JMEPEG (2000) 9:228-233

Structure and Friction-Reducing Property of the Sulfide Layer Produced by Ion Sulfuration

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(Submitted 3 May 1999; in revised form 24 June 1999)

Sulfide layers with a certain thickness were made on the surface of 1045 and 52100 steels by means of the low-temperature ion sulfuration technique. Metallography, scanning electron microscope (SEM) + energy-dispersive x-ray analysis (EDX), and x-ray diffraction (XRD) were adopted to analyze the structure of sulfide layers; the tribological properties of the layers lubricated by paraffin oil were also investigated on a reciprocating tester. The results showed that sulfide layer is porous, and its structure is mainly composed of FeS, FeS_2, and substrate phases. The sulfide layer possessed a remarkable friction-reducing effect; its friction coefficient was lower on average, by about 50%, than that of the surface without layer. With the increase of layer thickness, its friction coefficient was unchanged, and under low load conditions, its operational period was prolonged. Under the same experimental conditions, the operational period of sulfide layer on 52100 steel was longer than that on 1045 steel, and its friction coefficient was lower as well.

Keywords low-temperature ion sulfuration, sulfide layer, structure, friction reducing

1. Introduction

Tribological properties of machinery parts can be improved greatly by using sulfur-containing lubricants, because a FeS boundary film can be formed on the surface of parts due to the chemical reaction between sulfur and iron.[1–4] Although this boundary film is no more than 0.2 μm thick, it possesses remarkable friction-reducing and wear-resistant effects because of its special structure, high melting point, and low shearing strength. In order to obtain a much thicker FeS layer at the surface of ferrous metal parts, the sulfuration technique was developed. The sulfuration technique is known as a process specifically designed to produce sulfides at the surface of ferrous metal parts.[5] By means of this technique, a sulfide conversion layer several micrometers thick can be formed by introducing sulfur or sulfides onto or into the surfaces of metal parts. A traditional sulfuration technique is low-temperature electrolytic sulfuration, such as the "Sulf-BT" process.[6] A 190 to 200 ºC molten mixture of sodium and potassium thiocyanates is used as the electrolyte. The components to be treated are made the anode and the metal container for the electrolyte is the cathode. A sulfide conversion layer about 10 μm thick can be produced on the surface.[7,8] Obviously, besides easy aging of the molten mixture, another problem of this process is the pollution caused by CN^-. Thus, the propagation of this technique is limited. In recent years, a low-temperature ion sulfuration technique was developed. The operating temperature of this technique is low, no more than 200 °C, so the components can be treated with minimum distortion and without reduction in hardness. In addition, this technique is without pollution caused by CN^- in electrolytic sulfuration. Furthermore, its technological parameters can be easily controlled, and the surfaces of workpieces cannot be oxidized.[9,10] Therefore, this technique is a new sulfuration technology with great promise. The principles of ion sulfuration are basically the same as that of ion nitriding. The components are made up of the cathode and the container is the anode. Direct current voltage of about 500 to 600 V applied between the anode and the cathode ionizes the reactive gas and leads to glow discharge. Sulfur ions forced by electric field bombard the surface of components, which are heated. At the same time, nascent sulfur diffuses inward and reacts with iron. Then, the sulfide conversion layer can be formed. The reactive gases are generally H_2S, CS_2, or pure sulfur, as well as a little ammonia. At present, the ion sulfuration technique has been applied to many components, such as cutting tools, gears, bearings, dies, and piston cylinders. In China, more and more attention has been given to the low-temperature ion sulfuration technique owing to its many advantages.[10] In this paper, the structure and the friction-reducing property of the sulfide layer made by the ion sulfuration technique on the surface of 1045 and 52100 steel were studied.

