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Ordered molecular layer structure of lubricating oil adsorbed films①

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[Abstract] Low-angle X-ray diffraction has been applied to analyze the structure of stearic acid LB films and self-grown surface adsorbed films of aluminium product metalworking lubricants. The results show that LB films exhibit a good layer-like ordered structure in the normal direction of film-carrying surface, while in the tangential direction, they do not show a cyclically ordered molecular arrangement; as for the self-grown surface adsorbed films of aluminium sheet and strip metalworking lubricants, their molecules are orderly arranged to certain degree in both the tangential and the normal directions of film-carrying surface, and they have a short-range ordered structure. Moreover, the better the orientation of normal molecules is, the higher the oil film strength is, and the smaller the friction factor is.

[Key words] LB film; surface adsorbed film; molecular arrangement structure; lubricity
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1 INTRODUCTION

Boundary lubrication and thin-film lubrication are two lubricating states widely existing in metal plastic working process. In 1919 Hardy et al[1] first advanced the concept of boundary lubrication, in 1929 Tomlinson[2] disclosed the intermolecular effect of boundary lubrication. In 1950, Epstein, when studying the molecular orientation of long-chain organic compounds' surface films, put forward the "corn-cluster" structure model of mono-molecular layer, thinking due to the fact that the sectional area of long-chain organic compound molecule's polar group is larger than that of its chain, long-chain organic compounds' adsorbed films on base display the shape of "corn-cluster"[3]. There were also some scholars who thought that adsorbed films had a layer-like structure with multi-molecular layers, and advanced LB film as the structure model of boundary film[4]. In the past half of the 20th century, boundary lubrication theory and technology have made great progress. Bowden and Leben considered to analyze the lubricating state on metal surface with molecule size and known film thickness. Thin-film lubrication, advanced by Spike[5], in 1988, is a relatively new concept, and the study on it is still incomplete. Since boundary lubrication and thin-film lubrication involve the variation of the properties of a very thin surface layer, and many factors which are hard to control exist simultaneously, there is no general theory on boundary lubrication and thin-film lubrication mechanisms, and their applications still depend on experience. In this paper, the structure and lubricating performance of lubricating oil adsorbed films have been studied on the basis of experimental analysis, and a new way has been offered as a reference to developing new-type plastic metalworking lubricants.

2 EXPERIMENTAL

2.1 Preparation of stearic acid's LB films

Stearic acid was solvated into chloroform to form stearic acid chloroform solution, which was then dribbled by a microsyringe onto the surface of subphase liquid (super-pure water) to form film. Stearic acid's 7, 11 and 25 layers Y-type LB films had been prepared on LB105 Film-drawing Machine. Experimental parameters were as follows: the side pressure of film-pressing slider was 30 mN/m; the film-drawing rate was 0.4 cm/min; base plate was quartz glass; laboratory temperature was 20 ℃.

2.2 Preparation of oil samples' self-grown adsorbed films

Mono-ingredient additives—laurinol, hexanoic acid, lauric acid and stearic acid, multi-ingredient ones—CSA-1, CSA-B and CSA-FH were mixed with base oil (*jingling* sheet rolling oil) to make up lubricant samples with concentration of 3%, 5% and 7% respectively. The prepared lubricant samples were dribbled onto the aluminum plates with a drip pipe, and the oil films were homogenized by crushing with a glass bar. After being put for a while, lubricant molecules spontaneously adsorbed on the aluminum plates, so as to form self-grown adsorbed films.

2.3 X-ray diffraction

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In testing the molecular layers' orientation structure of adsorbed films in the normal direction of film-carrying surface, D500 X-ray diffractometer had been applied. Experimental conditions are graphite monochromater, Cr target, K_α ray, λ_{Cr} = 2.290 92 Å, scanned area 2θ = 2° ~ 30°, and diffractometer's angular instrument circle plane perpendicular to base plate.

