



# Friction and wear of Cr-doped DLC films under different lubrication conditions<sup>☆</sup>



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## ABSTRACT

**Keywords:**  
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In this paper, Cr-doped DLC films with various Cr contents were deposited on stainless steel plates by an ion beam deposition/magnetron sputtering hybrid method and the tribological performance of the samples was evaluated using a ball-on-disk tribometer. It was found that the influence of the Cr content in the Cr-doped DLC films on the friction coefficient when lubricated by PAO, 150SN, PAO + T307, or 150SN + T307 is insignificant while the friction coefficient of the Cr-doped DLC films under PAO + MoDTC or 150SN + MoDTC lubrication can be significantly reduced through the introduction of Cr at an optimum level into DLC films. The wear resistance of the DLC films under PAO, 150SN, PAO + MoDTC, or 150SN + MoDTC lubrication can be improved by the introduction of Cr into DLC films; but Cr doping is unbeneficial to the wear resistance of DLC films lubricated by PAO + T307 or 150SN + T307.

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## 1. Introduction

The improvement of antifriction and antiwear properties of mechanical parts is imperative for the development of modern machines [1]. Diamond-like Carbon (DLC) films are attractive wear resistant films for their high hardness, good wear resistance, and low friction coefficient [2]; but the friction and wear resistance of DLC films are affected by the environments, and their thermal stability is not good enough, hindering the applications of DLC films for severe service conditions [3]. Liquid lubricants can not only abate the disadvantageous effect of environments on the tribological performance of DLC films because they isolate the films from the atmosphere, but also they take away the wear debris and the heat generated during friction so that the demand for high temperature stability is relieved. Therefore, the tribological performance and service life of the DLC-coated mechanical parts can be greatly improved by suitable lubrication [4].

The interaction of lubricant additives with friction surface is closely related to the surface structure and the properties of the

friction-pair [5,6], but the tribological performance of DLC films with various doping elements under different lubrication schemes is not clearly understood. In order to fully utilize the excellent tribological performance of DLC films, it is dispensable to study the synergistic effect of the lubricant additives and the DLC films.

Cr-doped DLC films exhibit attractive tribological performance compared with undoped DLC films due to their low stress, high adhesion, and high thermal stability [7,8], and the interaction of the lubricant and the Cr-doped DLC films under boundary lubrication condition has been studied [9,10]. However, the effect of the Cr contents in the DLC films and the lubricant additives on the tribological performance of the DLC-coated samples is not clear.

In this study, Cr-doped DLC films with various Cr contents were first deposited, and then the influence of the Cr content in the DLC films on the friction coefficients and wear rates of the DLC-coated stainless steel samples under various lubrication conditions was studied.

## 2. Experimental

Cr-doped DLC films were deposited on 316 stainless steel plates in a size of 50 mm × 30 mm × 2 mm, polished to a surface roughness of Ra = 4 nm with a multifunctional coater (AS600DMTG) equipped with rectangular unbalanced magnetron sputtering targets, vacuum cathodic arc sources and linear anodic layer ion sources. Prior to the installation of these samples in the

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deposition system, the substrates were ultrasonically cleaned in the bath solution of water and metal cleaning agent, rinsed in deionized water and ethanol, and then dried in hot air. The sample surface was further etched by argon ions produced by an ion source and Cr ions produced with a vacuum cathodic arc source before the deposition in order to remove the undesirable oxide and contamination on the substrate surface. Then a gradual transition layer was deposited by ion beam assisted magnetron sputtering before depositing Cr-doped DLC films in order to enhance the adhesion between the DLC film and the substrate. During the deposition of the transition layer, the gas composition to the magnetron Cr target with a purity of 99.95% and the ion source was gradually changed from pure argon, to a mixture of argon and nitrogen, then a mixture of argon, nitrogen and methane, and finally a the mixture of argon and methane. After the deposition of the transition layer, Cr-doped DLC films with a thickness of about 1  $\mu\text{m}$  were synthesized by ion beam deposition (the inlet gas into the ion source was the mixture of argon and methane) combined with magnetron sputtering of the Cr target. The operation parameters of the ion source were determined on the basis of the deposition experience of undoped DLC films, and the Cr content in the films was obtained from 0 at% to 23.3 at% by controlling Cr target current. Argon with a purity of 99.999%, nitrogen with a purity of 99.999% and methane with a purity of 99.99% were used in the study.

