Tribological Properties of Diamond-Like Carbon Films with Surface Nano-Structure Formed by Femtosecond Laser Pulses

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We report tribological properties of diamond-like carbon (DLC) film of which surface has been nanostructured with femtosecond (fs) laser pulses. For this study, the fs-laser processing technology has been developed to produce a uniformly nanostructured DLC surface over a wide area of 15 x 15 mm^2. The results have demonstrated that the DLC surface has an excellent frictional performance by coating a MoS_2 layer on the nanostructured surface, where the friction coefficient of DLC surface was observed to decrease down to 0.07 from 0.18 for the steel ball and to 0.02 – 0.04 from 0.08 for the WC-Co ball used in the friction test machine.

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1. Introduction

Diamond-like carbon (DLC) is extensively used as protective films for hard disks and magnetic heads, because of its hardness, chemical inertness, and insulation properties close to those of diamond [1]. Recently, much attention has been focused on its excellent surface smoothness and low friction coefficient for the purposes of applications to tribological technology. Laser control of thin-film surface has been investigated to optimize its tribological properties. Several authors have reported the effect of laser texturing on the friction coefficient [2-4]. For example, Dumitru *et al*. have observed that the laser texturing consisting of shallow dimples of 25-μm in diameter and 15 – 20 μm in depth can greatly increase the lifetime of DLC film [4]. The laser texturing reported so far is limited to the size on a micrometer level, due most likely to the difficulty of creating smaller patterns less than the laser wavelength, and no study has been done of the tribological property for the texturing on a sub-micrometer and/or nanometer levels less than the film thickness. The nano-scale texturing of thin films should often be required to maintain the effective protection of the substrate.

In this paper we report the tribological properties of nanostructured DLC film, based on our recent findings of nanostructure formation on the hard thin films [5-10]. In our previous studies, the DLC film, as well as TiN film, has been demonstrated to be structured on a nanometer level when femtosecond (fs) laser pulses are irradiated at energy fluence slightly above the ablation threshold. The linearly polarized laser pulse produced arrays of fine slender granular structure on the ablated surface, while the circularly polarized light formed a fine dot-like periodic structure. The *nanostructure* size on the surface is 1/10 – 1/5 of the laser wavelength used and decreases with a decrease in the laser wavelength, whereas the structure size increases with an increase in the laser fluence. We have also found that the thin DLC film is modified into a glassy carbon (GC) layer with fs laser pulses under almost the same condition as for the nanostructure formation [7]. The GC is a kind of graphite having the sp^2 bonding structure and a small crystallite size of about 3 nm that leads to the high hardness. The physical and chemical properties of GC are similar to those of DLC, whereas it has additional properties of higher conductivity and thermal resistance than those of DLC [11]. The nanostructured DLC and/or GC layers are expected to improve the tribological property of thin film surfaces.

In the present study the tribological properties of the nanostructured DLC film have been measured with a ball-on disc friction test machine. For the measurements we have developed an experimental apparatus to form a wide and uniform nanostructured area on the DLC surface. The results have shown that the DLC film has an excellent frictional performance by coating molybdenum disulfide (MoS_2) on the nanostructured surface.