2. Experimental Method

Experimental materials were 1045 steel treated by quenching and high-temperature tempering, with a Rockwell hardness of C-26 to 30, as well as 52100 steel treated by quenching and low-temperature tempering, with a Rockwell hardness of C-57 to 62. The geometry of testpieces was 24 mm in diameter and 5 mm in thickness, and the average surface roughness was *Ra* 0.04 μm. Then, sulfide layers, which were about 4, 6, 8, and 10 μm thick, respectively, were produced on the surfaces of testpieces by means of the low-temperature ion sulfuration technique. X-ray diffraction (XRD) analysis was adopted to identify the structure of the sulfide layer, scanning electron microscrope (SEM) and energy-dispersive x-ray analysis (EDX) were used

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to analyze its morphology and compositon, and metallography was employed to measure its thickness. Wear tests were conducted on an Optimal-SRV reciprocating tester (made in Germany). The lower testpieces were sulfurated and unsulfurated discs, and the upper testpieces were 52100 steel balls (10 mm in diameter) with a Vickers hardness of 770. A normal load was given to the upper sample, which reciprocated on the lower sample. Tests were performed in a room-temperature and atmosphere environment with paraffin oil as a lubricant. Experimental parameters were that vibration frequency was 15 Hz, amplitude 1 mm, and the normal loads 20, 40, 60, 80, and 100 N. An X–Y recorder recorded the friction coefficient. When the friction coefficient increased suddenly, testing was stopped, and the wear time was recorded. If there was no change after 30 min of testing, then 30 min was considered as the wear life of the sulfide layer.

3. Experimental Results and Analysis

3.1 Morphology Features of Sulfide Layer

Figure 1 shows the surface morphology of the sulfide layer 12 μm thick on the 52100 steel. It can be seen that its surface is porous. Its composition analyzed by EDX is shown in Fig. 2 (unit of the ordinate representing intensity is arbitrary). Because the hardness of the sulfide layer is very low, only Vickers hardness 50 to 100,[11] the metallography sample was fairly difficult to prepare. Figure 3 shows the cross-sectional morphology of the sulfide layer on 1045 and 52100 steel substrate under light microscopy. The black strips are sulfide layers, whose thickness looks quite even, and the substrate is under the layer. Figure 4 shows the cross-sectional morphology of the sulfide layer on 52100 steel observed by SEM. Obviously, there is no transition layer between sulfide and the substrate, and the structure of the sulfide layer is loose. Using EDX to analyze the composition of the sulfide layer and the substrate in Fig. 4, the results are shown in Fig. 5. Combining with the results in Fig. 2, which indicated that a little Cr element still exists in the sulfide layer besides plenty of Fe, S elements, it can be ascertained that the substrate microstructure exists in the sulfide layer.

3.2 XRD Phase Structure Analysis

The phase structures of the 1045 and 52100 steel substrates and their sulfide layers analyzed by XRD are shown in Fig. 6. The α-Fe patterns of the 1045 and 52100 steel substrate correspond to the martensitic microstructures of both alloys after heat treatment. The strong peaks of α-Fe in the sulfide layer indicate that the main phase in the layer is α-Fe phase. Sulfide phases are composed of FeS and FeS_2. Other sulfide phases such as Fe_3S_4 reported by Ref 12 were not discovered. FeS, which has a hexagonal structure, can easily slide along its base plane, so FeS shows a very good lubrication property. When an x-ray penetrates a substance, the latter is weakened by scattering and absorption. Provided that the intensity of the incident x-ray is I_0, then the intensity of the diffracted ray is given by

$$I = I_0 e^{-\mu(2d\sin\alpha)} \quad (I < I_0)$$

where d is the penetration depth, α the incident angle, and μ the x-ray linear absorption coefficient.[13] Because $\mu_{Fe} >> \mu_s$ and Fe is the main element in the layer, the absorption coefficient of Fe to the Cu K_α ray is considered as that of the layer. The depth of $I/I_0 = 13\%$ is considered as the penetration depth of the x-ray. As a result, the maximum penetration depth of the Cu K_α ray in these tests is about 4 μm. In other words, the phase structure analyzed is almost all in the depth of 4 μm from the surface and is not involved in the substrate. So the apperance of α-Fe in the 10 μm thick sulfide layer indicated that μ-Fe is an ingredient of the layer. It can be seen from Fig. 6 that the FeS_2 phase appears with the increase of layer thickness. FeS_2, which has a cubic structure, does not show a self-lubrication property. As for the 52100 steel, both FeS and FeS_2 appear in the layer with either thickness, but carbide at the surface diminishs gradually with the increase of layer thickness.

