

Paper # 440, Session E5/D4

**SYNTHESIS OF SUPERLOW FRICTON CARBON FILMS FROM HIGHLY
HYDROGENATED METHANE PLASMAS***

A. Erdemir O. L. Eryilmaz, I. B. Nilufer, and G. R. Fenske
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

February 2000

Paper presentation at the International Conference on Metallurgical Coatings and Thin Films,
San April 9-14, 2000, Diego, CA

*Work supported by the U.S. Department of Energy, Office of Science under Contract
W-31-109-Eng-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SYNTHESIS OF SUPERLOW FRICTON CARBON FILMS FROM HIGHLY HYDROGENATED METHANE PLASMAS*

A. Erdemir^a, O. L. Eryilmaz^b, I. B. Nilufer^b, and G. R. Fenske
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

In this study, we investigated the friction and wear performance of diamondlike carbon films (DLC) derived from increasingly hydrogenated methane plasmas. The films were deposited on steel substrates by a plasma-enhanced chemical vapor deposition process at room temperature and the tribological tests were performed in dry nitrogen. Tests results revealed a close correlation between the hydrogen in source gas plasma and the friction and wear coefficients of the DLC films. Specifically, films grown in plasmas with higher hydrogen-to-carbon ratios had much lower friction coefficients and wear rates than did films derived from source gases with lower hydrogen-to-carbon ratios. The lowest friction coefficient (0.003) was achieved with a film derived from 25% methane-75% hydrogen, while a coefficient of 0.015 was found for films derived from pure methane. Similar correlations were observed for wear rates. Films derived from hydrogen-rich plasmas had the least wear, while films derived from pure methane suffered the highest wear. We used a combination of surface analytical methods to characterize the structure and chemistry of the DLC films and worn surfaces.

^a Corresponding author

^b Permanent address: Istanbul Technical University, Materials and Metallurgical Engineering Department, Ayazagi, Istanbul-Turkey.

Key words: DLC, highly-hydrogenated plasmas, super-low friction and wear.

INTRODUCTION

In recent years, there has been overwhelming interest in both the synthesis and diverse utilization of high-quality diamond and diamondlike carbon (DLC) films in a variety of tribological applications. Properties that make DLC very attractive for tribological applications include high mechanical hardness and strength, excellent chemical inertness, and a naturally low friction coefficient. Some of the current and future uses for these films include high-precision bearings, biomedical implants, mechanical seals, hard disks, microelectromechanical systems, gears, metal- and/or plastic-forming dies, etc. [1-4]. Unlike the very popular nitride and carbide coatings (e.g., TiN and TiC) which function more effectively under lubricated conditions, DLC can provide low friction to most sliding surfaces even without any lubrication [5-13]. Furthermore, these coatings can be made significantly harder and stiffer than most metal carbides and nitrides.

At present, DLC films are largely deposited by ion-beam deposition, DC and RF magnetron sputtering, arc-physical vapor deposition (arc-PVD), plasma-enhanced chemical vapor deposition (PECVD), and laser ablation [4,6,14,-16]. The deposition temperature may vary between subzero to 300°C. Depending on the source gas and/or the composition of gas discharge plasma, large amounts of hydrogen may be incorporated within the highly disordered or amorphous microstructure of the DLC films [1,3]. Films with very little or no hydrogen are also available and may be deposited by using laser ablation or arc-PVD methods [6,14].

Recent studies have confirmed that the tribological performance of DLC films is very sensitive to test

conditions. Specifically, it was found that the friction and wear coefficients of these films vary a great deal with test environments or temperatures. Hydrogen free DLC films work best in humid test environments while hydrogenated DLC films provide better performance in dry and inert test environments than in open air [17-20]. At elevated temperatures (i.e., 300°C and above), hydrogenated DLC films may gradually turn into graphite and hence wear out quickly [21]. The presence of certain dopants in the film microstructure (such as silicon, titanium, tungsten) may retard graphitization process and hence extend the durability of DLCs to much elevated temperatures.

In this study, we present a new deposition procedure that can lead to the formation of superlow friction DLC films. Procedure is very simple and essentially based on the creation of an increasingly hydrogenated methane plasma that allows synthesis of super-hydrogenated DLC films affording friction coefficients of 0.003 or less in dry N₂. In earlier studies [22,23], it was shown that regardless of the deposition process, the initial gas composition from which the DLC films were derived, was the most critical factor that affected friction and wear. In this study, we expanded this initial observation and further explored the effects of super hydrogenation on friction and wear of resultant DLC films. We hope that the results of this study will help in further optimization of the source gas compositions and will eventually lead to a much-improved DLC film affording super low friction and wear.

EXPERIMENTAL PROCEDURES

In this study, we used a PECVD method to produce DLC films on polished surfaces of AISI M50 balls and H13 steel substrates. The films were about 1 μm thick and were derived from methane (CH₄) and CH₄ + H₂ source gases. The procedure for forming DLC films on steel substrates by PECVD involved first sputter-cleaning of the substrates in an Ar plasma for 30 min by applying a

1200-1700V bias, then producing a 50 - 70 nm thick silicon bond layer, and finally depositing the film. The bond layer was applied by sputtering silicon from a Si target. In some cases, silane (SiH_4) gas was also used to form the bond layer on steel substrates. For the synthesis of DLC films, the carbon-bearing source gases were bled into the chamber until a gas pressure of 10 and 13 mtorr is attained. The RF bias applied to the specimen stage was 1600 V. Further details of the deposition process can be found in Refs. 22 and 23.