2. Experimental procedures

The DLC film was deposited on commercial pure titanium plate of 2-mm thickness with an unbalanced magnetron sputtering system using a pure carbon target at a bias voltage of 150 V in an atmosphere of the mixed gas of pure Ar and 5% CH_4. The coated DLC film was 1.4 μm in thickness, HV 3000 in hardness and 9 nm in surface roughness. This DLC film was irradiated in air with linearly-polarized, 800-nm, 100-fs laser pulses from a Ti:sapphire chirped-pulse amplification system operated at a repetition frequency of 1 kHz. The fs laser pulse energy of E = 110 – 200 μJ was focused on the DLC surface with a 50-cm focal-length parabolic mirror to ablate the film. The laser fluence at E = 110 μJ corresponds to about 0.14 J/cm^2 that is just above the ablation threshold of 0.11 J/cm^2 reported in Ref. [4]. The fluence at E = 200 μJ corresponds to about 0.25 J/cm^2. The DLC-coated plate was mounted on a precise X-Y stage and continuously translated at a constant speed to ablate an area of 15 x 15 mm^2 on the surface, while the laser pulses were irradiated at 1 kHz. The scan speed of the focal point was fixed at 1.6 μm/pulse for E = 110 μJ and 10 μm/pulse for E = 200 μJ. A single scan produced an ablated line zone with the width D ~ 240 μm for E = 110 μJ and D ~ 320 μm for E= 200 μJ. The parallel line scan of the focal spot was repeated with a periodicity L = D /2 ~ 120 μm for E = 110 μJ and L ~ 160 μm for E = 200 μJ to produce a uniformly nanostructured surface, so it was estimated that the fs laser pulses of about 150 shots for E = 110 μJ and 30 shots for E = 200 μJ were superimposed on the same point of the target, respectively. To see the effect of additional coating on the nanostructured DLC surface, a part of the ablated DLC surface was coated with MoS_2 of 0.5 – 1 μm in thickness with a different magnetron sputtering system.

Using an optical microscope, a field emission scanning electron microscope (SEM) and a scanning probe microscope (SPM), we carefully examined the morphology change of the DLC film surface ablated by the fs laser pulses. The bonding structure of the ablated DLC films was analyzed with Raman spectroscopy using the 514.5-nm line of an argon ion laser at a focused spot size of about 1 μm.

The friction coefficient of DLC surface was measured in air with a ball-on disc friction test machine (Rhesca Co., Ltd., FPR-2000) at the revolution up to 10^4. In the measurements we used two kinds of 6-mm-diameter balls made of hardened bearing steel (about HV 600) and hard metal (WC-Co, about HV 1600). The balls were rotated with the radius of 3 – 5 mm at a constant linear velocity of 0.03 m/s, keeping the load of 2N or 10 N applied on the DLC surface.

3. Results and discussion

3.1 Nanostructure and surface modification

Figure 1 shows the SEM images of DLC film surfaces ablated by the linearly polarized fs pulses at E = 110 μJ, where the microscope magnifications are (a) 30, (b) 10000 and (c) 20000. As seen in Fig. 1(a), the parallel belt like traces of which width is about 120-μm are created by the laser spot scanned at a constant speed. The surface undulation or roughness created by the laser scanning was less than 10 nm, which was measured with the SPM. Figures 1(b) and (c) represent the periodic fine structures, so-called nanostructures, that are almost oriented to the direction perpendicular to the laser polarization. The mean spacing D of the fine structure is measured to be D ~ 120 nm along the field polarization direction, which is much smaller than the laser wavelength of 800 nm, as in our previous observations [5-10]. The nanostructure was observed on the DLC surface over the whole area of 15 x 15 mm^2 that was irradiated at E = 110 μJ of the fs laser pulses.

