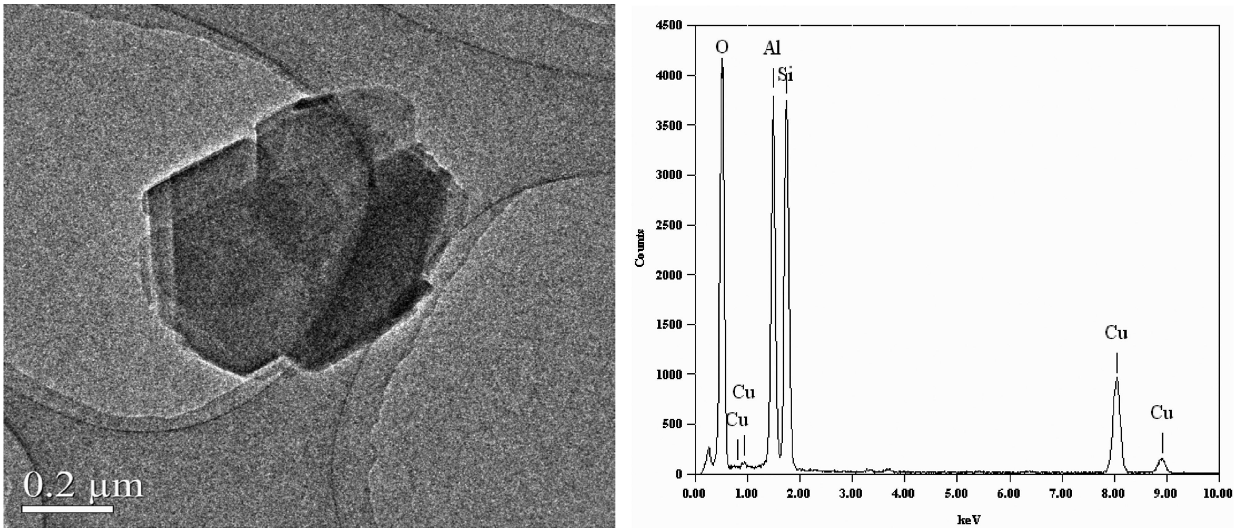

Fig. 2—TEM morphology and energy spectrum analysis of the mineral particle.

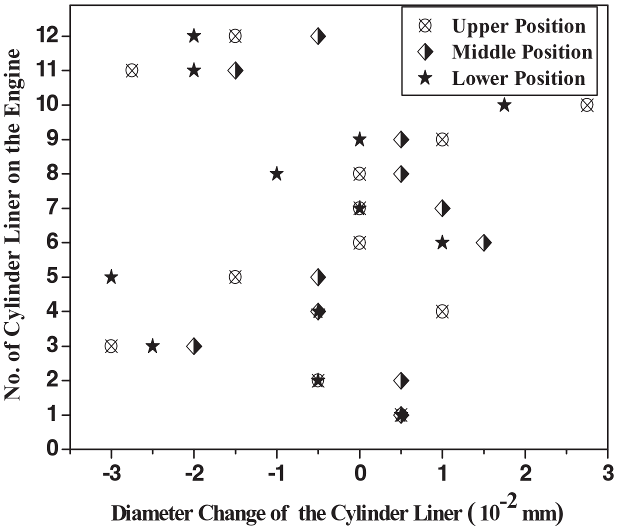

Fig. 3—Diameter change of three different locations of twelve cylinder liners on the engine after test.

The Roughness and Nanohardness of Worn Surface

The original surface roughness Ra of the cylinder liner is about 1 μm, whereas that of four different locations of the worn surface roughness became Ra = 36.9, 47.1, 112.5, and 31.0 nm, respectively. The measurement results by AFM are shown in Fig. 4. It can be considered that the surface roughness was significantly reduced in the friction and wear process.