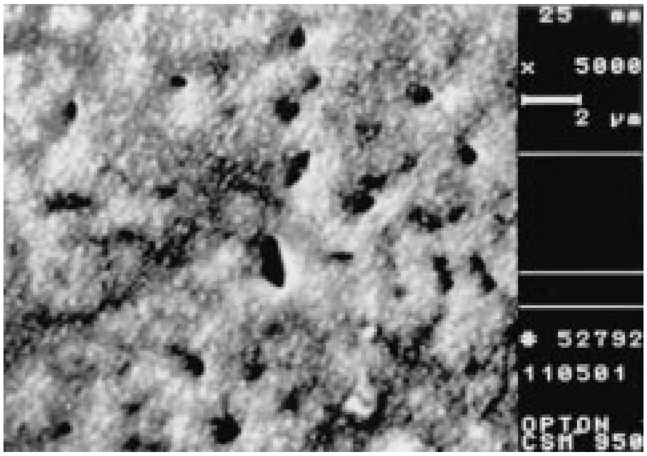


Fig. 1 Surface morphology of the sulfide layer on the 52100 steel

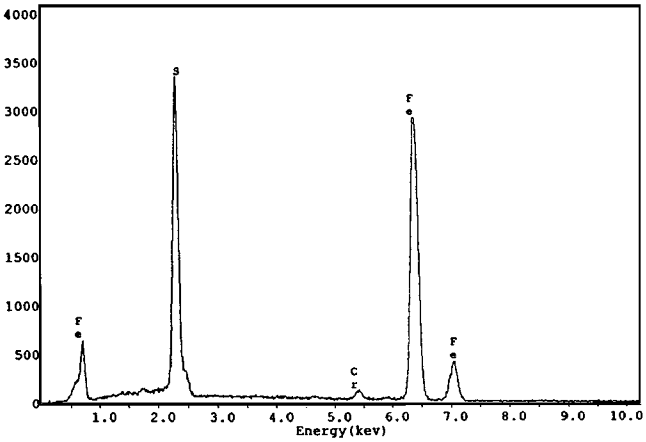
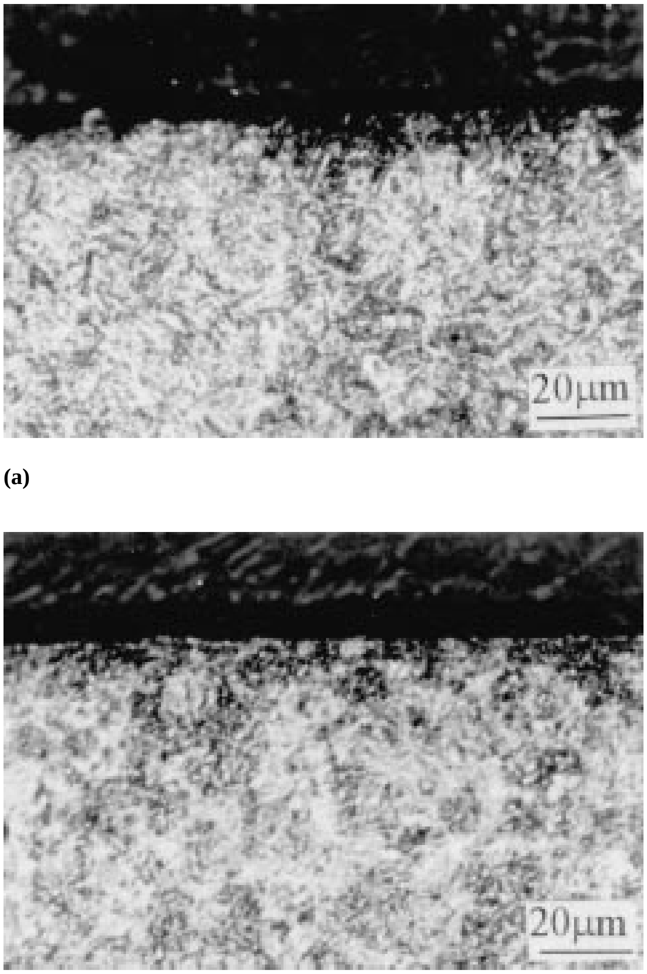