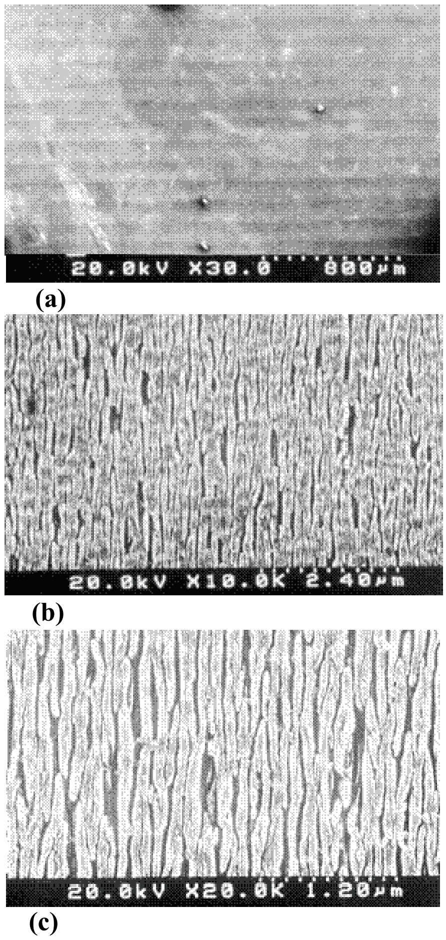

Fig. 1 SEM images of the DLC surfaces ablated with the fs laser pulses at E = 110 μJ. The magnifications are (a) 30, (b) 10000 and (c) 20000.

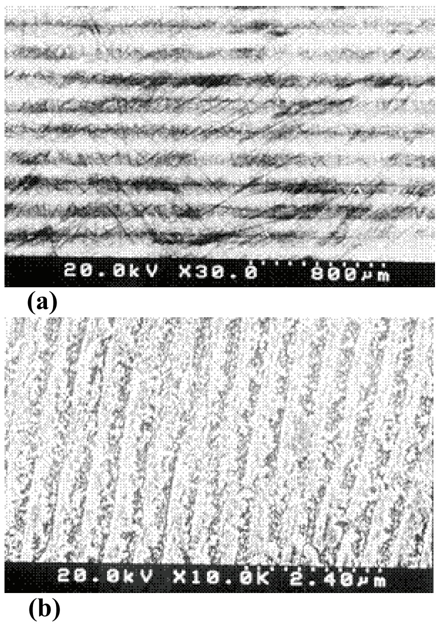

Fig. 2 SEM images of the DLC surfaces ablated with the fs laser pulses at E = 200 μJ. The magnifications are (a) 30 and (b) 10000.

Figure 2 shows the SEM images of DLC film surfaces ablated at the higher pulse energy of E = 200 μJ, where the magnifications are (a) 30 and (b) 10000. In Fig. 2(a), the width of laser traces of about 160 μm and the surface undulation of about 200 nm created by the laser scanning were larger than those formed at E = 110 μJ. At the higher pulse energy, the mean spacing of the periodic structures was increased to D ~ 480 nm, as shown in Fig. 2(b). This increase in D with an increase in E or the laser fluence is consistent with our previous observations [7,9].

To see the bonding structure change of the DLC, we observed Raman spectra of the laser-irradiated surface, and the results for those at E = 110 and 200 μJ are shown in Fig. 3(b) and (c), respectively, together with (a) the spectrum of non-ablated DLC film for comparison. As discussed in detail in our recent papers [7,8], Fig. 3(a) shows the typical spectrum of DLC which contains an asymmetric broad band, and Fig. 3(b) represents the typical one of GC that have two spectral peaks at 1355 and 1590 cm^{-1} [12]. On the other hand, the Raman spectrum of the DLC irradiated at the higher pulse energy of E = 200 μJ exhibits such a structure as superposed with those of GC and DLC and/or originated from the other carbonaceous materials [7]. The characteristic Raman spectra were observed on the whole area of 15 x 15 mm^2 on the DLC surface irradiated with the fs pulses.

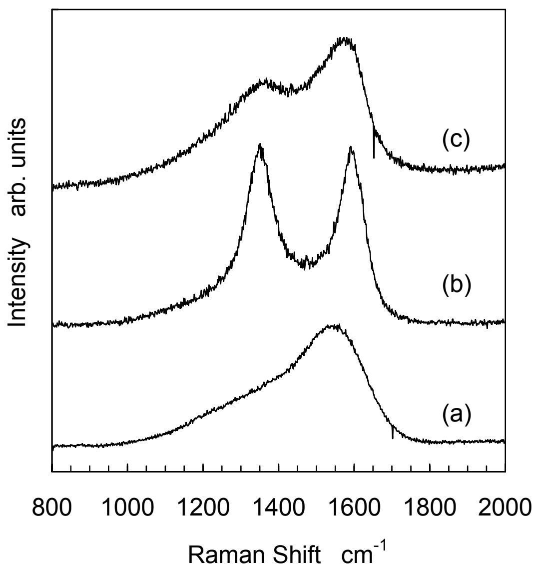

Fig. 3 Raman spectra of (a) the non-irradiated DLC film and those irradiated with the fs laser pulses at (b) E = 110 and (c) 200 μJ.