The average results of nanohardness and modulus at five different locations on the worn surface are shown in Fig. 5. The indentation depth of the conventional microhardness tester was more than 2 μm, much larger than the thickness of the repaired layer. The microhardness data must be influenced by the substrate. So it is necessary to measure the nanohardness of the repaired layer. The depth of indentation in the nanohardness test was 150 nm, which can reflect the true hardness of the repaired layer. The chromium-plated cylinder liner's hardness of the worn surface became a little lower than that of the substrate surface, but it was still above 10 GPa. It should be mentioned that the nanohardness and modulus data of the worn surface were more scattered than that of the substrate surface, which indicated that

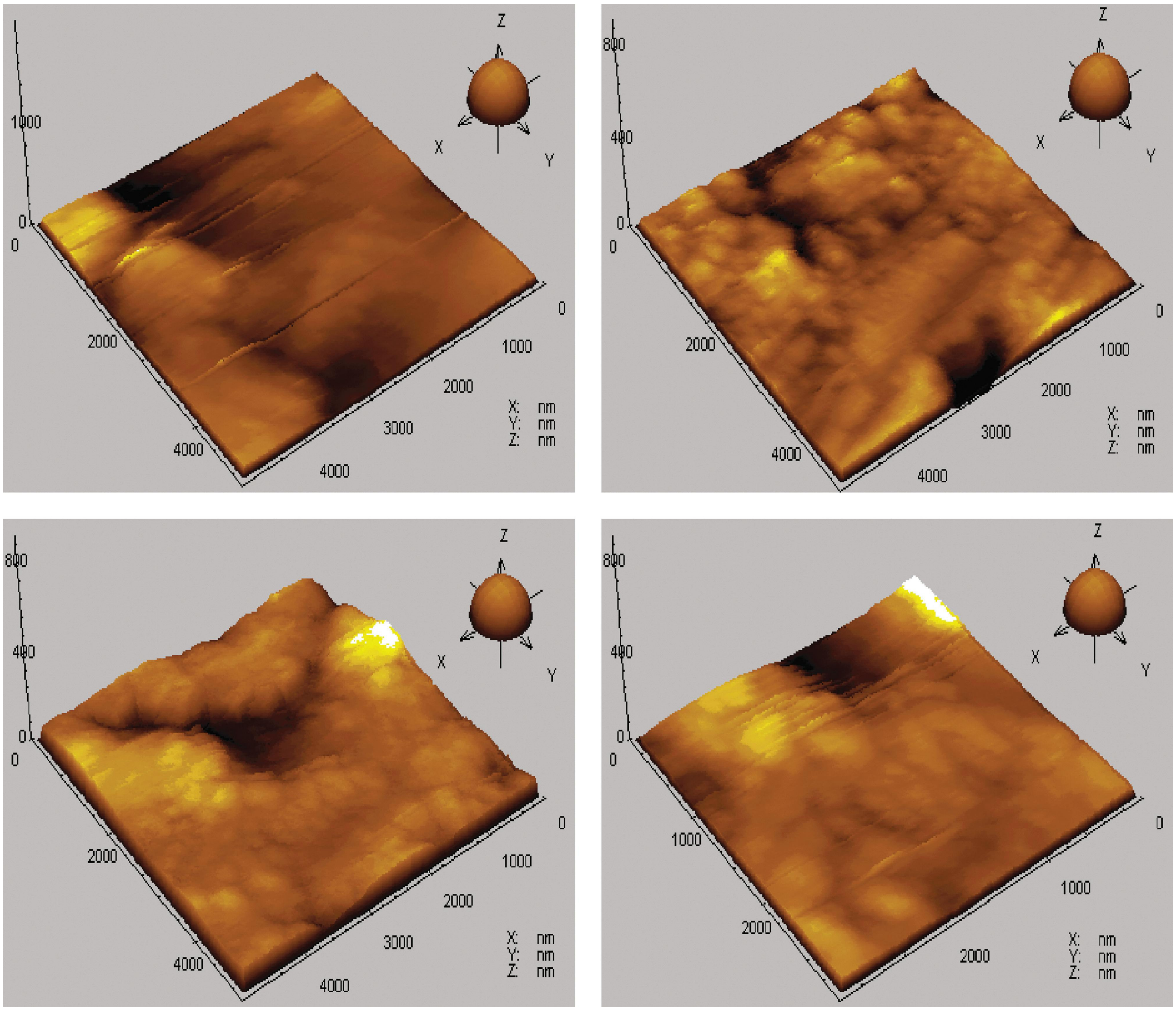

Fig. 4—Morphology of friction surfaces of the cylinder liner.