Fig. 2 Surface composition of the sulfide layer on the 52100 steel



(a)

(b)

Fig. 3 Cross section of the sulfide layer on **(a)** 1045 and **(b)** 52100 steel substrates under light microscopy. The black strip is the sulfide layer, and the substrate is under the layer

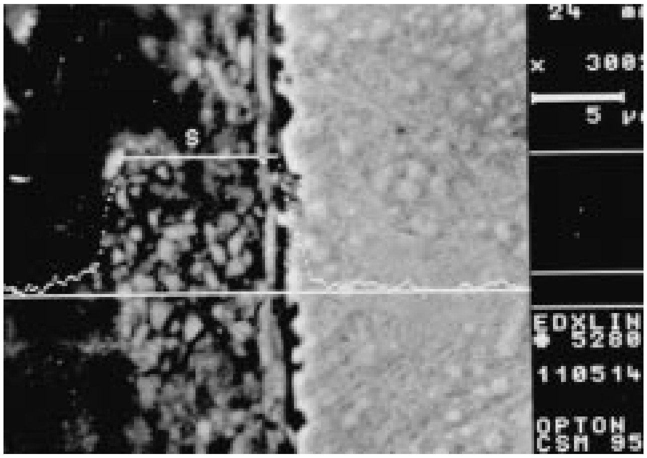
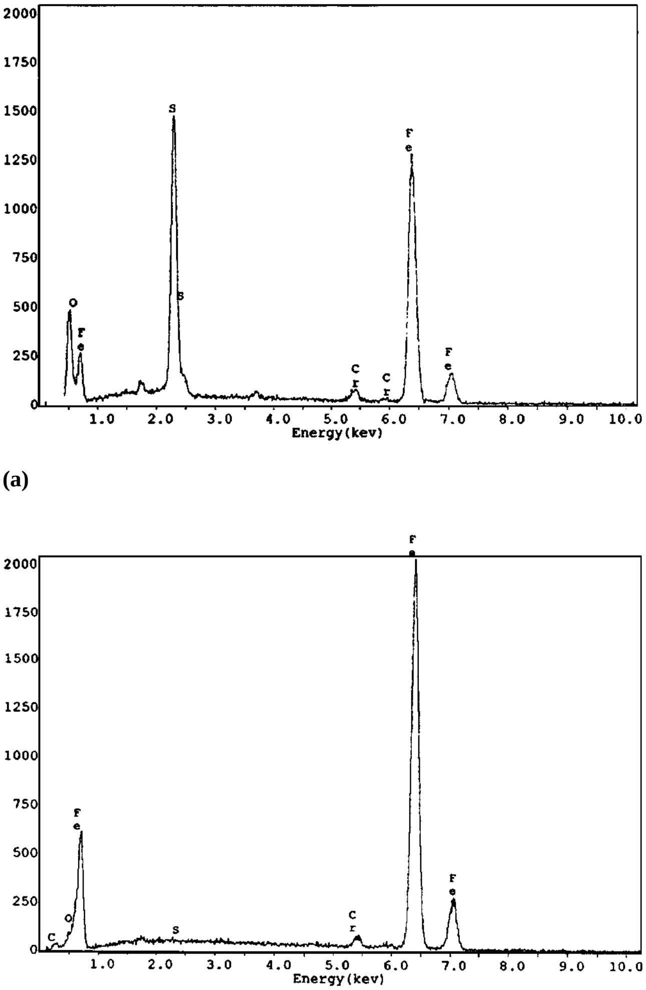


Fig. 4 Cross-sectional morphology of the sulfide layer on the 52100 steel. The content of sulfur in the layer is very high, and the substrate is on the right of the layer