The friction and wear testing of DLC-coated steel substrates was done on a ball-on-disk tribometer. These tests were performed in a dry nitrogen environment under a 10 N load (which created a peak Hertz pressure of 1.04 GPa) and at a sliding velocity of 0.5 m/s for a distance of 5 km. To measure the true friction coefficient of the DLC coating against itself (not against steel), AISI M50 steel balls (9.5 mm in diameter) were also coated with DLC and rubbed against the coated H13 steel substrates. The Vickers hardness of the substrates and balls was ~ 8 GPa and their surface roughness was better than 0.1 μm centerline average (CLA). Each coating was tested twice in dry nitrogen (0% humidity). The test chamber was purged with dry nitrogen for at least two hours after 0% humidity was shown on a hygrometer display unit. Wear volume (W_b) of the steel balls was determined with an optical microscope. Specifically, wear scar diameter and the diameter of the ball were used in the equation: $W_b = 3.14d^4/64r$, where r is the ball radius, d is the diameter of the wear scar, and W_b is the wear volume. To simplify the calculations, we assumed that the wear scar was flat.

EXPERIMENTAL RESULTS

The Raman spectra of the films derived from pure and increasingly hydrogenated CH_4 gas discharge plasmas are shown in Figure 1. They all reveal broad Raman features ranging in positions from 1502 to 1570 cm^{-1} and shouldered features at a range from 1320 to 1350 cm^{-1} . The broad and shouldered

features are somewhat less pronounced on films produced in pure CH_4 plasmas, but the films derived from plasmas that contained higher and higher amounts of H_2 exhibited well defined Raman features shifted to higher wave numbers. Overall, these Raman features were typical of DLC films and were consistent with the Raman spectra presented elsewhere [24,25]. SEM micrograph in Figure 2 shows the structural morphology of a film derived from 25% methane and 75% hydrogen. In general, the films produced in our study were structurally amorphous, free of volume defects, and had very good bonding to their substrates.

Figure 3 summarizes the results of hardness measurements on various DLC films produced in this study. Elastic modulus of each film was also measured and included in this figure. Standard deviations as well as mean values of hardness and elastic modulus of each film are provided in Table 1. It looks that there is a close correlation between mechanical properties (i.e., hardness and elastic modulus) of the films and the composition of gas discharge plasmas from which these films were derived. In general, the higher the amount of hydrogen in gas discharge plasma, the lower the hardness and elastic modulus.

Figure 4 compares the frictional performance of DLC films derived from pure CH_4 and 25% CH_4 + 75% H_2 . The complete results from all the friction and wear tests run on various DLC films are summarized in Table 1. For comparison, the friction coefficients of C_2H_2 - grown and hydrogen-free DLC are also included in this Table. The values shown in Table are based on the average of the steady-state portion of the actual frictional traces shown in Fig. 3 and reflect the means and standard deviations of two to three repeat tests. As is clear from Fig. 4 and Table 1, the friction coefficient of the film grown in pure CH_4 plasma is rather high (i.e., 0.015) but that of the film grown in 25% CH_4 + 75% H_2 is very low (i.e., 0.003 ± 0.0005). The friction coefficient of an uncoated M50 ball against the H13 steel disk in dry nitrogen was ~ 0.8 . A film grown in a 10% CH_4 + 90% H_2 plasma is around

0.004, but its wear rate is the lowest of all.

The wear rates of DLC-coated M50 balls during sliding against DLC-coated H13 disks in dry nitrogen are shown in Table 1. It is interesting to note that these rates show a similar trend to that of the friction results. Specifically, test data show that balls coated with pure methane-grown films suffer the most wear (i.e., $9 \times 10^{-9} \text{ mm}^3/\text{N} \cdot \text{m}$), whereas those balls coated with 25% methane+75% hydrogen-grown films suffer the least wear (i.e., $4.6 \times 10^{-10} \text{ mm}^3/\text{N} \cdot \text{m}$). The wear rate of an uncoated M50 ball against the uncoated H13 disk was $4.6 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$ when tested under the same conditions. The wear rates of balls coated with DLC in CH_4 + increasing amounts of hydrogen were moderate, but still significantly higher than those of the balls coated with DLC in a 25% methane+75% hydrogen plasma. Wear rates of those balls coated with hydrogen free DLC or C_2H_2 -grown DLC were significantly higher than those of the balls coated with DLCs derived from increasingly hydrogenated CH_4 plasmas.

Microscopic examination of sliding contact surfaces of the DLC-coated balls and flats revealed very shallow wear tracks and scars. Some wear debris particles were visible around the edges of the wear scars, but the wear scars themselves were relatively clean and there was no detectable evidence of the presence of a transfer or debris layer on sliding surfaces. Figure 5 shows the typical Raman spectra of wear debris particles found around the edges of the wear tracks.