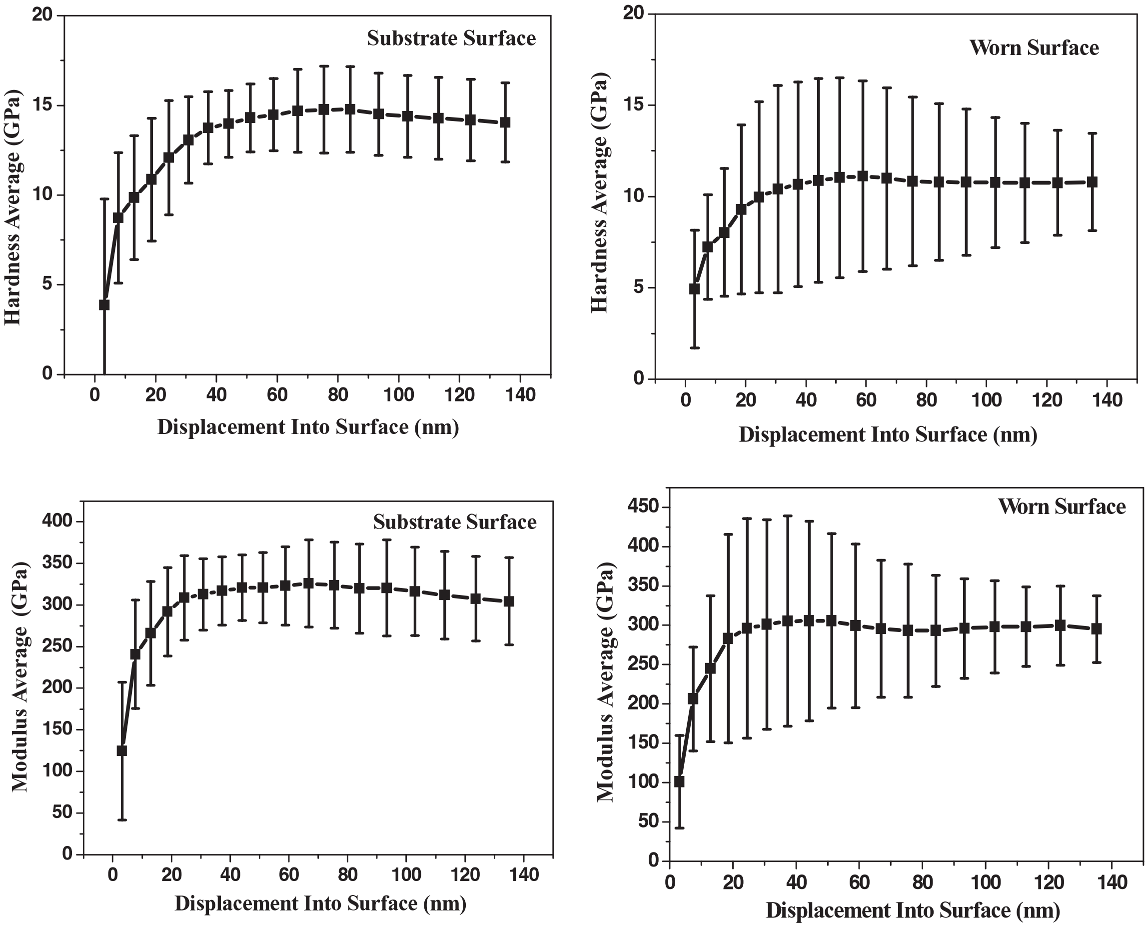

Fig. 5—Nanohardness and modulus comparison of the substrate and the worn surface.

the effect of the silicate additive possessed certain selectivity at different locations of the worn surface.

