CHARACTERIZATION OF TRANSFER LAYERS ON STEEL SURFACES SLIDING AGAINST DIAMONDLIKE CARBON IN DRY NITROGEN*

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DISCLAIMER

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ABSTRACT:

Transfer layers on sliding steel surfaces play important roles in tribological performance of diamondlike carbon films. In this study, we investigated the nature of transfer layers formed on M50 balls during sliding against diamondlike carbon (DLC) films (1.5 μm thick) prepared by ion-beam deposition. Long-duration sliding tests were performed with steel balls sliding against the DLC coatings in dry nitrogen at room temperature, ≈22±1°C, and zero humidity. Test results indicated that the friction coefficients of test pairs were initially ≈0.12 but decreased steadily with sliding distance to 0.02-0.03 and remained constant throughout the tests, which lasted for more than 250,000 sliding cycles (≈30 km). This low-friction regime appeared to coincide with the formation of a carbon-rich transfer layer on the sliding surfaces of M50 balls. Micro-laser-Raman spectroscopy and electron microscopy were used to elucidate the structure and chemistry of these transfer layers and to reveal their possible role in the wear and friction behavior of DLC-coated surfaces.

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INTRODUCTION

Diamond-like carbon (DLC) or amorphous hydrogenated carbon coatings offer unique mechanical and physical properties that make them very desirable for a wide range of triblogical applications. Mechanically, these materials are extremely hard. Reported microhardness values for DLC coatings vary between 2000 and 9000 kg/mm^2 [1-4]. Furthermore, DLC coatings are chemically very inert, hence provide excellent resistance to corrosive attack in acidic and saline media [1,2,4,5]. Recent tribological tests indicate that these coatings can afford very low friction and high wear resistance to sliding tribological interfaces [6-13]. The reported friction coefficients of DLC coatings sliding against metallic and ceramic materials may range from 0.005 to 0.4, depending on test environment, deposition methodology, and temperature [8-10,13]. Furthermore, compared to other popular hard coatings; such as TiN and TiC; DLC coatings can last 2 to 3 orders of magnitude longer in a typical wear test. The relative humidity of the test environment were found to play a significant role in the friction and wear performance of DLC coatings. In dry air, N_2, and inert gases, the friction coefficients were found to vary between 0.005 to 0.04 [8-10]. However, with increasing relative humidity, the friction coefficients of DLC films may increase to 0.3 [6,7,10].

Some of the previous studies have indicated that the wear scars of counterface materials are often covered with a carbon-rich transfer layer during sliding against the DLC coatings. Moreover, in most cases, the formation of these carbon-rich transfer layers on wear scars always coincided with a substantial reduction in friction coefficients [9,11,14-16]. For example, Erdemir et al. [11] found carbon-rich transfer layers on the wear scars of 440C steel balls after a long period of sliding, ie.e., 25 km. In their sliding tests, the friction coefficients of 440C balls against the DLC coated 440C disks were initially 0.17 but decreased to ≈0.05 to 0.07 after a carbon-rich transfer layer formed on the wear scars. It is possible that an understanding of the chemical and physical nature of such transfer layers may provide some insight into the otherwise complex friction and wear mechanisms of DLC coatings. Furthermore, very long endurance lives afforded by these coatings may be due to a mechanism involving first the generation, then the transfer of such a highly shearable layers at sliding interfaces of pins and disks.

In this study, we attempt to elucidate the physical and chemical nature of these carbon-rich transfer layers formed on the surface of M50 balls during sliding against DLC coatings (1.5 μm thick). For this purpose, a series of long-duration sliding tests (250,000 revolutions, ≈30 km) were performed in dry nitrogen at room temperature, ≈22±1°C. After reaching a low steady-state friction regime, the balls were taken out the test machine and the structural chemistry of the transfer layers formed on the balls was examined by micro-laser-Raman spectroscopy and electron microscopy.

EXPERIMENTAL PROCEDURES

Test Materials

The ball and disk specimens used in this study were fabricated from AISI M50 steel. The disk specimens were 50 mm in diameter and 5 mm thick. They were ground to a surface finish of 0.05±0.01 μm centerline average (CLA). The counterface balls were 9.5 mm in diameter with a surface finish of better than 0.01 μm CLA. Ball and disk specimens had a Vickers hardness value of about 8.0±0.2 GPa. Prior to friction testing, M50 balls were ultrasonically cleaned sequentially in hexane + 10 vol.% toluene, acetone for 1 min each, then dried in an oven at 100°C for 10 min.

Ion-Beam Deposition of Diamondlike Carbon

Thin DLC films (≈1.5 μm thick) were ion-beam deposited on M50 disks at room temperature in a vacuum chamber equipped with a broad-beam ion source. A schematic illustration of this deposition system is shown in Fig. 1. In this deposition system, methane, the carbon source, was fed through a cylindrical ion source (see Fig. 1) and ionized by energetic electrons produced by a hot filament wire.