The surface morphology of the DLC films was observed with scanning electron microscopy (SIRON-200). The chemical bonding status of the DLC films was analyzed using X-ray photoelectron spectroscopy (PHI Quantera), and Mg  $K\alpha$  radiation was used as the exciting X-ray. The sample surface was etched with argon ion for 10 nm in order to avoid the effect of surface contaminants. The hardness and elastic modulus were measured using a nano-indentation tester (MTS XP) with an indentation depth of 1000 nm; the hardness and elastic modulus was determined according to the platform values from 100 nm to 300 nm, and the average value was obtained from five times measurement results.

The friction coefficients and wear rates of the DLC-coated stainless steel samples under different lubrication conditions were evaluated using a ball-on-disk tribometer (MS-T3000). The counterpart was a  $\text{Si}_3\text{N}_4$  ball of 4 mm in diameter. The DLC-coated stainless steel plate was fixed on a rotary sample stage with a rotation rate of 400 rpm and the diameter of the wear trace was 8 mm. The load was 9.80 N. Polyalphaolefin synthetic oil (PAO-4) and paraffin base mineral oil (150SN) were chosen as the base lubricant oil. The kinematic viscosity at 40  $^\circ\text{C}$  of PAO-4 and 150SN is 16.68  $\text{mm}^2/\text{s}$  and 28–32  $\text{mm}^2/\text{s}$ , respectively. The viscosity index of PAO-4 and 150SN is 124 and 98, respectively. A friction modifier

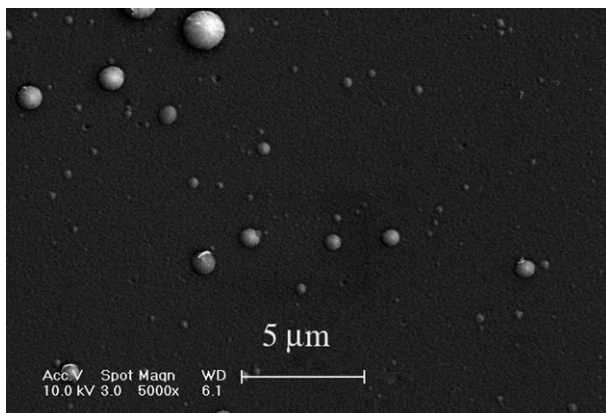


Fig. 1. Surface morphology of Cr-doped DLC films.

