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Friction and adhesion behavior of polycrystalline diamond films deposited on metals

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Abstract

Polycrystalline diamond films with different grain sizes and thickness are coated on copper with a titanium interlayer. Friction and wear behavior of the coatings against steel is tested using a block-on-ring tribotester. Raman spectroscopy is used to characterize the diamond quality and to access residual stress in the coatings being tested under different wear loads. More non-diamond phases are found in thinner film, which still exhibits high wear resistance as evidenced by scanning electron microscopy. It is shown that the friction coefficient is proportional to the diamond grain size and the wear load. After the wear tests, the diamond coatings still adhere to the substrate. However, Raman spectra show a smaller shift in the diamond peak than that before the test; this may imply an actual decreasing in the coating adhesion, or it could relate to graphitization in the wear test. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Diamond film; Friction; Adhesion; Wear

1. Introduction

Diamond possesses many extreme properties [1]. It is the hardest material ever known. Its thermal conductivity is approximately five times that of copper and it is chemically inert. In addition, it has a low thermal expansion coefficient and is almost optically transparent from UV to far IR regions. These properties combined with the success in low-pressure synthesis of diamond by chemical vapor deposition (CVD) make diamond thin films very attractive in coating applications. Therefore, as one of the basic topics, the tribological performance of CVD diamond has been under investigation for many years [2–10]. Generally, it has been realized that the mechanical and tribological properties of CVD diamond films depend on their microstructure — such as grain size and grain boundary strength — the presence of non-diamond phases and the coating-substrate adhesion. However, the experimental results reported in the literature are often in disagreement. This is possibly due to the different test conditions and materials used by the authors. Thus, some tribological properties of CVD diamond still needs to be confirmed.

The present investigation is undertaken to determine the effect of the diamond grain size and film thickness on the wear and friction behavior. Furthermore, since the adhesion of diamond is extremely important in most tribological applications, it is necessary to determine how the wear process influences the coating adhesion. Instead of a simple fail (film delamination)–

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pass (adherence) observation of the coatings after the wear tests, we propose using micro-Raman spectroscopy to evaluate the adhesion status of the diamond films. It is shown that a change in the coating adhesion caused by the wear load will lead to a different shift in the diamond Raman line even though the film still attaches to the substrate.

2. Experimental details

The substrates used for the diamond deposition were polycrystalline copper foil (99%) 1 mm thick and 5×5 mm^2. They were polished with a sequence of SiC sand papers down to 600# grid, then ultrasonically cleaned in acetone for 10 min and dried in an oven at 100°C. Before the diamond deposition, the substrates were coated with a titanium layer (approximately 0.6 μm thick) by DC sputtering. Diamond synthesis was conducted using an ASTeX 2.45 GHz microwave plasma CVD system. The process gases were H_2, CH_4, and O_2. Typical deposition conditions were as follows: microwave power, 2500 W; gas pressure, 90 Torr; gas flow rate, $H_2 = 469$ sccm, $CH_4 = 30$ sccm, and $O_2 = 1$ sccm. The substrate temperature was not an independent parameter in this system, it was controlled mainly by microwave power. Diamond films with different thickness were obtained by changing the deposition time.

The wear resistance and friction coefficient (f) of the diamond films were tested using a block-on-ring tribotester, as shown in Fig. 1. A load of 76–376 N was applied to the stationary sample against a rotating steel ring of 12 cm in diameter. The rotating speed was ~300 rev./min. A mineral oil Shell Helix 20W was used as lubricant. The temperature at the sample/steel wheel contact region was approximately 200°C. The friction force was automatically recorded through a load cell and the f value was calculated from the friction force divided by the load. The film morphology and the surface chemical composition were observed using a Hitachi 4100 scanning electron microscope (SEM) equipped with an energy dispersion spectrometry (EDS). A Reneshaw 2000 Raman spectroscopy system with a 633-nm He–Ne laser was used to evaluate the diamond films and their stress status. At this laser wavelength the Raman spectra of non-diamond phases of carbon are enhanced because of a resonance effect, in which the non-diamond forms of carbon scatter more effectively than diamond [11].

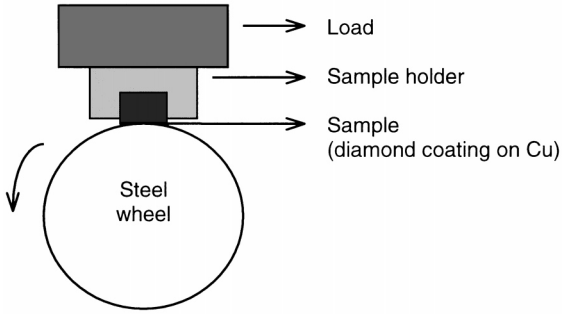


Fig. 1. Illustration of the block-on-ring tribotester.