Microanalysis of Worn Surface

Figure 6 and Fig. 7 show the optical and SEM morphologies of the chromium-plated cylinder liner substrate and worn surface. It can be seen clearly that some reticular cracks were present on the substrate surface and worn surface of chrome-plated layer under optical microscope (see Figs. 6(a) and 6(b)), and the cracks were still found on the substrate surface under SEM (see Figs. 7(a) and 7(b)); however, on the worn surface they basically disappeared under SEM (see Fig. 7(c) and 7(d)). This phenomenon indicated

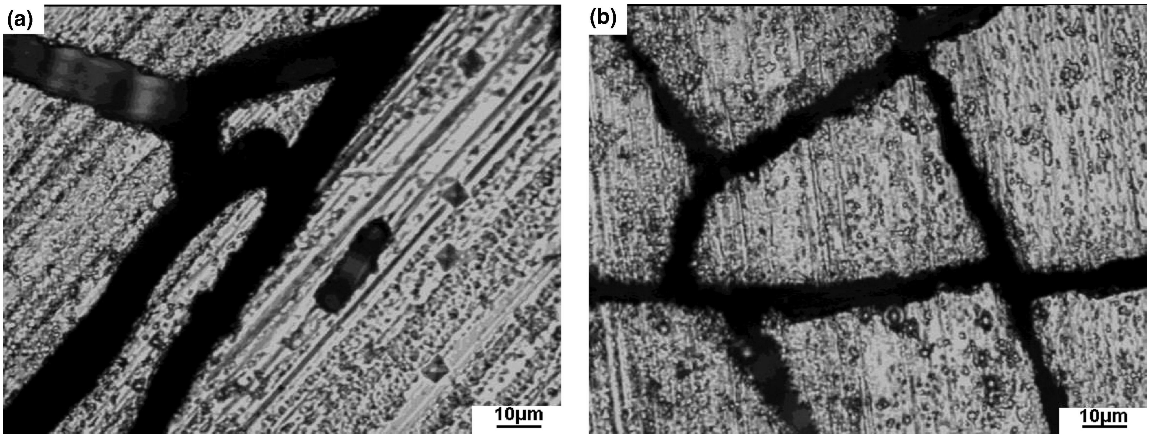

Fig. 6—Optical morphologies of substrate and worn surface on chromium-plated cylinder liner: (a) substrate surface, (b) worn surface.