The M50 substrates were positioned directly beneath the ion source and sputter-cleaned with a 1 keV, 2.5 mA/cm^2 Ar-ion beam for ≈3-5 min. Subsequently, an intermediate hydrogenated-silicon carbide (SiC:H) bondlayer was sputter-deposited on these substrates by rotating the samples out of the beam and into the sputter-coating position, as illustrated in Fig. 1. Simply, methane is bled into the vacuum chamber and the 1 keV argon beam is allowed to sputter the silicon target shown in the figure. The thickness of the SiC bond layer was about 20 nm. Without the SiC layer, strong bonding could not be achieved between DLC films and M50 substrate.

Finally, the deposition of DLC was started by rotating the disk samples back to a position directly beneath the ion beam. Operating conditions were adjusted to give an ion beam with an acceleration energy of 450 eV and a current density of ≈ 2.5 mA/cm^2. Under these operating conditions, the deposition rate was ≈ 3 µm/hr. Deposition was continued until a 1.5-µm-thick DLC film was obtained. Substrates were water-cooled via their mounting plates.

Friction and Wear Tests

Sliding friction and wear tests were performed with pairs of M50 balls and DLC-coated M50 disks on a ball-on-disk Tribometer in dry N_2 at room temperature, 23 ± 1°C for a sliding distance of about 30 km. A few short distance tests (i.e., 1 km) were also run with M50/M50 and M50/DLC-coated M50 pairs to provide comparison between their friction and wear performance in dry N_2. The sliding velocity was kept at 0.5 m/s. The dead weight applied on balls was 5 N, which created an initial mean Hertzian contact pressure of approximately 0.54 Gpa. Frictional force was monitored with the aid of a linear variable-displacement transducer and was recorded on chart papers throughout the tests. The diameter of the wear track varied between 30 and 35 mm during these tests, producing steadily decreasing nominal pressures far below the initial mean Hertzian pressures.

Wear-volume calculations on the balls were based on microscopic determination of the diameter of the circular wear scars, combined with the assumption that the wear scar is flat. The wear of disk specimens was estimated from the traces of surface profiles across the wear tracks. Two to three tests were run under conditions described above to check the reproducibility of the friction and wear data. The results were quite reproducible, with deviations of ≈ ± 6 to ± 15%. Wear scars and tracks were examined with a scanning electron microscope and analyzed with a micro-laser Raman spectroscope.

RESULTS AND DISCUSSION

Figure 2 shows the microstructural details of the DLC films tested in this study. As is evident, this DLC film appears very dense and free of volume defects. The structural morphology of this film is essentially featureless. Also, at the magnification shown, there is no evidence of a gap or discontinuity at the film/substrate interface, suggesting that this DLC film had excellent adhesion.

Fig. 3 gives the micro-laser Raman spectrum of the DLC film shown in Fig. 2. It reveals a peak at ≈1356 cm^{-1} (appearing as a shoulder) and another broad peak centered at ≈1502 cm^{-1}. The shouldered peak at ≈1350 cm^{-1} may be representing amorphous carbon. The peak at 1550 cm^{-1} is most likely due to the disordered graphite precursor. In general, these peaks are typical of the carbon films designated as DLC and are consistent with the Raman data provided in refs. 1,4, and 17.

Figure 4 shows the variation of the friction coefficients of M50/M50 and M50/DLC-coated M50 test pairs during short duration sliding tests. As is evident, the friction coefficient of a pair without a DLC coating is higher than 1 in dry N_2. However, the friction coefficient of the M50/DLC-coated M50 pair is very low. As can be noticed, initially friction coefficient of this pair is around 0.12, but decreased steadily as sliding continues and reaches a value of about 0.07 toward the end of the 1-km test. The average specific wear rate ((wear volume (mm^3) divided by contact load (N) and total sliding distance (m)) of the M50 ball slid against the uncoated M50 disk was ≈$9.8x10^{-6}$ mm^3/N.m. Whereas, the wear rate of an M50 ball slid against the DLC-coated M50 disk was $6X10^{-9}$ mm^3/N.m which translates into a factor of 1600 reduction in the wear rate.

Figure 5 shows the variation of the friction coefficient of a M50/DLC-coated M50 pair as a function of sliding cycles in a long-duration test. Initially, the friction coefficient of this pair was 0.13, but decreased substantially after about 50,000 sliding cycles and eventually reached a steady-state value of about 0.03 after 100,000 cycles and remained constant for the reminder of the test. The average specific wear rate of counterface ball was 4.6×10^{-10} $mm^3/N.m$. Surface profilometry trace over the wear track revealed very little wear on the DLC film itself.