3. Results and discussion

Three samples with different diamond film thickness, 6 μm (sample A), 18 μm (sample B), and 60 μm (sample C), were used in the tests. Raman spectra taken from the samples are shown in Fig. 2. It can be seen that the thinner film (sample A) exhibits much higher background and more non-diamond phases than the thicker films, indicating that the film quality improves with the diamond growth. SEM images of the films are also given in Fig. 2. It can be seen that at different growth stages, the diamond films possess quite different grain sizes and, therefore, grain boundary/volume ratios. The structure of the grain boundary is different from the grain interior and usually many defects and non-diamond phases exist in the grain boundaries that may contribute to the high background and many ill-defined wide bands in the Raman spectra. Therefore, in thinner films, the effect of grain boundary is expected to be stronger. Thus, the tribological properties of these films are quite a practical concern.

3.1. Wear resistance

Samples A, B, C were tested under loads of 76, 176, 276 and 376 N. For each load the test time was 30 min, corresponding to a wear distance of approximately 3400 m. The surface of the samples after the wear tests is shown in Fig. 3. Almost no wear in the films can be observed, indicating that even the thinner film (sample A) that contains the highest level of non-diamond phases and grain boundaries is hard enough to resist the wear. As a comparison, a clear groove was observed in the steel wheel, indicating that significant wear to the steel wheel occurred. After the tests, the samples were ultrasonically cleaned in acetone for 10 min, and EDS was performed to check the residues left in the film surface. With the exception of an obvious carbon peak, no other elements were detected. Even for iron, its signal intensity was only in a range of noise level, implying that the iron debris could not adhere to the diamond films. Therefore, the diamond films serve as super abrasives.

It was found that when the load increased to 376 N, small cracks appeared in thinner films, samples A and B. An example is shown in Fig. 4. However, no crack was observed in the thickest film, sample C. Such kind