In testing the molecular layer's orientation structure of adsorbed films in the tangential direction of film-carrying surface, similar D500 X-ray diffractometer had been applied. Experimental conditions were as follows: graphite monochromater, Cu target, K_α ray, λ_{Cu} = 1.541 82 Å, scanned area 2θ = 2° ~ 30°, and diffractometer's angular instrument circle plane forming an angle of 5° with base plate's film-carrying surface.

2.4 Test of oil film strength and friction factor

Data of oil film strength had been measured by MS-Ⅲ four-ball friction testing machine. Lubricant samples' friction factors had been measured by MPX-2000 disc-pin friction & abrasion testing machine.

3 RESULTS AND DISCUSSION

3.1 Molecular orientation state of LB film in normal direction of base plate's film-carrying surface

The X-ray diffraction patterns of stearic acid's 7, 11 and 25 layers Y-type LB films had been obtained. Fig. 1 shows the diffraction pattern when angular instrument's circle plane is perpendicular to base plate's film-carrying surface. From Fig. 1, it can be seen that, a series of equidistant diffraction peaks are shown on the diffraction patterns of 11-layer and 25-layer Y-type LB films in the range of 2θ = 2° ~ 18°. Diffraction strength as a whole decreases sharply. The strength of odd peak is larger than that of the even peak immediately before it. And an apparent fluctuation of odd and even peaks is displayed. These show that the prepared LB films have indeed a very orderly-arranged cyclic structure in the normal direction of film-carrying surface. Since each diffraction peak corresponds with one diffraction surface, if the peaks in Fig. 1 are translated into indexes, from small angle to big (001), (002), (003), …, (00l), and the corresponding d_{hkl} of a diffraction peak is d_{00l}, then the identical period of LB film can be expressed as follows:

$$D = l \cdot d_{00l} \quad (1)$$

where d_{00l} can be calculated by Bragg equation $2d_{00l}\sin\theta = \lambda$, therefore

$$D = \lambda / 2\sin\theta \quad (2)$$

where θ can be read out by the location of diffraction peak. In Y-type LB films, one identical period comprises two mono-molecule layers, so the thickness of one layer of LB film is calculated by halving the identical period.

Averaging the identical periods calculated by each diffraction peak according to the equations as above, the identical period of stearic acid's 11-layer and 25-layer LB films are obtained, respectively, 40.14 Å and 40.3 Å, therefore the thickness of one molecule layer is respectively 20.07 Å and 20.15 Å. Compared with documented value 49.4 Å[6] and 47.0 Å[7], the data as above are 7~ 9 Åsmaller. Reasons might be: 1) the facilities and parameters of film-drawing utilized are different, e.g. film-drawing machine's type, film pressure and film-drawing velocity; 2) the diffraction peaks start in X-ray scan's low angle area, where may exist relatively big errors; 3) the diffracting surface of sample oil deviates from correct place. When sample surface deviates from correct place by a minute angle, i.e. film plane's "advance" or "lag", relatively larger error is produced. The calculated results show that 0.01° disparity in angle can bring about 1 Åerror.

Since pure stearic acid's LB films contain only light atoms, its diffraction ability is very weak. Thus, when layer number decreases to a certain de-