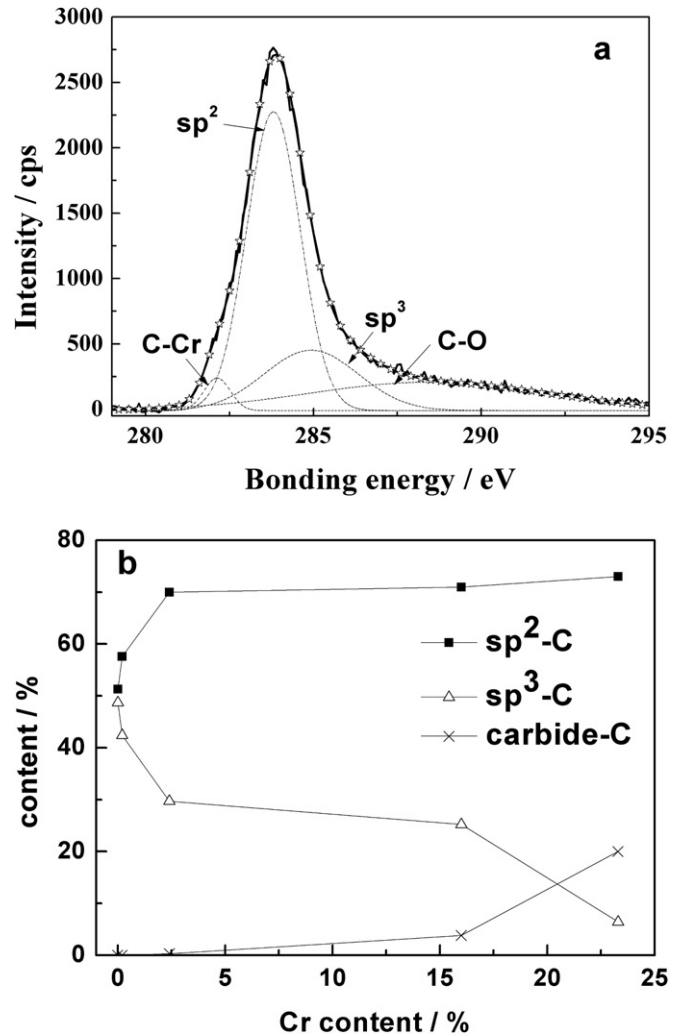


Fig. 2. XPS analysis of Cr-doped DLC films: (a) C1s spectrum of DLC films containing 16 at% Cr, (b) content of carbon atoms with different chemical bonding status as a function of Cr content.

additive of molybdenum dithiocarbamate (MoDTC) and an extreme pressure antiwear additive of amine sulfuric-phosphate diester (T307) were added as the lubricant additives into the base lubricant oil with a concentration of 1% in weight. The average value was obtained from three times result.

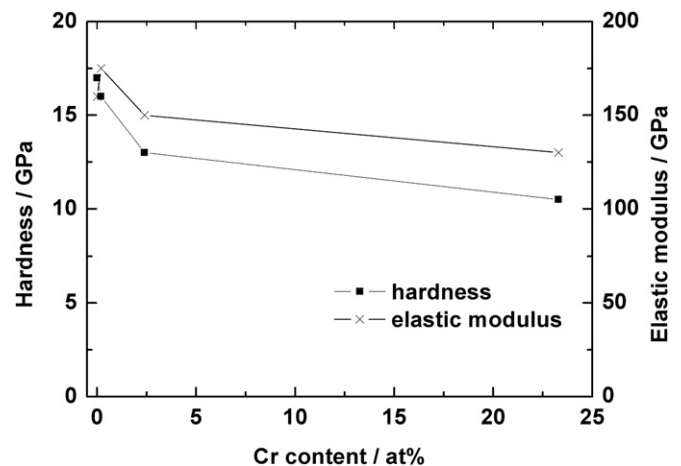


Fig. 3. Hardness and elastic modulus of DLC films as a function of Cr content.

3. Results and discussion

Typical surface morphology of the Cr-doped DLC films is shown in Fig. 1. It can be seen that some macroparticles with a size less than 2 μm in diameter exist on the surface of the Cr-DLC films, which make the sample surface rougher. The composition analysis of the macroparticles and flat zones show that the composition of the macroparticles is similar to that of flat zone in the Cr-doped DLC films and the transition layer, but the composition of the macroparticles and flat zone in the bond layer, so the macroparticles may be produced by arcing during depositing the bond layer using

vacuum cathodic arc source. The root mean square (RMS) roughness of the polished stainless steel is about 4 nm, but the RMS roughness of the coated samples is 15–45 nm (20 nm for the undoped DLC films, 15–45 nm for the Cr-doped DLC films). When the DLC-coated samples with different Cr contents were compared, it was found that the surface morphology or the RMS roughness of the DLC films with different Cr contents was similar.