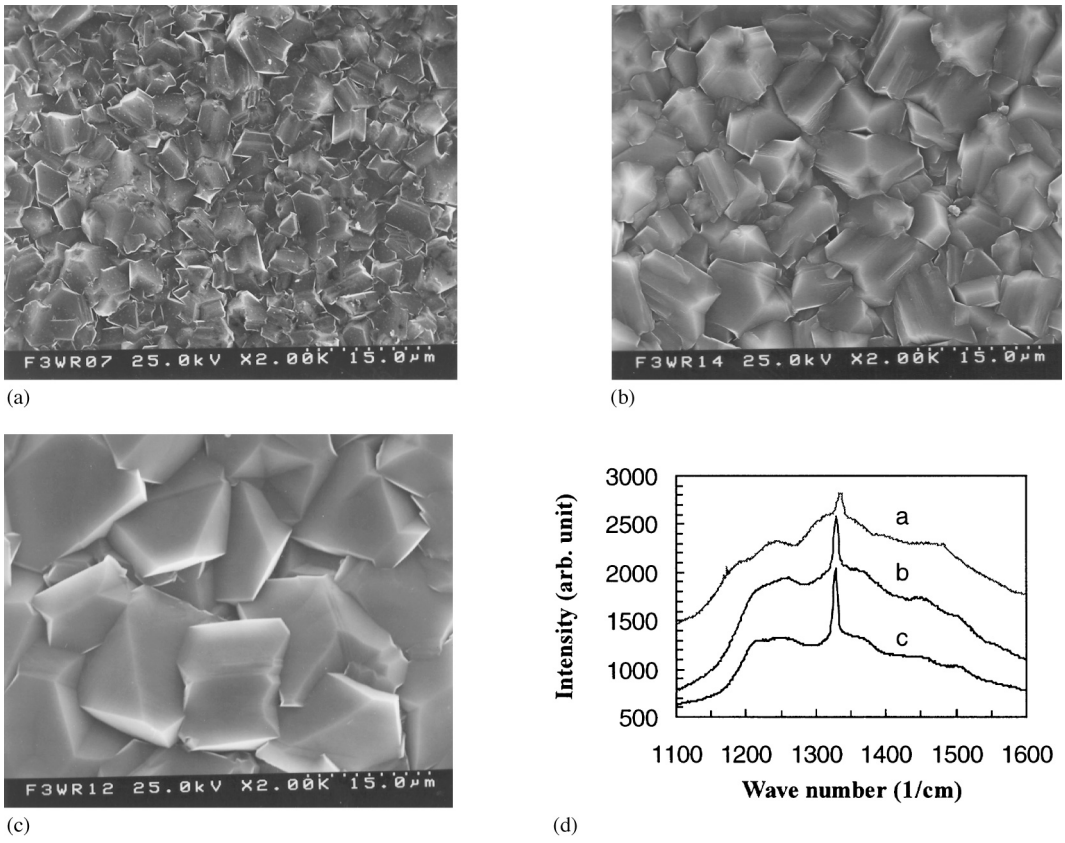


Fig. 2. SEM images of sample A (a), sample B (b), sample C (c) and their Raman spectra (d).

of local crack is probably induced by the substrate collapsing beneath the film. It is interesting to note that at some points the crack is trans-granular, indicating that the chemical bonds at the grain boundary could be as strong as those in the grain.

3.2. Friction coefficient (f)

The friction properties were obtained from testing samples A, B, and C. Fig. 5 shows the f dependence on the wear time for different samples under the same load of 76 N. Fig. 6 shows the f dependence on the wear time for sample C under different loads. The initial variation of f is connected to the starting procedure of the test. It can be seen that although the friction coefficient increases with increase in the grain size (sample A < sample B < sample C) and with increase in the load, it almost does not change with the wear time. This implies that the coating stands the wear, as confirmed in Fig. 3. The slight decrease in f with the wear time is probably due to smoothening of the steel wheel and filling the sample surface with worn materials during the wear tests.

It is noted that samples A, B and C have a grain size of approximately 3.5, 6 and 12 μm, respectively. Plotting the f dependence on the grain size D and making a best fitting, we find that the f–D curves are in linear relationship, as shown in Fig. 7. Note that the f is an average value for each sample tested under each load for 30 min. The slope of the curves increases with the load. This can be related to the roughness of the film surface. A larger grain size normally results in a rougher film surface. Therefore, the sharp grains penetrate deeper into the steel wheel under a higher load, leading to an increase in the friction coefficient f. It is interesting to note that although f depends strongly on the load, all the curves show a similar intercept on the vertical axis, approximately 0.08. We suppose that when the grain size approaches zero, the geometry of the film surface becomes similar to a single crystal. We may, therefore, deduce that the friction coefficient of a bulk diamond sliding on the steel will be approximately 0.08 and it will be almost independent of the wear load used in the present work.

3.3. The coating adhesion and residual stress

A microscopic observation showed that the diamond coatings stood the wear with no delamination and film removal, except some local cracks in thinner films (samples A and B) after being tested with a higher load of 376 N (see Fig. 4). Such a simple fail–pass evaluation leads to the conclusion that the coating adhesion seems sufficient. A question, therefore, arises — is