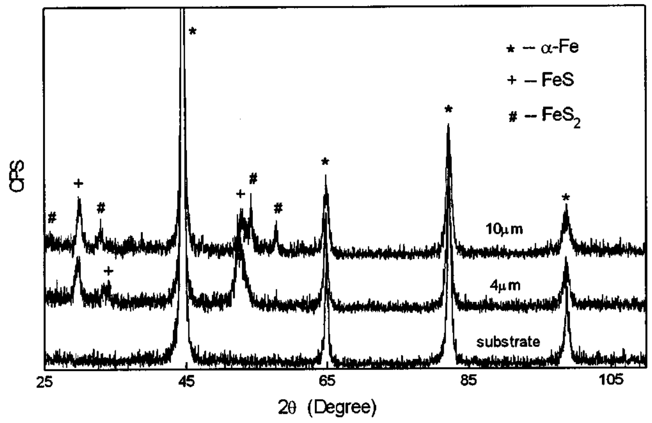
(a)

(b)

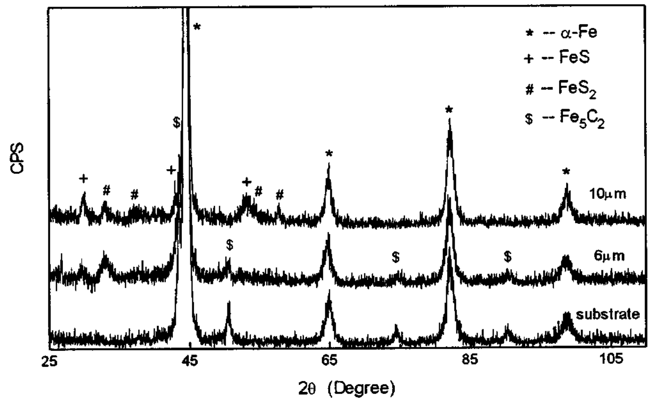
Fig. 5 Composition of the **(a)** layer and **(b)** substrate in Fig. 4

3.3 Wear Test Results

The variation of the friction coefficient of the sulfide layer with wear time is shown in Fig. 7. After a certain period of test, the sulfide layer was worn away and lost its effects, and then the metallic surfaces came into direct contact, which led to the sharp rise and large fluctuation of the friction coefficient. The operational period t_c and the μ_1 of the sulfide layer were considered as the indexes to evaluate the friction-reducing property of the sulfide layer. The test results are shown in Fig. 8 and 9. Obviously, at the initial stage when the sulfide layer could fully play its role, the μ_1 of the layer was only about 50% that of the plain surface. This indicated that the sulfide layer showed a remarkable lubrication effect. With the increase of layer thickness, μ was basically unchanged, and at low loads, t_c was prolonged. Under the same experimental conditions, the μ_1 of the 1045 steel sample was higher and the t_c was shorter than that of the 52100 steel sample. In addition, with the increase of load, μ_1 was decreased and t_c was shortened.



(a)



(b)

Fig. 6 Phase structure of the **(a)** 1045 steel and **(b)** 52100 steel substrate and sulfide layers on them. CPS—counts per second—indicates the intensity value