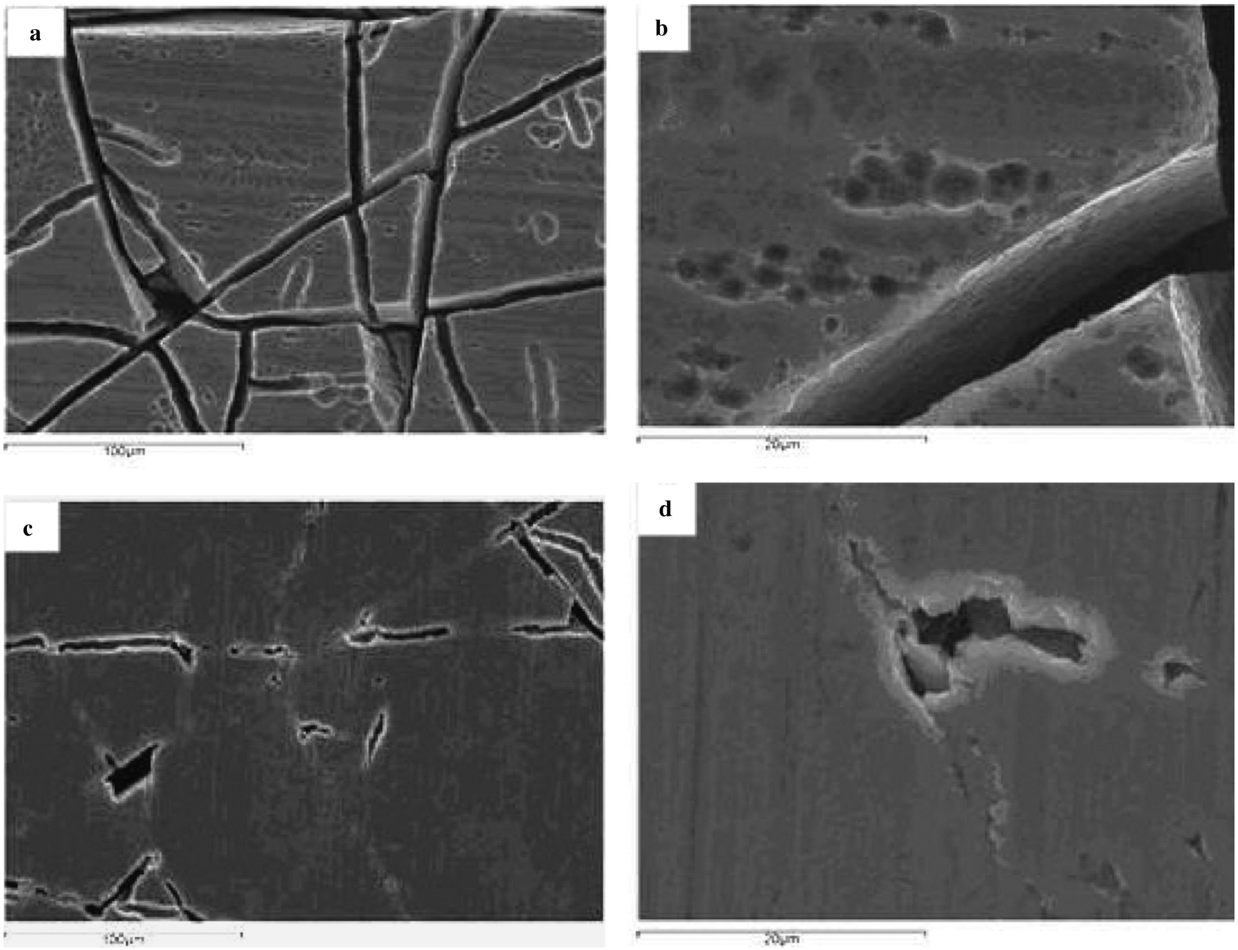

Fig. 7—SEM morphologies of substrate and worn surface on chrome-plated cylinder liner: (a), (b) substrate surface; (c), (d) worn surface.

that the worn surface was covered indeed by a thin transparent film due to different principles of image formation under SEM. The electron beam of SEM was acting only with the top surface of the sample, and the observed morphology reflected just the thin transparent film, while the optical microscope could observe the original cracks through the transparent film because of the higher transmission power of the visible light.

It is interesting to note that the EDS analysis data of the worn surface suggested a new viewpoint: No other elements were detected besides that of the substrate on the worn surface, and the carbon content in the repaired layer was obviously higher than that in the substrate. That means that the silicate additive played only the role of catalyst in the tribochemical reactions and did not participate in the formation of the repaired layer. Such a repaired layer was completely different from the boundary lubrication film formed through the reaction of substrate with the additives.

A translucent repaired layer was suggested to be formed on the worn surface; therefore, the accurate composition of this layer should be analyzed by AES. Six points on the worn surface were selected to do AES tests as shown in Fig. 8. Points 1, 2, and 3 were on the edge of cracks; point 4 was on the end edge of the cracks; point 5 was on the flat area; point 6 was on a pitting area. The full Auger spectra of six points showed that the chromium peak

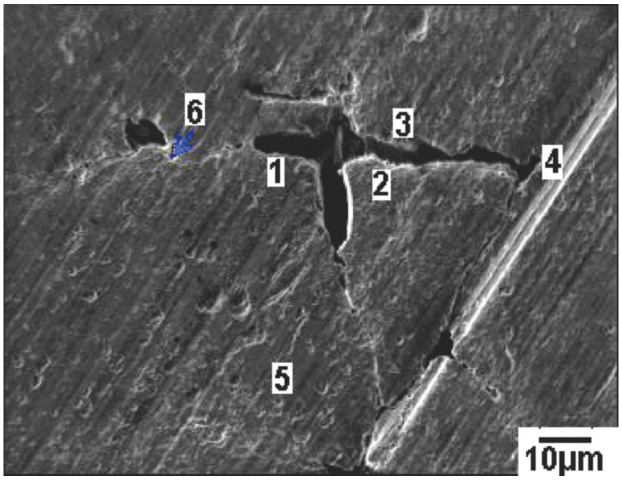

Fig. 8—SEM morphologies at the AES tested points.