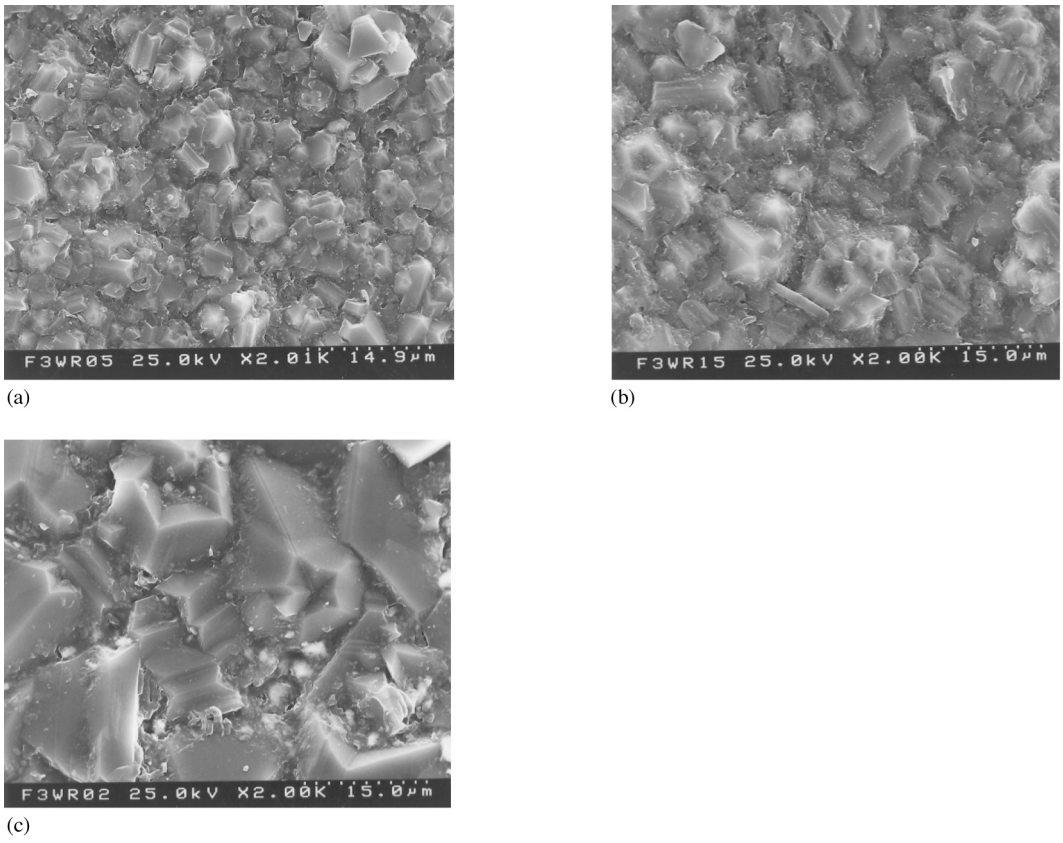


Fig. 3. The surface of sample A (a), B (b), and C (c) after the wear test under loads 76, 176, 276 and 376 N. For each load the test duration is 30 min.

there any change in the coating adhesion and in residual stress after the wear tests with different loads? To answer this question we performed Raman spectroscopy measurements on the samples before and after each wear load test. It was found that samples A, B and C showed a diamond Raman shift at wave numbers higher than 1332 cm^{-1} before the tests. This implies that the films were subjected to a compressive stress due to their adherence to the substrates [12]. The compressive stress is believed to be due mainly to thermal mismatch between the film and the substrate [13]. After the wear tests, the diamond Raman line shifted to lower wave numbers. It approached 1332 cm^{-1} with an increase in the wear load. An example is shown in Fig. 8.

It is known that the Raman shift is proportional to the biaxial stress, σ, in the diamond films with relationships shown as follows [12–14],

$$\sigma = -1.08(\nu_s - \nu_0)\ (\text{GPa}) \quad \text{for singlet phonon} \qquad (1)$$

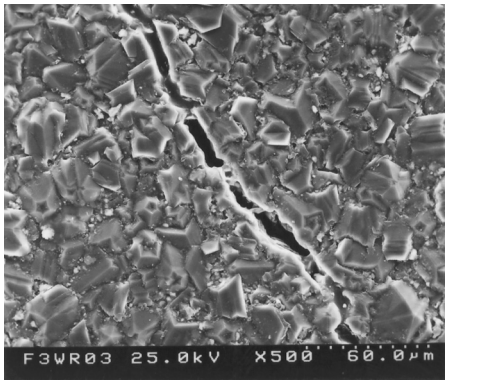


Fig. 4. An example of small cracks in the diamond film (sample B) after the wear test under a load of 376 N.

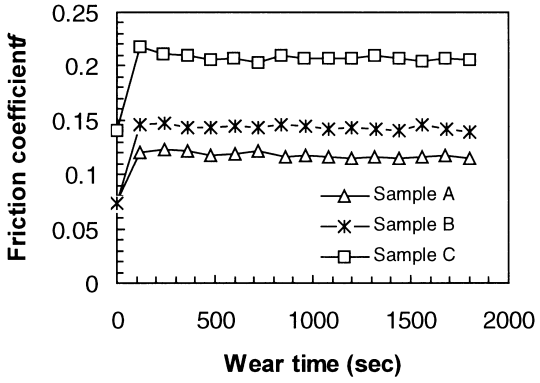


Fig. 5. The friction coefficient dependence on the wear time and grain size. The load is 76 N.