C1s spectrum of the Cr-doped DLC films with a Cr content of 16 at% is shown in Fig. 2a. The C1s spectrum can be deconvoluted into four components centered at 282.1 eV, 283.8 eV, 284.9 eV, and 288.4 eV, which correspond to C–Cr bonded carbon (C–Cr), sp<sup>2</sup>

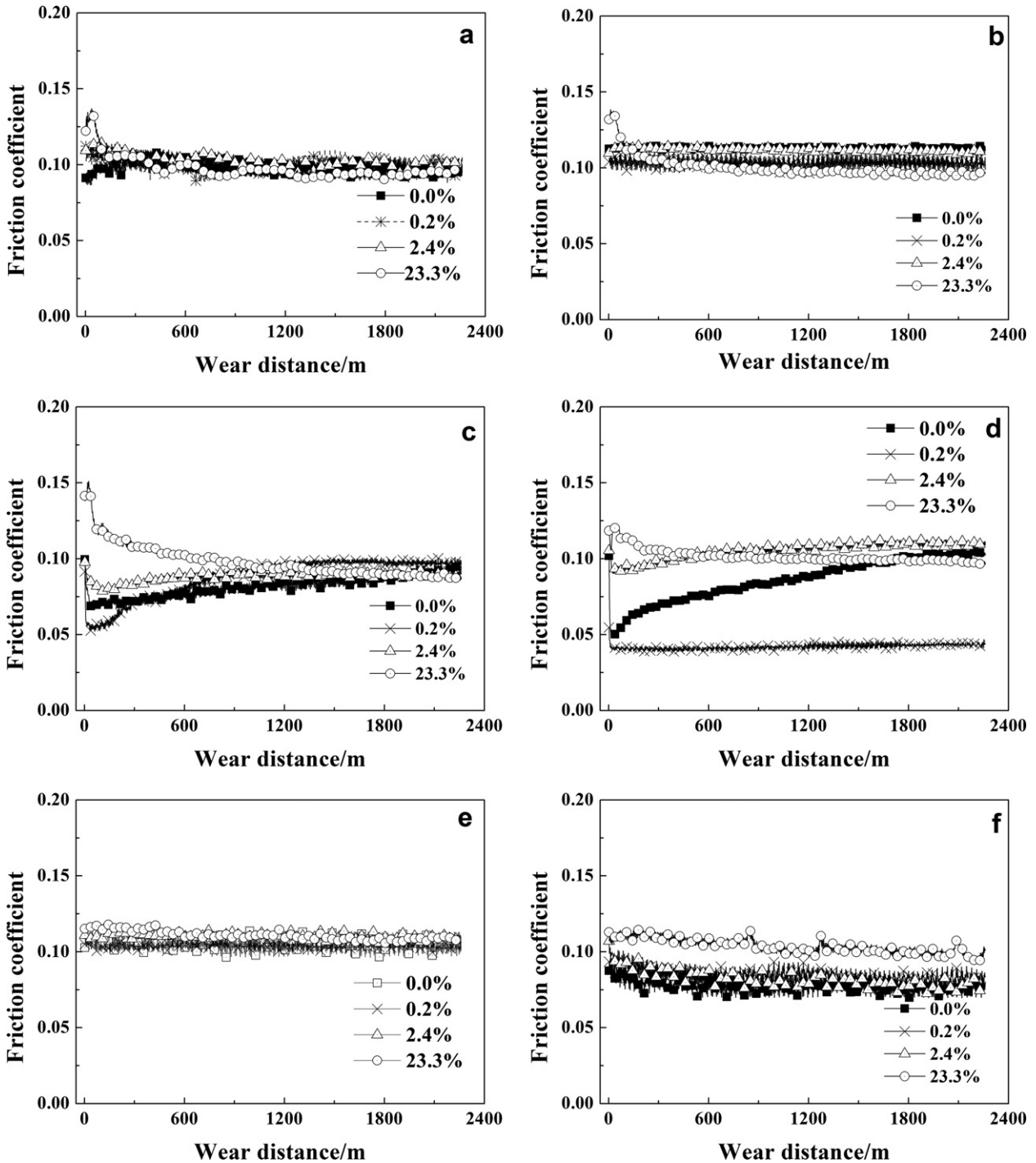


Fig. 4. Friction coefficients of DLC-coated stainless steel plates under the lubrication conditions: (a) PAO, (b) 150SN, (c) PAO + MoDTC, (d) 150SN + MoDTC, (e) PAO + T307, (f) 150SN + T307.

bonded carbon ( $sp^2$ -C),  $sp^3$  bonded carbon ( $sp^3$ -C), and C–O bonded carbon (C–O), respectively. The content of carbon atoms in a specific chemical bonding status can be established according to the ratio of its area to the total area of C 1s peak, and the influence of the Cr content on the content of carbon atoms with different chemical bonding status is shown in Fig. 2b. It can be found that the content of  $sp^3$ -C clearly decreases and the content of  $sp^2$ -C increases with the increase of the Cr content in the films from 0 at% to 2.4 at%, but when the Cr content in the films is beyond 2.4 at%, the influence of Cr content on the content of  $sp^3$ -C and  $sp^2$ -C becomes less pronounced. When the Cr content is beyond 2.4 at%, the percentage of carbon atoms existing in chromium carbide is increased with the increase of the Cr content. The increase of the  $sp^2$ -C content and the decrease of the  $sp^3$ -C content lead to the reduction of the hardness and elastic modulus of the DLC films, as shown in Fig. 3, but the appearance of hard chromium carbide in the films seems to slow down the decrease of the hardness and elastic modulus of the DLC films.