3.2 Tribological properties

First we measured friction coefficient α of the DLC surfaces, using different ball materials in the test machine. Figure 4 shows the results of α measured at a load of 10 N with (A) the steel ball at 2000 revolutions and (B) the WC-Co ball at 10^4 revolutions, where the samples (a), (b) and (c) are the non-irradiated DLC, and those irradiated at E = 110 μJ and 200 μJ, respectively. We define the friction coefficient α_0 of the non-irradiated DLC at each condition for the measurement. As seen with (A) in Fig. 4, the friction coefficient α of the DLC films irradiated at E = 110 (b) and 200 μJ (c) was reduced down to α ~ (4/5)α_0 and (3/5)α_0, respectively. This result appears to demonstrate that α is certainly reduced by the fine structure on the DLC surface. However, in comparison with the results for (b) and (c), the larger structure size reduces α more than the smaller one. This observation is attributed to the relatively high adhesive property of the steel ball, since the surface hardness is decreased for the modified and structured surface layer produced by the laser pulses. In fact, when α was measured with the steel ball at the revolution of 10^4, this modified surface layer was observed to wear away, and α for the three samples (a), (b) and (c) was increased to almost the same value of α ~ 0.24. On the other hand, such strong wearing of the structured surface was not observed with the WC-Co ball even at 10^4 revolutions. As seen with the results (B) in Fig. 4, however, the friction coefficient α of the DLC films (b) and (c) is α ~ α_0 and (3/2)α_0, respectively. For the WC-Co ceramic ball having the higher hardness and the lower adhesive property than the steel ball, the coefficient α is inversely increased with the decrease in the hardness of the modified layer and with the increase in the structure size. The friction coefficient α of the DLC film (b) is higher than α_0 of the non-irradiated film (a) during the early stage of the wear test, but α reaches α_0 at about 5000 revolutions, since the thickness of the modified layer of (b) is thinner than that of (c).

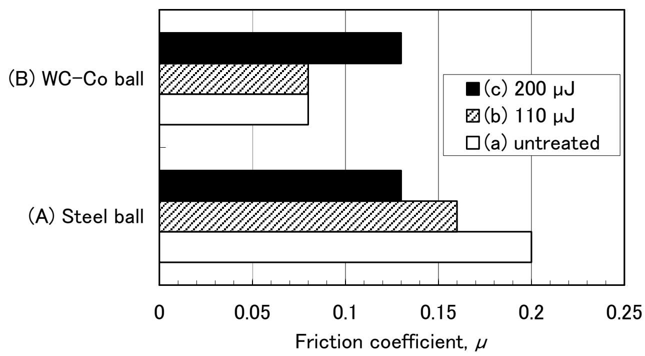

Fig. 4 Friction coefficients of (a) non-irradiated DLC film and those irradiated with the fs laser pulses at (b) E = 110 and (c) 200 μJ measured with the ball-on-disk friction test machine at a load of 10 N. (A) indicates the results for (a) , (b) and (c) at 2000 revolutions with the bearing steel ball, and (B) at 10^4 revolutions with the WC-Co ball.