DISCUSSION

In general, the results presented above demonstrate that the DLC coatings evaluated in this study are capable of imparting very low friction coefficients and wear rates to sliding steel surfaces during both the short duration and long-duration tests in dry N_2. In general, high mechanical hardness and very slippery nature of these coatings may have been largely responsible for their excellent friction and wear performance. Even after 250,000 sliding cycles, the film tested in this study was still intact, further verifying that these films wear at a very low rates.

In order to understand the physical and chemical nature of sliding contact interfaces that provided very low friction and wear, we employed micro-laser Raman spectroscopy and electron microscopy on rubbing surfaces. In our test schedule, we first allowed each sliding test to continue until a fairly low steady-state friction coefficient, i.e., ≈ 0.03, was established between M50 balls and DLC films. As shown in Fig. 4, the friction coefficient of M50/DLC-coated M50 pairs is about 0.07 after sliding for 1 km, but it further decreased to 0.03 during long-duration test (see Fig. 5). This observation suggests that short-duration tests do not necessarily reflect the real steady-state friction coefficient of

DLC films.

When we examine the wear scars on balls after long-duration test under a scanning electron microscope, we immediately noticed that the scars were covered by long streaks of transfer layers with an orientation parallel to the sliding direction (see Fig. 6a). Figs. 6b, 6c, and 6d are the secondary electron image, C, and Fe X-ray maps, respectively, of a transfer layer found in this scar at a much higher magnification. The X-ray map in Fig. 6c suggests that this transfer layer is rich in C. According to Fig. 6d, the transfer layer is Fe deficient. Fig. 7 shows the micro-laser Raman spectra of the base DLC coating, transfer layer, and black deposit found in the upper right corner of the wear scar shown in Fig. 6a. The Raman spectroscopy of a graphite standard is also provided in this figure as a reference. As is clear, the structural chemistry of black deposit and transfer layer is very different from that of the DLC coating, but is similar to that of graphite. Note that the Raman line positions of black deposit around the edge of scar and transfer layer essentially match those of the graphite standard. It is also important to note that the Raman line shapes of the transfer layer and black deposit are not as sharp as those of the graphite. This type of broadening is thought to result from phonon damping and is related to the degree of structural disorder in graphitic precursors as discussed in ref. 18.

Similar microscopic inspection of the wear scars on balls used in short-distance tests (i.e.., 1 km) of Fig. 4 did not reveal any type of transfer layer. It is possible that a very thin transfer layer may have also formed on the wear scars of these balls, but it may have been too thin or beyond the detection limit of our electron microscope and Raman spectroscope. In short, based on the results of this preliminary investigation, we conclude that the transfer layers forming on the surface of M50 balls have a disordered graphite structure. Furthermore, it is possible that much lower steady-state friction coefficients observed during long duration tests may have been related to the formation of such layers.

CONCLUSIONS

1. DLC films used in this study afforded very low friction coefficients and low wear rates to sliding steel surfaces. During short-duration sliding tests, the friction coefficient was around 0.07, but reduced further to 0.03 during long-duration tests.

2. Low friction coefficients in long-duration test correlated with the formation of a transfer layer on counterface balls.

3. The transfer layers are rich in carbon and have a graphite-like structure.

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FIGURE CAPTIONS

Fig. 1. Schematic of ion-beam deposition system.

Fig. 2. Cross-sectional SEM micrograph of DLC film used in this study.

Fig. 3. Micro-laser-Raman spectrum of DLC film used in this study.

Fig. 4. Variation of friction coefficient of an M50 ball during sliding against an M50 disk and against a DLC-coated M50 disk during short-duration sliding tests under 5 N and in dry N_2.

Fig. 5. Variation of friction coefficient of an M50 ball during sliding against a DLC-coated M50 disk during long-duration test under 5 N and in dry N_2.

Fig. 6. (a) Scanning electron photomicrograph of a wear scar formed on M50 ball during

long-duration test, (b) higher magnification SEM micrograph, (c) C X-ray map, and (d) Fe X-ray map of transfer layer on the wear scar.

Fig. 7. Micro-laser Raman spectra of DLC coating, transfer layers, black deposit around the edge of wear track, and graphite standard, suggesting that the transfer layer and black deposit have a graphitelike structure.