4. Discussion

4.1 Formation and Structure of Sulfide Layer

From the Fe-S binary diagram[11] it can be known that the solubility of S into Fe is very low. At 930 °C, the solubility of S into α-Fe is only 0.02%, and it is almost zero at 700 °C. So only FeS can be formed at the 200 °C sulfuration temperature. FeS_2 can also be formed if activated sulfur is saturated. The formation course of the sulfide layer is shown by the scheme in Fig. 10. In the process of ion sulfuration, sulfur-containing gases are ionized, and sulfur ions, neutral particles, electrons, and other particles are produced. Sulfur ions accelerate in the cathode zone and bombard the surface of the cathode. Then, the cathode is heated, and its surface is in the activating state due to the bombardment of high-energy particles. Sulfur reacts with iron, and iron sulfide is formed. Because of the large radius of the sulfur atom (1.02nm) and the very low solubility of sulfur into iron, sulfur can only diffuse into iron substrate along defects. Due to the bombardment of ions, a high-density defect zone, which is favorable to the diffusion of sulfur atoms and/or ions into the substrate, is formed at the surface. However, because of the very low solubility of sulfur into iron, sulfur can easily aggregate on the surface and FeS appears as islands at the initial stage of sulfuration. With the diffusion of sulfur and its aggregation, a continuous sulfide layer can be formed on the surface of the component. The analysis results of EDX for the sulfide layer on the 52100 steel showed that Cr was present in the layer. Combining with the results of XRD analysis mentioned above, it could be confirmed that the sulfide layer is the mixture of the sulfide and the substrate phases. When the layer thickened, the diffusion time of sulfur toward the Fe/FeS boundary was prolonged and sulfur could easily aggregate on the surface, so the FeS_2 phase could be formed. In this research, the transition layer between the sulfide layer and the substrate, which had been described in Ref 14, was not observed. It was probably because of the ion bombardment effects, which led to the formation of intrinsic stress and high-density lattice defects at the surface, that the sulfide layer was easily and homogeneously formed.

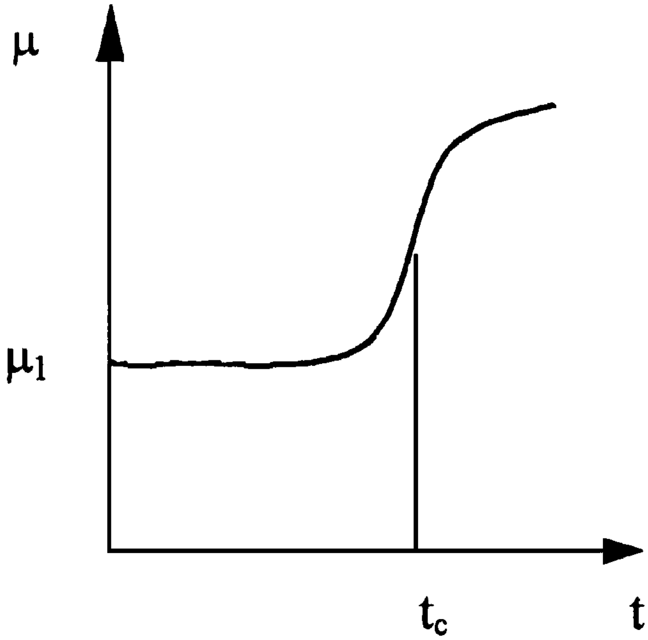
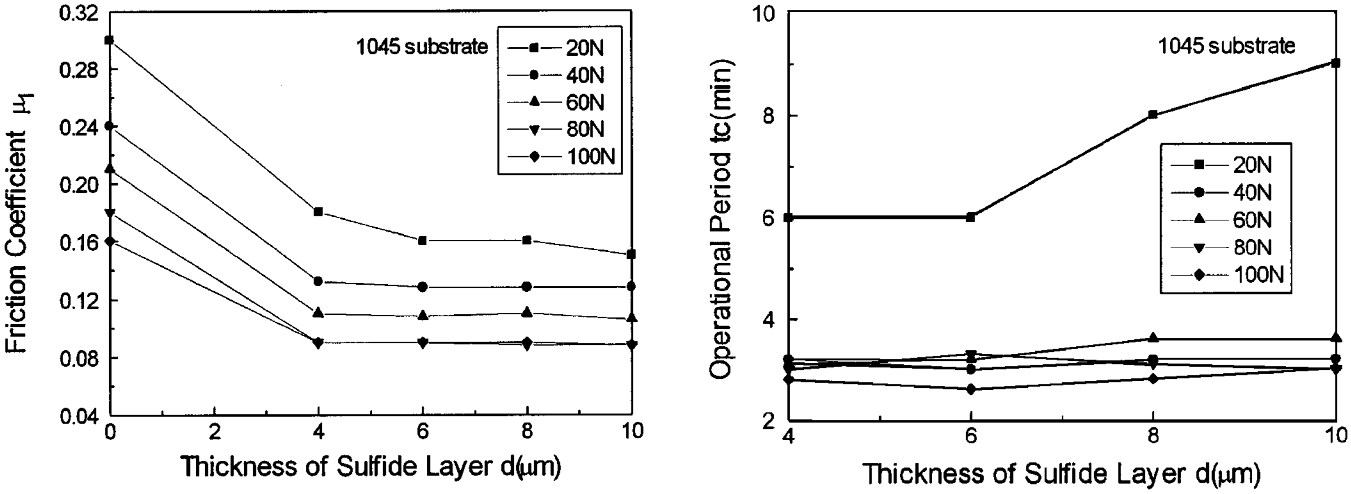