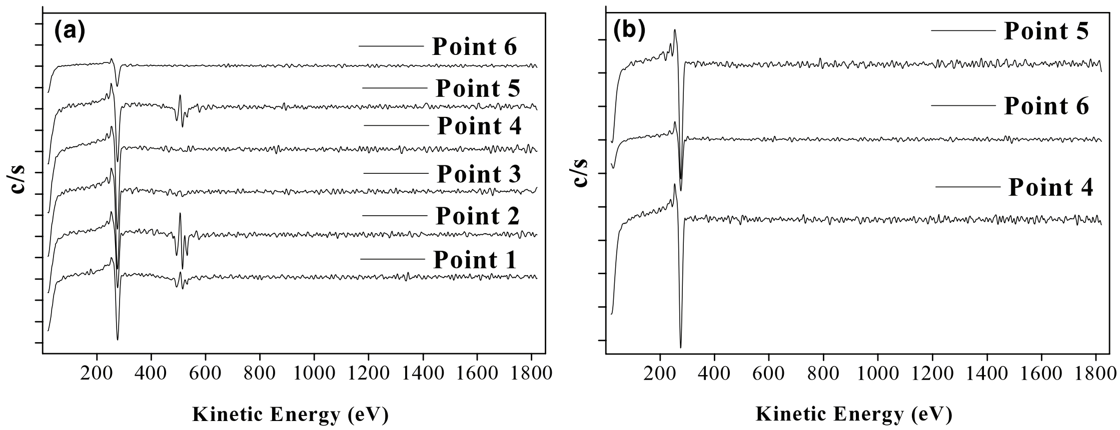

Fig. 9—Full auger spectra of the worn surface: (a) the top surface; (b) sputtered 3.6 nm.

and carbon peak were found on points 1, 2, and 5, and only the carbon peaks were found on points 3, 4, and 6. However, only the carbon peak appeared on all six points after sputtering 3.6 nm as shown in Fig. 9. This means that the top of the worn surface was composed of a little chromium and a lot of carbon.

The variations of elemental content of points 4, 5, and 6 with the sputtering depth were analyzed by AES as shown in Fig. 10. Only the carbon, oxygen, and chromium elements were found on the worn surface, which were corresponding to the above EDS analysis results. At the top surface, carbon content was very high; then it decreased with the sputtering depth; the thickness of the carbon-rich repaired layer was uneven it was about 250 nm on the flat area and about 400 nm at the end edge of cracks. Nevertheless, the curves of three elements on the pitting area were