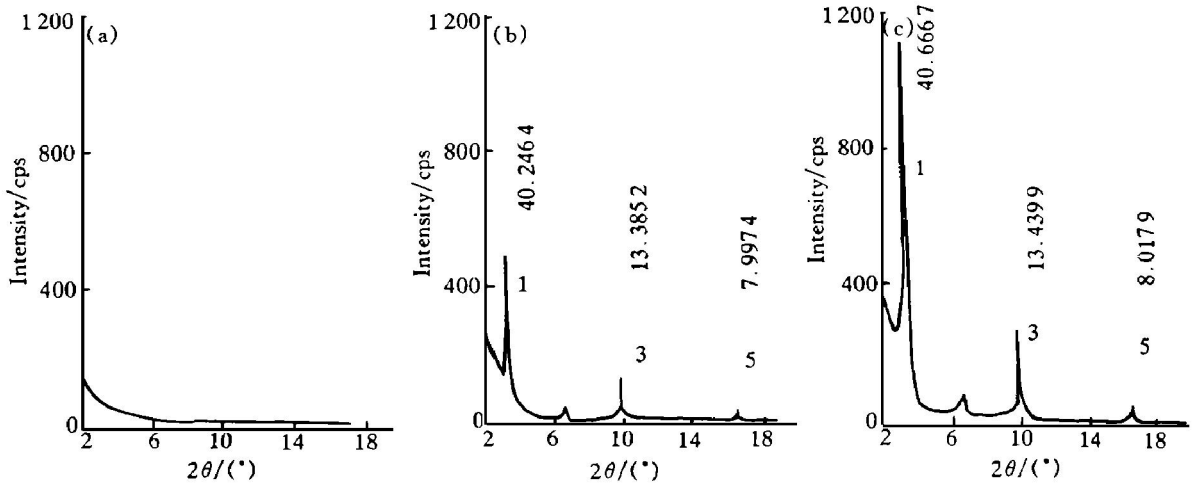

Fig. 1 X-ray diffraction patterns of stearic acid LB films in normal direction of film-carrying surface

gree, it is difficult to observe diffraction peaks. The experimental results show that, the diffracting ability of 7-layer stearic acid's LB film on quartz glass plate is very weak, hardly any diffraction peak is observed.

3.2 LB film's molecular arrangement structure in tangential direction of film-carrying surface

Because the LB film adsorbed on base plate is very thin, it is very difficult for X-ray beam to penetrate a film exactly paralleling with it. Therefore, the method that make X-ray diffractometer's angular instrument circle plane form an angle of 5° with base plate's film-carrying surface is applied to approximately obtain the diffraction patterns of LB film in the tangential direction of film-carrying surface.

Fig. 2 shows the diffraction patterns of LB films when the diffractometer's angular instrument circle plane form an angle of 5° with the film-carrying surface. From Fig. 2 it can be seen that no matter it is 7-layer, 11-layer or 25-layer, no diffraction peak is shown. This means that the molecules of LB films prepared are not orderly arranged in the tangential direction of film-carrying surface. Therefore, LB films have a layer-like structure that is ordered in the normal direction but chaotic in the tangential direction.

3.3 Molecular arrangement structure of self-grown adsorbed films

Fig. 3 shows the diffraction patterns of the six oil samples attending testing in the normal direction of film-carrying surface. In the diffraction patterns of the six oil samples as above, apparent diffraction peaks are shown, and their peak tops smooth, their peak-widths relatively big. This shows that oil films on aluminum base plates have an orderly-arranged molecule layer structure in the tangential direction. As for LB films, because of its ordered molecular arrangement in the normal direction and its apparent cyclic structure, in its X-ray diffraction pattern, every certain 2° angle there is a peak. This is similar to the ordered state of molecules (or atoms) in complete crystal, i.e. long-range order. For the self-grown ordered molecules in lubricating adsorbed film, however, such an analogous structure exists only in a small range. But because few diffraction peaks are shown in the pattern, and diffraction peak spans are wide, it is very difficult to determine which grade of diffraction they are. So their identical period cannot be calculated accurately.

In Fig. 3, the patterns of multi-component additives CSA-1 and CSA-B show only one diffraction peak, their peak strengths are respectively 40.1 (CSA-1) and 164.1 (CSA-B); but two diffraction peaks show on the pattern of CSA-FH, their spans are narrow and their peak strengths are 116.1 and 18.4 respectively. The more the diffraction peaks there are, the narrower the span is, and the higher the peak strength is, then the better the ordered structure of the corresponding adsorbed film is. Obviously, CSA-FH's adsorbed film has the best ordered-structure in the normal direction of film-carrying surface, CSA-B's the mediate, CSA-1's the worst.