Fig. 7 Variation of the friction coefficient μ of the sulfide layer with time t

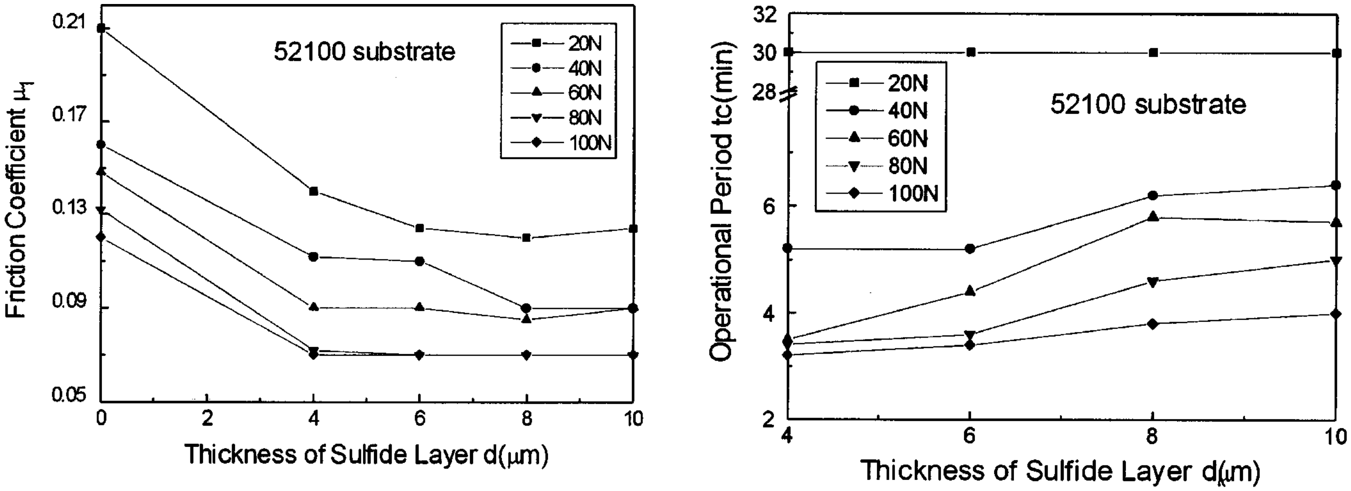
4.2 Friction-Reducing Effect of Sulfide Layer

The friction-reducing effect of the sulfide layer shown by wear test results is due to the following reasons. (1) FeS, which has a hexagonal structure, lattice constants a = 5.97nm, c = 11.74nm, can easily slide along its base plane and shows low shear strength and high melting point (1100 °C). Thus, it is an excellent solid lubricant. (2) The FeS layer can impede the direct contact of rubbing surfaces and alleviate the adhesion. (3) The sulfide layer, which shows a loose and porous structure, can easily absorb lubrication oil and form oil film. (4) In the wear process, FeS probably can be decomposed and liberate activated atomic S due to the actions of friction heat and mechanical force. A part of the activated atomic S is oxidized, and another part can react with Fe to produce FeS again; there-



(a) (b)

Fig. 8 Wear test results of the sulfide layer on the 1045 steel substrate; variation of **(a)** the friction coefficient μ_1 and **(b)** the operational period t_c with layer thickness and load