The friction coefficients of the Cr-doped DLC films with various Cr contents under different lubrication conditions are shown in Fig. 4. When lubricated by the base oil such as PAO (Fig. 4a) or 150SN (Fig. 4b), except the DLC films with a Cr content of 23.3 at%, the friction coefficient is stable during friction and the difference amongst the friction curves of the DLC films with different Cr content is minimal. For the DLC films with a Cr content of 23.3 at%, the friction coefficients increase rapid first, and then decrease quickly to a stationary value. The rapid change of the friction coefficients at the start could be related to the difficulty in the formation of a boundary lubrication film. It is clearly that the Cr content in the films has no influence on the friction curves of DLC films under either PAO or 150SN lubrication.

For the undoped DLC films, the friction coefficient under PAO + MoDTC (Fig. 4c) or 150SN + MoDTC (Fig. 4d) lubrication decreases to the lowest value rapidly and then increases to a stable value slowly. For the DLC films with a Cr content of 0.2 at%, the friction behavior under PAO + MoDTC is similar to that of undoped DLC films under PAO + MoDTC or 150SN + MoDTC lubrication, while the friction coefficient under 150SN + MoDTC lubrication abruptly decreases to a low value of 0.04 and then remains at the low value for a quite long period. For the DLC films with a Cr content of above 2.4 at%, the friction coefficient under PAO + MoDTC or 150SN + MoDTC lubrication first decreases to a stable value and no obvious minimum point appears in the friction curves; the lowest friction coefficient is found for the DLC films with Cr content of 0.2 at%.

Under PAO + T307 lubrication (Fig. 4e), the DLC films with different Cr content exhibit similar friction coefficients and the fluctuation of friction coefficient is small. Under 150SN + T307 lubrication (Fig. 4f), the trend of friction coefficient for the DLC films with the Cr content below 2.4 at% is similar but the friction coefficient for the DLC film with the Cr content of 23.3 at% is obviously higher.