In Fig. 3, mono-ingredient additive laurinol's pattern also shows only one diffraction peak, whose peak strength is 84.4; hexanoic acid's pattern shows almost no diffraction peak with a fairly wide span; stearic acid's shows three diffraction peaks with relatively narrow spans, and the peak strengths of which are 32, 116.1 and 18.4 respectively. Therefore, stearic acid's adsorbed film has the best ordered-structure in the normal direction of film-carrying surface, laurinol's the mediate, and hexanoic acid's the worst.

From Fig. 4 we can see that in the diffraction patterns when angular instrument circle plane form a 5° angle with film-carrying surface, all six oil samples attending test show obvious diffraction peaks, with smooth peak tops and relatively wide spans. This means that in the tangential direction of film-carrying surface, there exists ordered adsorbed film structure, molecular arrangement displays short-range order and quite obviously differs from the totally chaotic state of LB film in the tangential direction.

In the six oil samples, no matter multi-ingredient additives or mono-ingredient ones, only one diffraction peak displays on their patterns. The peak strengths of multi-ingredient additives CSA-FH, CSA-B and CSA-1 are respectively 446.3, 366.2 and 321.8. And those of mono-ingredient additives laurinol, lauric acid and stearic acid are 482.1, 198 and

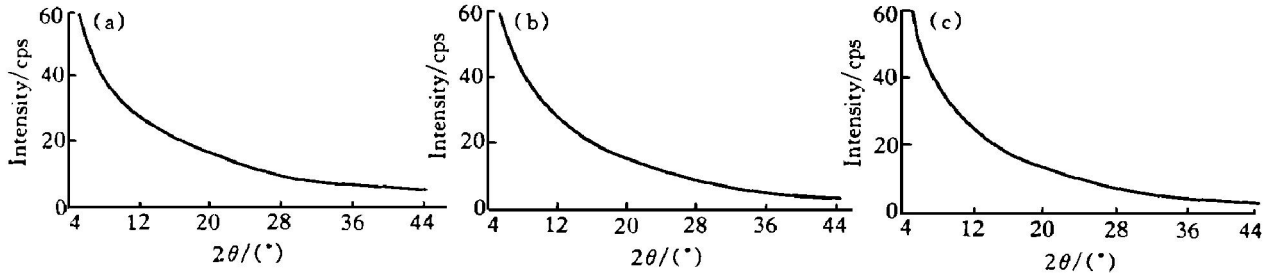

Fig. 2 Stearic acid LB films' X-ray diffraction patterns when angular instrument circle plane form 5° angle with film-carrying surface