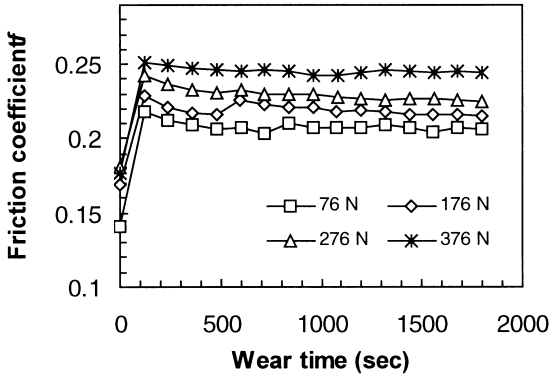


Fig. 6. The friction coefficient dependence on the load for sample C.

$$\sigma = -0.384(\nu_d - \nu_0)\ \text{(GPa)} \quad \text{for doublet phonon} \quad (2)$$

$$\sigma = -0.567(\nu_m - \nu_0)\ \text{(GPa)} \quad \text{for unsplitted peak} \quad (3)$$

where $\nu_0 = 1332\ \text{cm}^{-1}$, ν_s and ν_d are Raman shifts for singlet and doublet phonon, ν_m is the measured diamond Raman line once there is no peak splitting. Combining Fig. 8 and Eqs. (1)–(3), we can see that stress relaxation has occurred during the wear test. The decrease in the biaxial stresses can be related to a few factors. First, plastic deformation in the substrate may happen under the wear load since the substrate (Cu) is a relatively soft material. Second, the temperatures developed during sliding can be locally high enough to drive the graphitization process. The observed increase in the background around the 1332 cm^{-1} diamond peak (see Fig. 8) for the worn surfaces would support this suggestion. The conversion of an sp^3 carbon bond to an sp^2 bond can lead to stress relaxation. Third, the films may partially detach from the substrate in the wear test and consequently become less stressed. Obviously a higher load causes an increase in the degree of the film detachment. Thus, the shift in the diamond

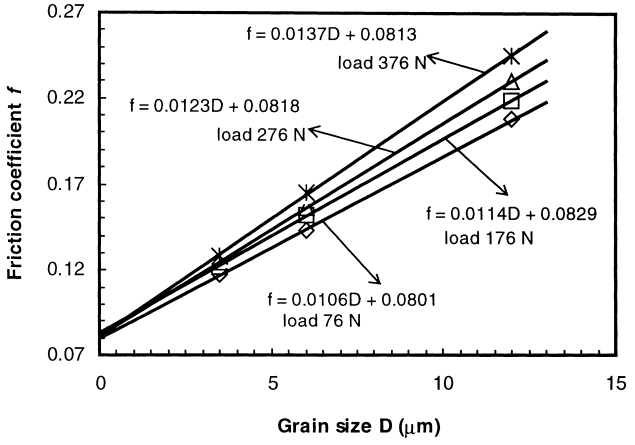


Fig. 7. The friction coefficient f dependence on the grain size D of the diamond films. Symbols *, △, □, ◇ are experimental results. The continuous lines are from the best fitting as indicated in the figure.

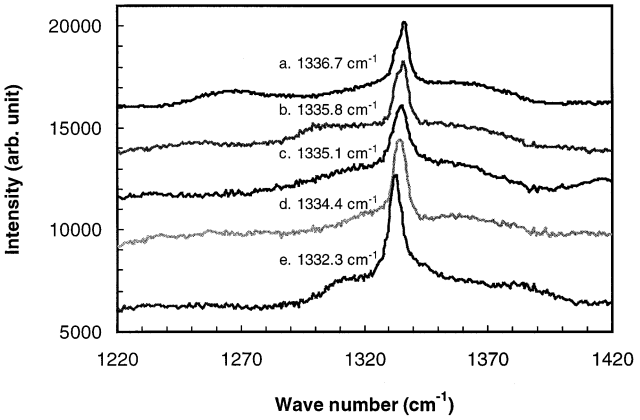


Fig. 8. Raman spectra taken from sample B before the wear test (a), after the wear test with load 76 N (b), with load 176 N (c), with load 276 N (d), and with load 376 N (e). The Raman peak position is labeled in the figure.

Raman line indicates not only the stress status, but also the film adhesion. We, therefore, deduce that there is actually a decrease in the coating adhesion after the wear tests although the films still attach to the substrate. Further work to distinguish the effect of the above-mentioned factors on the coating adhesion and on the residual stress is under consideration.

4. Conclusions

Diamond films of different thickness show different grain sizes and grain boundary/volume ratios. However all these films exhibit high wear resistance against steel. Friction coefficients of the diamond films are proportional to their grain size and proportional to the wear load. The diamond Raman line shift can be used to compare qualitatively the coating adhesion, although other mechanisms (such as graphitization) may occur and need to be identified.

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