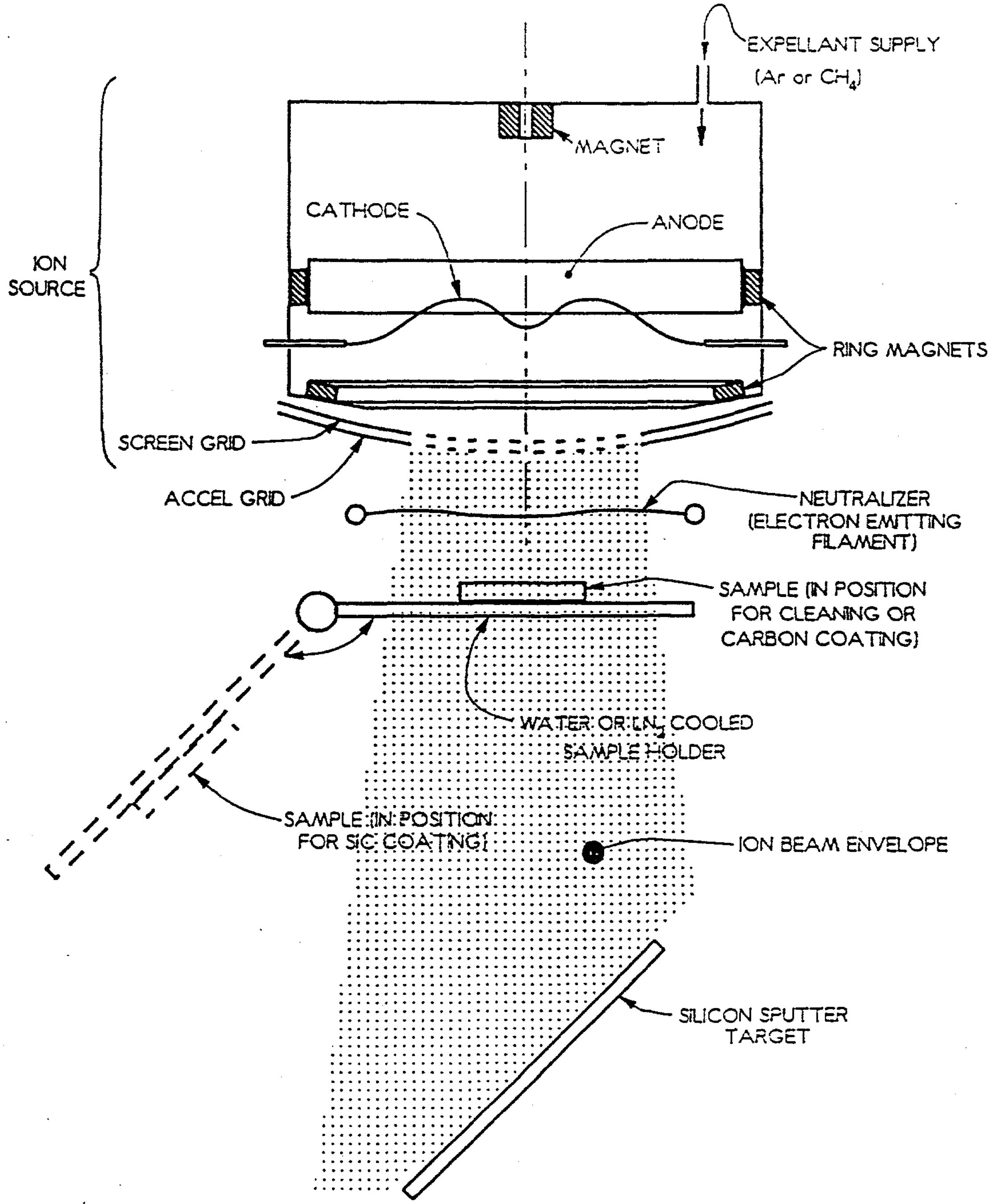
EXPELLANT SUPPLY
(Ar or CH_4)
MAGNET
CATHODE
ANODE
ION
SOURCE
RING MAGNETS
SCREEN GRID
ACCEL GRID
NEUTRALIZER
(ELECTRON EMITTING
FILAMENT)
SAMPLE (IN POSITION
FOR CLEANING OR
CARBON COATING)
WATER OR LN_2 COOLED
SAMPLE HOLDER
SAMPLE (IN POSITION
FOR SiC COATING)
ION BEAM ENVELOPE
SILICON SPUTTER
TARGET