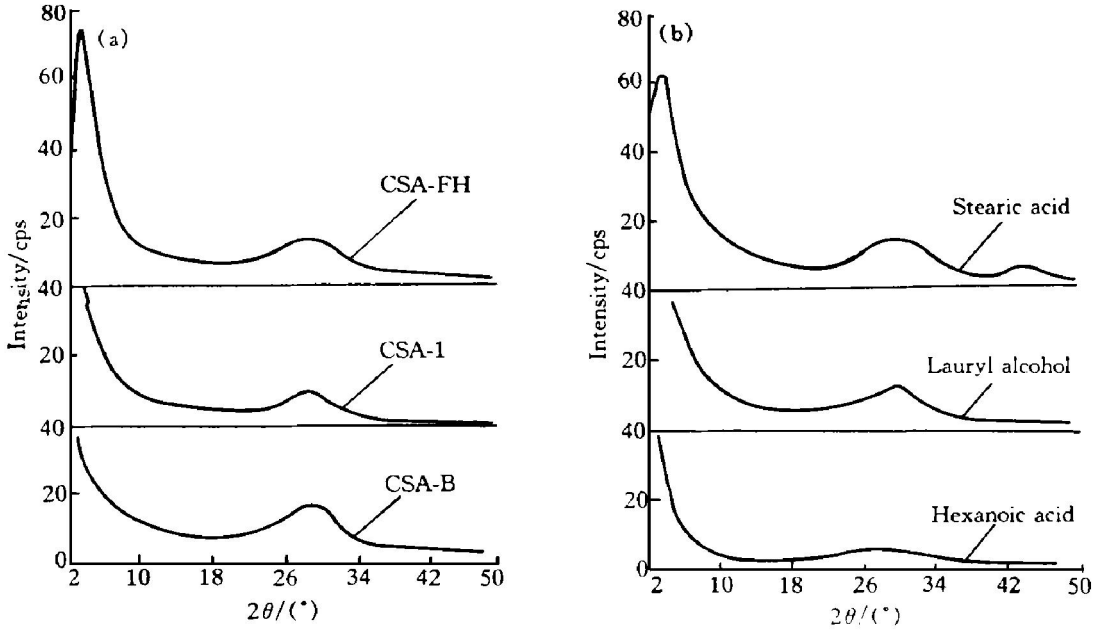

Fig. 3 Diffraction patterns of self-grown film in normal direction of film-carrying surface (concentration 3%), Cr target

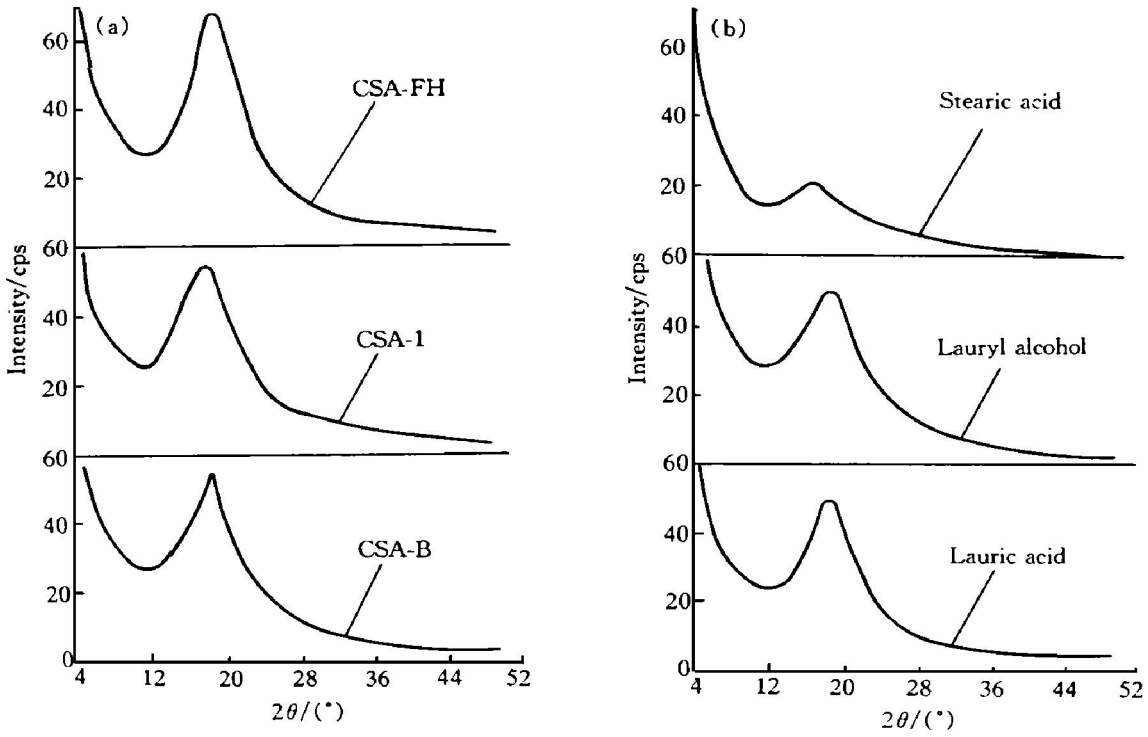

Fig. 4 Diffraction patterns of self-grown film in tangential direction of film-carrying surface (concentration 3%), Cu target

62 respectively. Since the multi-ingredient additives as above are mixed by alcohols and esters with weak polarity, their adsorption on aluminum surface is physical adsorption. However, stearic acid and lauric acid have –COOH– groups which have a relatively strong polarity, their adsorption on aluminum surface is mainly chemical adsorption, and with the increase of the length of hydrocarbon chain, the chemical adsorption becomes stronger. Apparently, chemically adsorbed film has a poor molecular arrangement structure in the tangential direction of film-carrying surface, but physically adsorbed film has a much better one in that direction.