Utilizing the steel ball and WC-Co ball, the friction coefficient α of the DLC films was also measured after coating a MoS_2 layer on the non-irradiated DLC surface and the nanostructured one at E = 110 μJ. Figure 5 shows the results of α for the non-irradiated DLC film with no coating (a), the non-irradiated one with the MoS_2 coating (b) and the nanostructured DLC with the MoS_2 (c), where the group (A) is those measured with the steel ball at 10^4 revolutions under a load of 2 N applied on the surface, and (B) and (C) are with the WC-Co ball at 4000 and 10^4 revolutions, respectively, under a load of 10 N. As seen with (A), the friction coefficient α of the MoS_2-coated DLC film (b) was $\alpha \sim (3/4)\alpha_0$ with the coefficient α_0 of the sample (a). The nanostructured DLC film with the MoS_2 coating (c) shows a larger decrease in α down to $\alpha \sim (2/5)\alpha_0$. In Fig. 5, similar large decreases in α are also demonstrated for the groups (B) and (C) that have been measured with the WC-Co ball. The friction coefficient of the MoS_2-coated DLC film (b) is $\alpha \sim (1/2)\alpha_0$ and $(3/4)\alpha_0$, as measured at 4000 and 10^4 revolutions, respectively, and the nanostructured DLC film with the MoS_2 coating shows a further decrease in α to $\alpha \sim (1/4)\alpha_0$ and $(1/2)\alpha_0$, respectively. The absolute friction coefficients of the nanostructured and MoS_2-coated DLC film are measured to be 0.07 with the steel ball and 0.02 – 0.04 with the WC-Co ball. The extremely small friction coefficient of DLC surfaces is attributed to the following two effects. One is of the nanostructure formed with the fs laser pulses that could store the MoS_2 layer on the surface acting as a lubricant reservoir for MoS_2, and the other is of the softened surface layer modified to GC that would improve the bonding interface between the DLC and MoS_2 layers.

The present results demonstrate that the MoS_2 coating after nano-structuring the DLC surface with the fs laser pulses provides an extremely effective way to improve tribological properties of DLC surfaces.

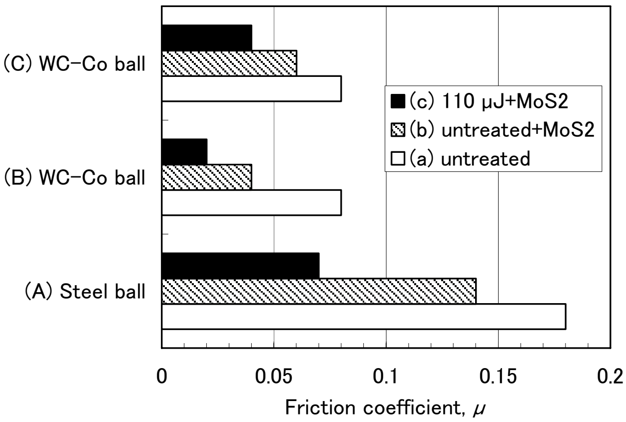

Fig. 5 Friction coefficients of (a) the untreated DLC film, (b) the MoS_2-coated DLC film and (c) the MoS_2-coated DLC film nanostructured at E = 110 μJ. (A) represents the results at 10^4 revolutions with the bearing steel ball at a load of 2 N, and (B) and (C) at 4000 and 10^4 revolutions, respectively, with the WC-Co ball at a load of 10 N.

4. Conclusions

We have developed the fs-laser processing technology to produce a uniform nanostructured DLC surface over a wide area and investigated the tribological properties of the structured surfaces, together with the fundamental nature on the structure size and the bonding structure change. The results obtained are summarized as follows.

1) The nanostructure has been formed uniformly on the DLC surface over the area of 15 x 15 mm^2.
2) The structured surface at E = 110 μJ near the ablation threshold is uniformly modified to the GC layer.
3) The friction coefficient of the structured DLC film has shown a small decrease for the steel ball but a small increase for the ceramic WC-Co ball.
4) A large improvement of the friction coefficient of the DLC surface has been achieved by coating the MoS_2 layer on the nanostructured DLC surface. The measured friction coefficients of the surface were 0.07 with the steel ball and 0.02 – 0.04 with the WC-Co ball.

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