Fig. 1

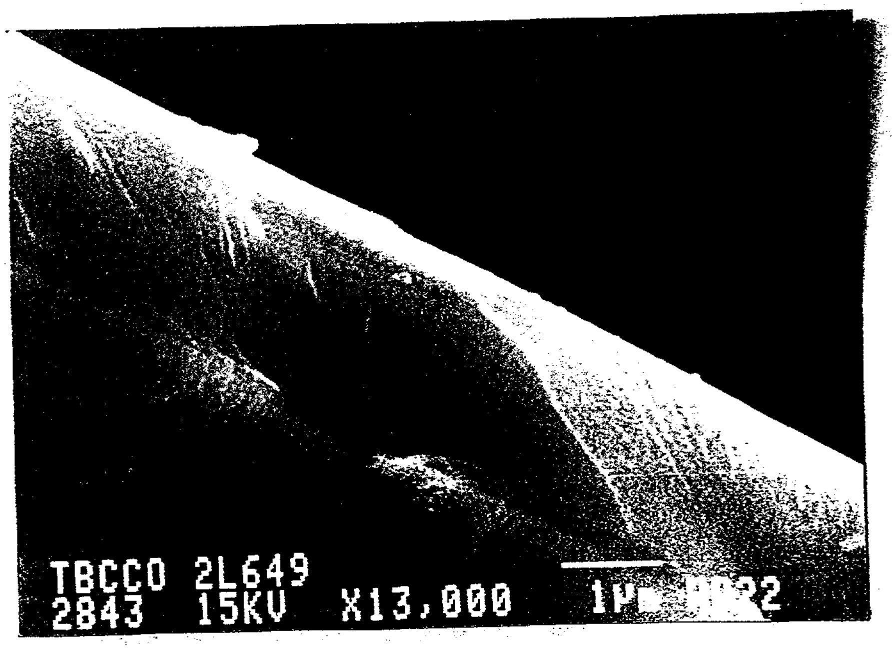
TBCCO 2L649
2843 15KV X13,000

Fig. 2

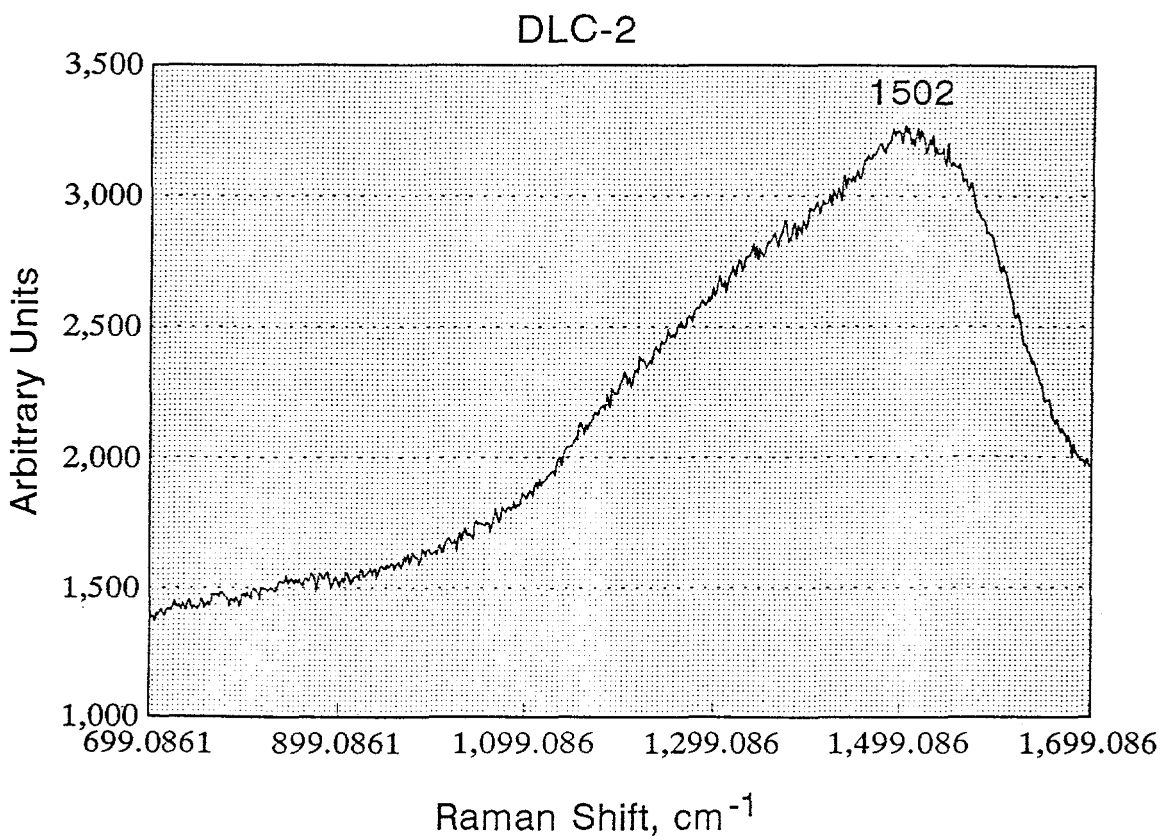
DLC-2
1502
3,500
3,000
2,500
2,000
1,500
1,000
Arbitrary Units
699.0861
899.0861
1,099.086
1,299.086
1,499.086
1,699.086
Raman Shift, cm⁻¹