The wear volumes were calculated from the wear track profile obtained using a white-light interference profilometer for 3 times. The wear rates of the DLC-coated stainless steel under different lubrication are shown in Fig. 5. It is shown that the wear rate of DLC films lubricated by PAO, 150SN, PAO + MoDTC, or 150SN + MoDTC can be obviously reduced through the introduction of Cr into DLC films at an optimal level. The optimal Cr content is different under different lubrication conditions. Under PAO or 150SN lubrication, the Cr-doped DLC films with a Cr content from 0.2 at% to 16 at%, respectively, have the lowest wear rate; but under PAO + MoDTC or 150SN + MoDTC lubrication, the lowest wear rate is obtained for Cr-doped DLC films with a Cr content of 0.2 at%, the optimal Cr content range of Cr-doped DLC films lubricated by PAO + MoDTC or

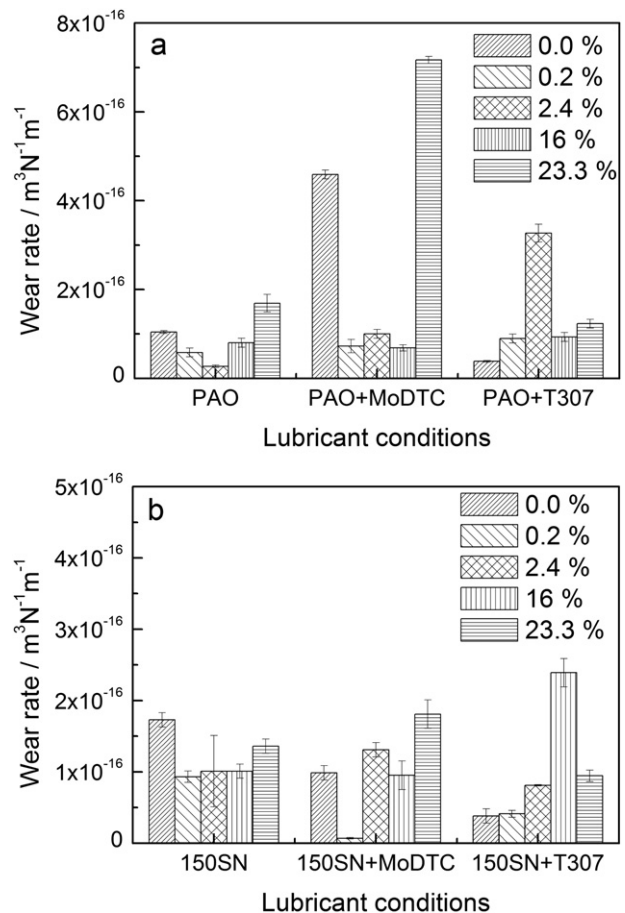


Fig. 5. Wear rate of DLC-coated stainless steel plates as a function of Cr content: base lubricant oil was (a) PAO and (b) 150SN.

150SN + MoDTC is much narrower than that by PAO or 150SN. But when DLC films is lubricated by PAO + T307 or 150SN + T307, the wear rate of DLC films increases by Cr doping, and the largest wear rate is found for Cr-doped DLC films with a moderate Cr content. Judging from both charts, the DLC films doped to 0.2 at% seem to have low wear rates. This result may be explained by their high hardness (Fig. 3).

#### 4. Conclusions

Cr doping has little effect on the friction coefficient of the DLC films lubricated with PAO, 150SN, PAO + T307, or 150SN + T307. The introduction of 0.2 at% Cr into DLC can clearly reduce the friction coefficient of DLC films under PAO + MoDTC or 150SN + MoDTC lubrication, and the low friction remains for a long period under 150SN + MoDTC lubrication. The introduction of Cr into DLC films at an optimal level can improve the wear resistance of DLC films lubricated by PAO, 150SN, PAO + MoDTC, or 150SN + MoDTC; but when the samples are lubricated by PAO + T307 or 150SN + T307, the undoped DLC films exhibit the lowest wear rate. Overall, doping Cr to about 0.2% retains high hardness of the DLC and hence results in low wear.

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