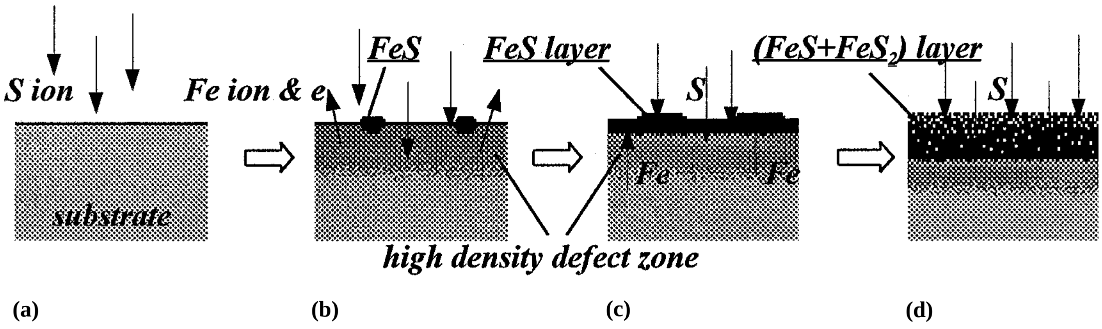


(a) (b)

Fig. 9 Wear test results of the sulfide layer on the 52100 steel substrate; variation of **(a)** the friction coefficient μ_1 and **(b)** the operational period t_c with layer thickness and load

fore, the operational period of the sulfide layer is prolonged. When FeS is decomposed and regenerated, the iron oxide film can also be formed. The boundary lubrication film composed of iron sulfide and oxide can remarkably increase the load-carrying capacity.[15-18] Under low load condition, the thicker the layer, the longer the operational period t_c. When the load becomes higher, the sulfide layer is worn away faster, and its solid lubrication effect is no longer present. But the decomposition and regeneration of FeS may occur. The lubrication effect of newly generated boundary film can affect the relationship of the operational period t_c with the original thickness of the sulfide layer. Therefore, it is unnecessary to produce a very thick layer on the surface of the component for high load condition. Especially, with the increase of thickness, FeS_2 phase, which is with cubic structure and without self-lubrication effect, can appear in the sulfide layer. This phenomenon can cause the friction coefficient to no longer be reduced with the increase of layer thickness. Moreover, FeS_2 may transform into FeS in the wear process to prolong the operational period of sulfide layer.

In addition, under the same conditions, the operational period of the sulfide layer on the 52100 steel surface was longer than that on the 1045 steel surface, and μ_1 was also lower. Probably it was because the higher hardness substrate of the 52100 steel could support the sulfide layer more strongly, and also the plastic deformation at the surface was less. Therefore, the higher hardness of the substrate is a key factor for fully playing the friction-reducing role of the sulfide layer.



(a) **(b)** **(c)** **(d)**

Fig. 10 Schematic diagram of ion sulfide layer formation. **(a)** S ions bombard the surface of the substrate. **(b)** Fe ions and electrons are sputtered out; FeS and the high-density defect zone are formed. **(c)** FeS islands, which connected with each other, form a continuous layer; at the same time, S ions and Fe ions continue to diffuse toward the layer. **(d)** As the layer becomes thicker, S is rich in the surface, and FeS_2 is formed

5. Conclusions

- The sulfide layer produced by low-temperature ion sulfuration technique is composed of sulfide and substrate phases. The sulfide phases mainly include FeS and FeS_2. With the increase of layer thickness, FeS_2 is easily formed.
- The sulfide layer can make the friction coefficient of 1045 and 52100 steels decrease remarkably under the paraffin oil lubrication condition. Thus, the sulfide layer shows an obvious friction-reducing effect.
- With the increase of the sulfide layer thickness, the friction coefficient was no longer reduced due to the presence of FeS_2.
- Under the same experimental condition, the operational period of the sulfide layer on the 52100 steel is longer than that on the 1045 steel, and the friction coefficient of the former is also a little lower.

Acknowledgments

The authors received great help from Miss Xu Gui-Zhen, Department of Mechanical Engineering, and Professor Tao Kun and Mr. Li Bin, Department of Material Science and Engineering, Tsinghua University. We would like to thank them for their help.

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