When testing the structure of stearic acid LB film in the normal direction, it is found that the strength of X-ray diffraction peak decreases sharply with decreasing normal ordered molecule layers, and that no obvious diffraction peak is shown on its diffraction pattern when it is less than 7 layers (Fig. 2 (a)). However, there are obvious diffraction peaks on self-grown adsorbed films' diffraction patterns. This indicates that the number of ordered molecule layers of self-grown adsorbed films in the normal direction is not smaller than 7. And considering the fact

that LB film has a better normal molecular orientation than self-grown adsorbed film, then the number of ordered molecular layers of self-grown adsorbed film in the normal direction is far larger than 7.

The analysis as above shows that ordered molecular arrangement of self-grown adsorbed films exists not only in the normal direction but also in the tangential direction. Therefore, self-grown adsorbed film has some structure between crystal and non-crystal, which is very possible to display a "multi-layer corn-cluster" state (Fig. 5).

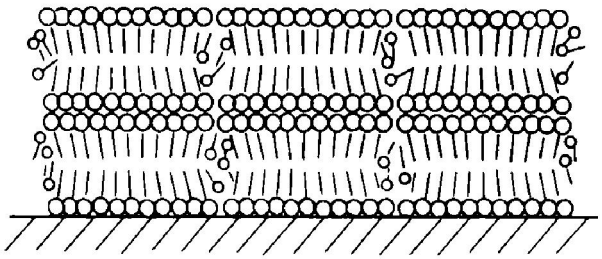

Fig. 5 Illustration of self-grown adsorbed film's "multi-layer corn-cluster" structure model

3.4 Relationship between lubricant adsorbed films molecular arrangement and lubricating performance

Table 1 shows the friction factors and oil film strengths of the six oil samples as above. From the data in the table it can be seen: the oil sample containing hexanoic acid has a low oil film strength and a big friction factor; the oil sample containing either stearic acid or CSA-FH has a small friction factor and a high oil film strength. Fig. 4 illustrates that hexanoic acid oil sample's diffraction peak is the weakest, but stearic acid and CSA-FH oil samples' diffraction peaks are the strongest, and several diffraction peaks are shown. Therefore, the data in Table 1 and Fig. 3 show that good corresponding relationship exists between oil samples' lubricating performance and adsorbed film's normal molecular arrangement microstructure, that is, the better the normal molecular arrangement of self-grown adsorbed film is, the better the lubricating performance is.

Table 1 Friction factors and oil film's strengths of six oil samples (concentration 3%)

Oil sample	Film strength/N	Friction factor
Hexanoic acid	140	0.24
Lauric acid	270	0.098
Stearic acid	310	0.085
CSA-B	270	0.097
CSA-FH	300	0.086
CSA-1	280	0.093

Both hexanoic acid and stearic acid have a strong-polar – COOH – group. However, because the length of their non-polar hydrocarbon chain is different, stearic acid's adsorbed film has a relatively good multi-layer cyclic arrangement structure in the normal direction, but hexanoic acid's adsorbed film's molecular arrangement is poor and has few ordered molecule layers. Although CSA-FH is composed of weak-polar alcohols and esters[8], and the length of its non-polar hydrocarbon chain is equivalent to that of laurinol, because of the addition of some ring-shaped hydrocarbon ester (non-polar ring-shaped hydrocarbon has a big sectional area), which acts as skeleton in adsorbed film, and thus can effectively prevent long hydrocarbon chain from falling over and curling, its adsorbed film also has a relatively good multi-layer cyclic orientation structure in the normal direction. Therefore, the additive molecule's polar group polarity, hydrogen bond, shape and length of hydrocarbon chain, and sectional area of non-polar hydrocarbon chain and polar group are all factors influencing the molecular orientation of adsorbed film.

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