Fig. 3

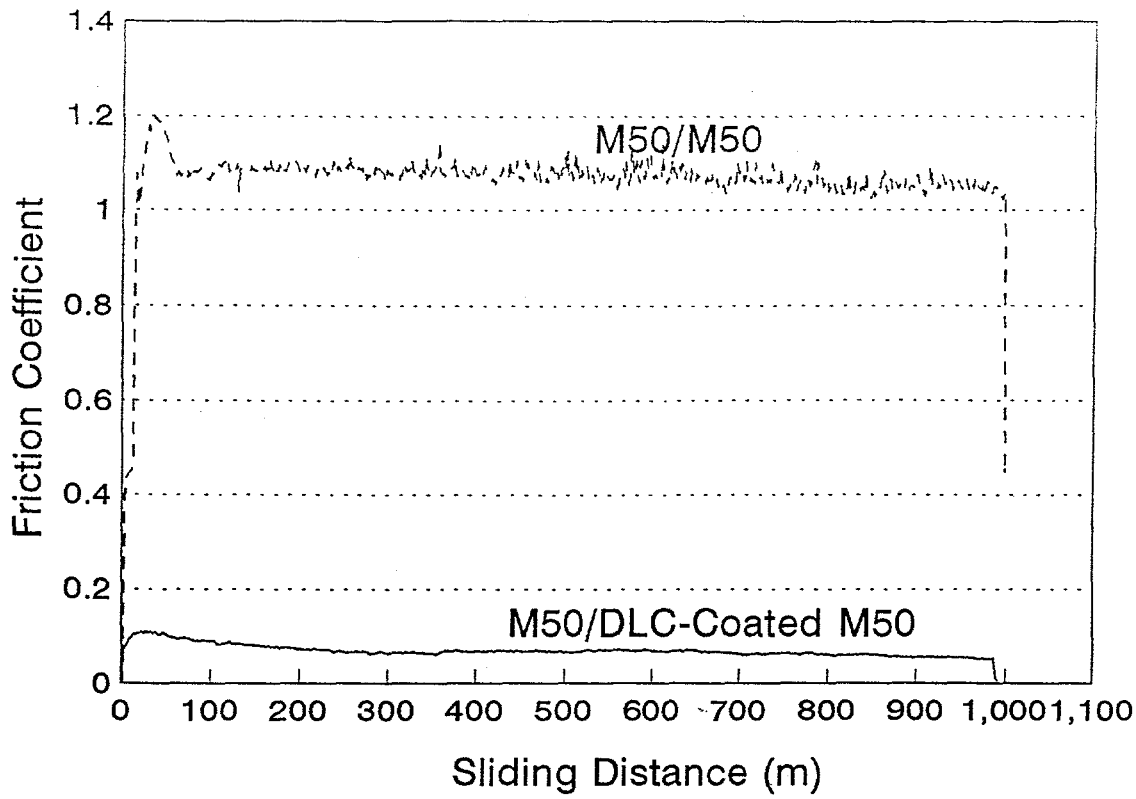
M50/M50
M50/DLC-Coated M50
Friction Coefficient
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
800
900
1,000
1,100
Sliding Distance (m)

Fig. 4

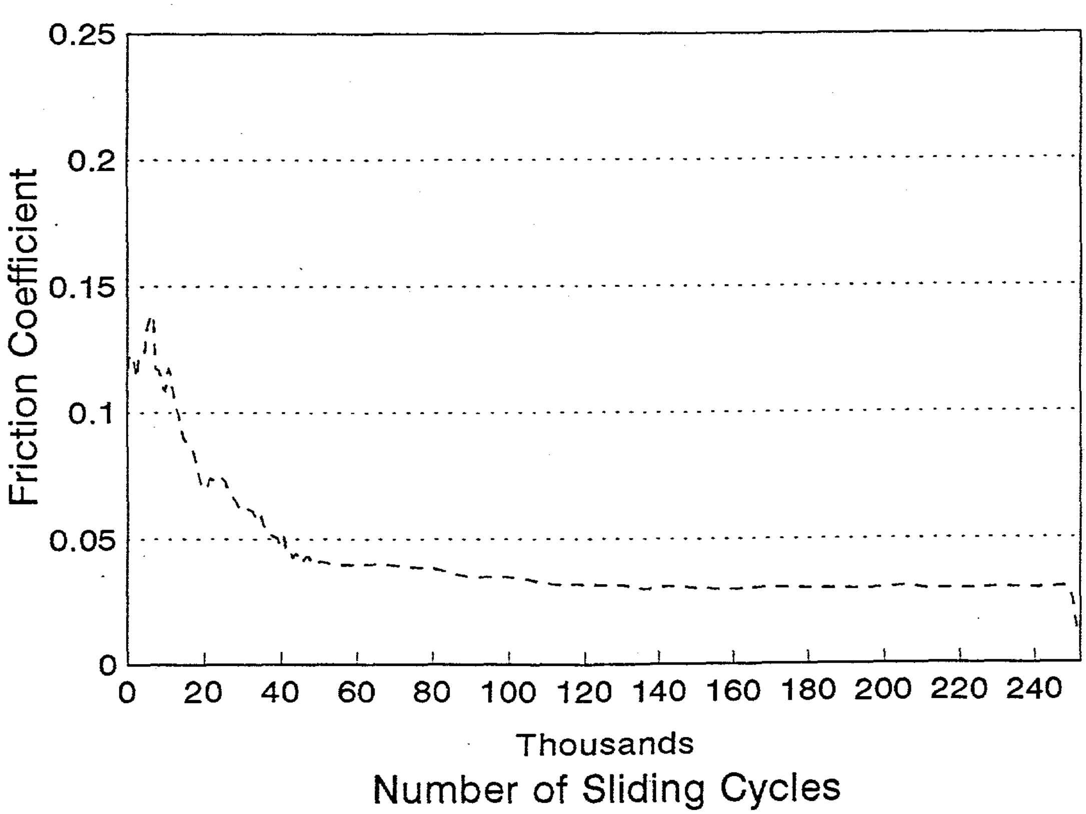
Friction Coefficient
0.25
0.2
0.15
0.1
0.05
0
0
20
40
60
80
100
120
140
160
180
200
220
240
Thousands
Number of Sliding Cycles