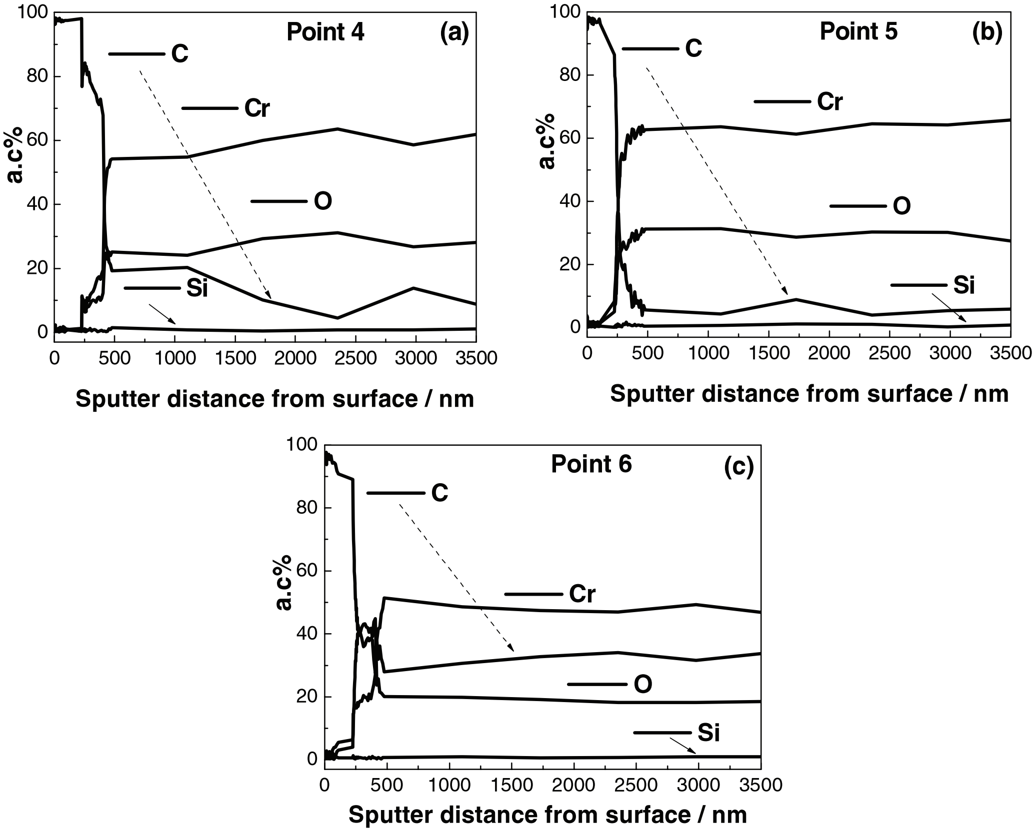

Fig. 10—Variations of chromium-plated cylinder liner's element contents with the sputtering depth: (a) point 4; (b) point 5; (c) point 6.

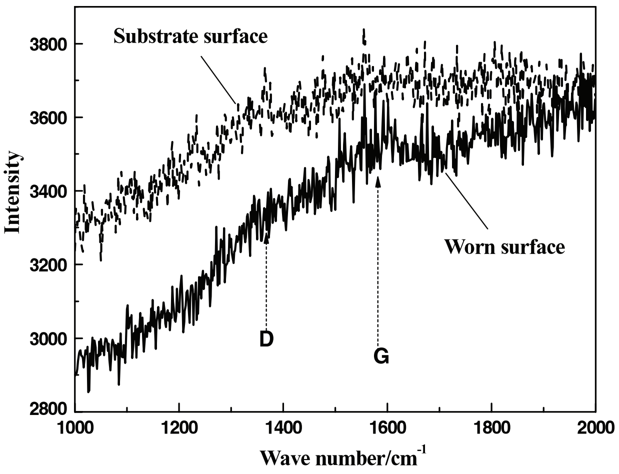

Fig. 11—Raman spectra of the substrate surface and worn surface.

different from those of the flat area and cracks, which indicated that the microcracks of pitting were covered by the transparent repaired layer. This was why the cracks disappeared under SEM observation.

The carbon structure of the repaired layer was analyzed by Raman spectroscopy and is shown in Fig. 11. Specific peaks D and G were found on the worn surface, but the intensity of them was relatively weak, whereas nothing was found on the substrate surface. Peak D represents amorphous carbon structure, and Peak G represents graphite structure. Therefore, the most likely structure of the carbon-rich layer was considered to be amorphous carbon structure, including some microcrystalline graphite.

DISCUSSION

A carbon-rich repaired layer of several hundred nanometers was formed on the worn surface of the chromium-plated cylinder liner, but its depth was uneven. The depth of the repaired layer on the flat area is lower than that on the end edge of cracks, and the depth at the pitting area was in the middle level. So it could be inferred that the depth of the repaired layer was dependent on the wear intensity; in other words, it was related to the surface energy. That was also the reason for the scattered nanohardness and modulus data of the worn surface. However, the carbon content of the Cr substrate was nearly zero (Wang, et al. *(14)*); Pina, et al. *(15)*). It could be certainly imagined that the carbon element of the repaired layer was not coming from the substrate, but from another channel: the lubricating oil pyrolysis product during the wear process. Aluminum and silicon elements of silicate particles were not found in the repaired layer, which means that the elements of silicate particles did not participate in the formation of the repaired layer. The solid silicate particles possessed enough chemical inertia; they were very difficult, even impossible, to react with the metal surface. The silicate particles could act only as a catalyst to promote a series of complex tribochemical reactions to form an amorphous carbon structure on the worn surface under high temperature and pressure in the friction and wear process; therefore, the mechanism of the silicate particles as the lubricating oil additive was very different from that of traditional extreme pressure additives. However, further studies should be done to deeply explore the mechanism of this novel silicate additive. Such studies include the accurate structure of the repaired layer, chemical and physical reactions between the worn surface and silicate particles, and thermodynamic modeling.