Fig. 5

Fig. 6a

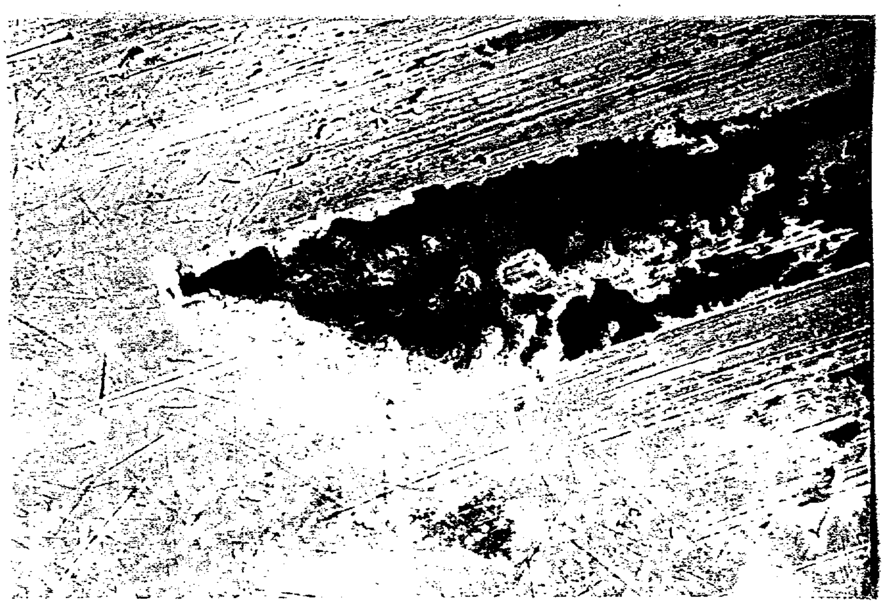

Fig. 6b

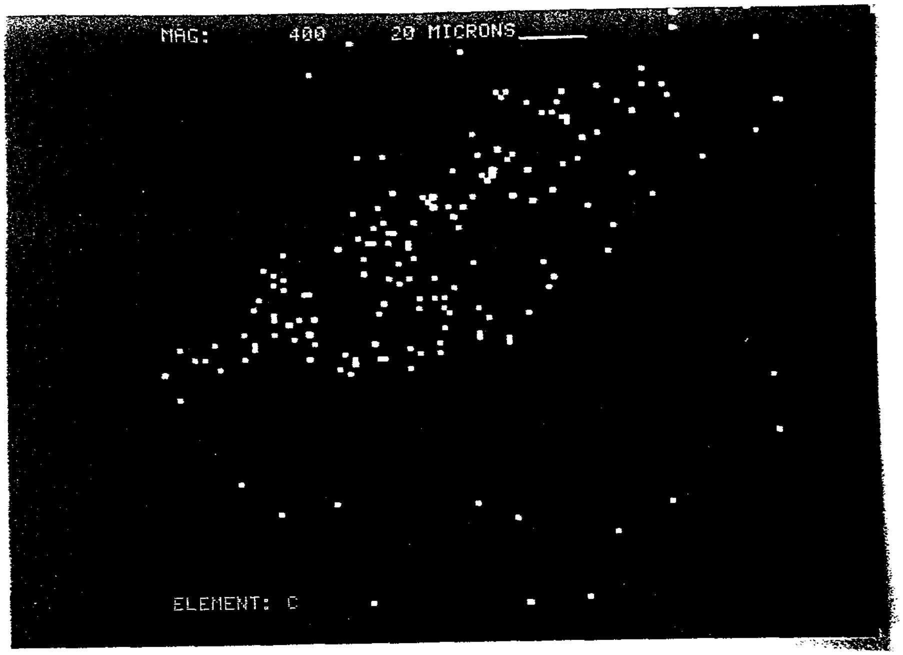

Fig. 6C

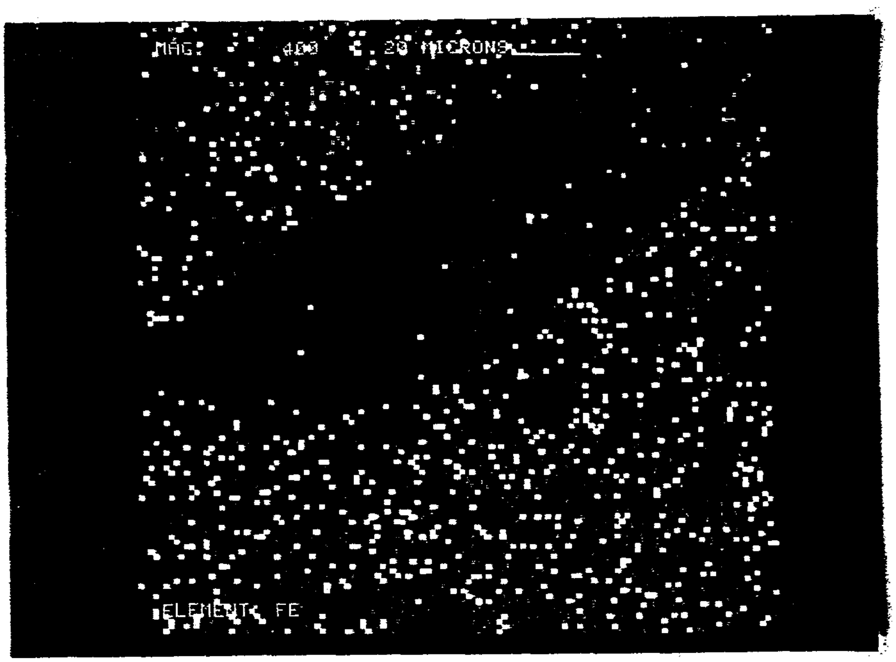

Fig. 6d

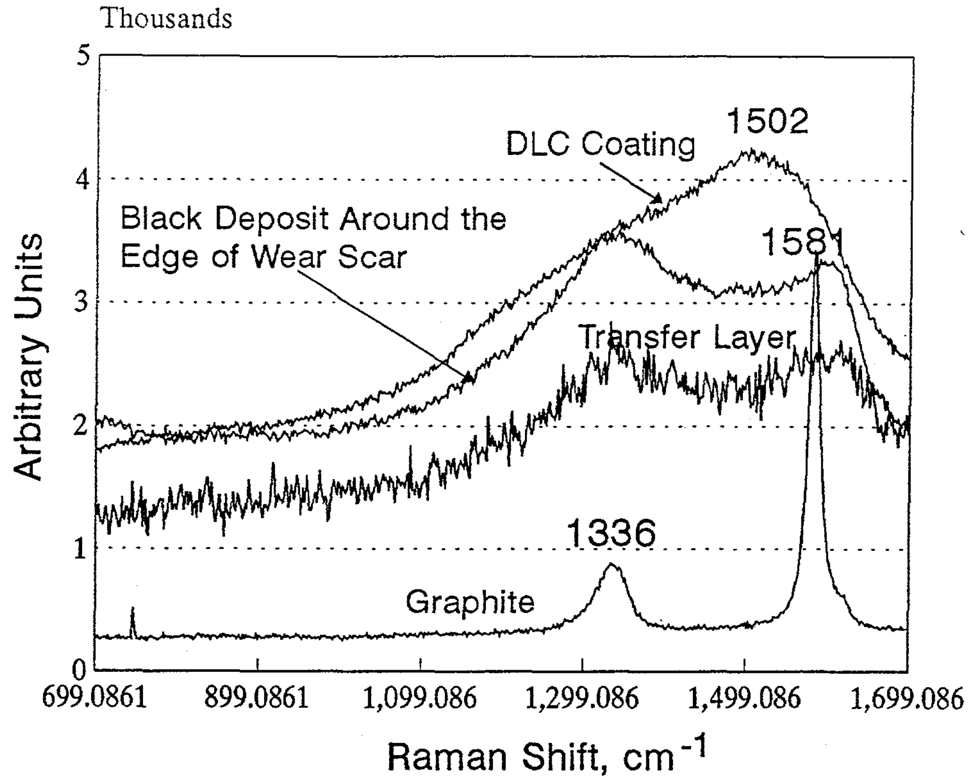
Thousands
5
4
3
2
1
0
Arbitrary Units
DLC Coating
1502
Black Deposit Around the
Edge of Wear Scar
1581
Transfer Layer
1336
Graphite
699.0861
899.0861
1,099.086
1,299.086
1,499.086
1,699.086
Raman Shift, cm-1

Fig. 7