CONCLUSIONS

From the investigation results, the following conclusions can be drawn:

1. The silicate additive can act as a catalyst to promote a series of complex tribochemical reactions to form an amorphous carbon-rich layer on the worn surface.
2. The silicate additive shows an obvious effect on the tribological performances of rubbing pairs through forming a self-repaired or regenerated layer with lower roughness and higher hardness.
3. The silicate additive can obviously repair the pits and cracks on the worn surfaces of the cylinder liners; in general, it may maintain a zero-wear in the service life of the engine.

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REFERENCES

(1) Liu, J. (1993), *The Theories of Materials Wear and Their Wear Resistance*, Tsinghua University Press, Beijing.

(2) Spikes, H. (2001), "Tribology Research in the Twenty-First Century," *Tribology International*, **34**, 789-799.

(3) Hsu, S. M. (2004), "Molecular Basis of Lubrication," *Tribology International*, **37**, 7, 553-559.

(4) Chen, S. and Liu, W. (1999), "Preparation and Characterization of Surface-Coated ZnS Nanoparticles," *Langmuir*, **15**, 23, 8100-8104.

(5) Chtourou, M., Frikha, M. H., and Trabelsi, M. (2006), "Modified Smectitic Tunisian Clays Used in the Formulation of High Performance Lubricating Greases," *Applied Clay Science*, **32**, 210-216.

(6) Liu, J. and Guo, F. (2004), "The Application and Analysis of a New Self-Repairing Technology on the Frictional Surface," *China Surface Engineering*, **66**, 3, 42-45, 47.

(7) Jin, Y., Li, S., Zhang, Z., Yang, H., and Wang F. (2004), "In Situ Mechanochemical Reconditioning of Worn Ferrous Surfaces," *Tribology International*, **37**, 561-567.

(8) Xu, J., Wang, F., and Liu, Z. (2007), "Investigation of the Tribology Behaviors of Auto-Restoration Additive Under Heavy Loading Conditions," *Surface Review and Letters*, **14**, 2, 329-334.

(9) Wang, F. (2005), "Research on Microstructure of the Auto-Restoration Layer of Worn Surface of Metals," *Materials Science and Engineering A*, **399**, 271-275.

(10) Yang Y., Jialin, G., Feiyu, K., Xianqing, K., and Wei, M. (2007), "Surface Restoration Induced by Lubricant Additive of Natural Minerals," *Applied Surface Science*, **253**, 7549-7553.

(11) Tian, B., Wang, C., Gu, Y., Yue, W., Ma, X., and Liu, J. (2006), "Effect of a Cermet Additive in Lubricating Oil on Tribological Performance of Steel/Steel Friction Pair," *Transactions of Materials and Heat Treatment*, **27**, 3, 132-136.

(12) Yue, W., Wang, C., Tian, B., Gu, Y., and Liu, J. (2006), "Effect of Ceramic Additive in Lubricating Oil on Contact Fatigue and Wear Performance of Steel/Steel Friction Pair," *Transactions of Materials and Heat Treatment*, **27**, 6, 118-123.

(13) Nikolaevich, A. S., Valentinocich, B. V., and Abbas-Ogli, G. E. (2001), "Method of Treatment of Friction Surfaces of Friction Units," World Patents, WO 01/38466.

(14) Wang, L., Kim, D. S., Nam, K. S., Kim, M., and Kwon, S. C. (2005), "Microstructure of Electroplated Hard Chromium Coatings After Plasma Nitrocarburizing," *Surface and Coating Technology*, **190**, 151-154.

(15) Pina, J., Dias, A., Francois, M., and Lebrun, J. L. (1997), "Residual Stresses and Crystallographic Texture in Hard-Chromium Electroplated Coatings," *Surface and Coatings Technology*, **96**, 148-162.