A long-duration lifetime test was run with a ball and disk pair that was coated with the best DLC film derived from 25% CH_4 + 75% H_2 . The result of this test is shown in Fig. 6. This test was let go for a duration of 32 days during which 17,500,000 sliding passes (translating into more than a 1200 km sliding distance) had elapsed. Test was terminated only because the electrical brushes in DC motor providing sliding motion had burnt. In short, under condition where a superlow friction coefficient was maintained, the films derived from a mixture of 25% CH_4 and 75% H_2 would last for a long time.

DISCUSSION

The extent of friction between two sliding surfaces is generally governed by the physicochemical nature of the microcontact interfaces, contact stresses, and surrounding environment. Low friction on such surfaces is normally achieved by liquid or solid lubrication. The situation with liquid-lubricated surfaces is rather complex and may involve surface reaction films and several intrinsic and extrinsic parameters. However, lubrication by soft metals and lamellar solids is largely attributed to the easy shear characters of these solids. Because of their high mechanical strength and rigidity, diamond and DLC coatings cannot undergo bulk shear, hence similar lubrication mechanisms cannot be used to explain the very low friction nature of these materials.

The extent of interactions between chemical species in surrounding test environments and the sliding contact surfaces of diamond and DLC plays a major role in frictional behavior of diamond and DLC films. It is now generally agreed that the low friction nature of these films are due to the fact that their sliding surfaces are covered by a layer of adsorbed gas molecules (such as hydrogen, oxygen, hydroxyl and other active chemical species), so that they are chemically very inert, hence, cannot exert high adhesive bonding across the sliding interface. Hydrogen is perhaps the most suitable element providing the best passivation and also hydrogen-carbon bonding is perhaps the strongest (stronger than carbon-carbon single bond). In short, these films provide low friction by an interface shear mechanism where pins or balls slide over a chemically passive carbon surface with very little interactions. Micrographitization and formation of transfer layers on sliding surfaces have also been proposed to explain the frictional behavior of certain diamond and DLC films [26-29].

In our study, we found that there is a clear and very close correlation between friction and the source

gas composition used during DLC deposition. Specifically, the higher the amount of H_2 in source gas plasma, the lower the friction coefficient. Clearly, the friction and wear test results in Table 1 suggest that DLC films produced in source gases with higher amounts of hydrogen exhibit superior friction and wear performance. DLC films grown in a 25% CH_4 + 75% H_2 plasma provided the lowest friction coefficient (0.003 at steady-state), whereas films grown in a pure methane provided much higher friction coefficient. The friction coefficients of films grown in increasingly higher amounts of H_2 containing plasma fall between those of the pure CH_4 and 25% CH_4 + 75% H_2 in terms of their frictional characteristics. We attempted to deposit films at much higher H_2 concentrations, but the deposition rate became so low that beyond 90% H_2 , it was not possible to deposit any film. The friction coefficient of a film grown in 10% CH_4 + 90% H_2 was around 0.004. As shown in Figs. 1 and 3, this film exhibited a graphitic Raman spectrum and was also very soft. The hydrogen-free DLC and the DLC grown in pure C_2H_2 exhibited very high friction and short wear lives under the same test conditions. Overall, the DLC films derived from hydrogen rich plasmas provided the best performance.

We believe that the increasingly lower friction coefficients of the DLC films produced in this study are primarily due to the increasingly inert nature of their sliding contact surfaces. The extent of inertness in each film is mainly governed by the amount of hydrogen that was available to passivate the carbon atoms at or near the sliding surfaces. In other words, the films provided the lowest friction were inherently saturated with a species that readily passifies the dangling surface bonds of carbon that can otherwise cause high adhesive interactions and hence friction. Apparently, when the dangling bonds are passivated, the adhesion component of friction is drastically reduced. In fact, the low-friction mechanism of diamond is largely attributed to the highly passive nature of its sliding surface [30-32]. When hydrogen and other species are desorbed or removed from the sliding surfaces of

diamond (e.g., by ion-beam sputtering and/or high-temperature annealing in vacuum), the friction coefficient increases significantly, presumably because the reactivated dangling bonds cause strong adhesive interactions between the diamond and the counterface ball or pin surface [33,34].

The wear resistance of DLC films correlates well with their friction performance. Specifically, films with higher friction coefficients suffer higher wear rates (see Table 1). The difference between wear rates of balls coated with methane + 75%hydrogen-grown DLC and those coated with methane-grown DLC films is more than an order of magnitude (i.e., $9 \times 10^{-9} \text{ mm}^3/\text{N} \cdot \text{m}$ for methane-grown film vs. $4.6 \times 10^{-10} \text{ mm}^3/\text{N} \cdot \text{m}$ for 25%methane + 75% hydrogen-grown film). Also, this film with the lowest friction last more than 17.5 million cycles, suggesting that under conditions where a super low friction coefficient is maintained, these films can last for a very long time. Raman studies of sliding surfaces and debris particles suggested that worn particles had a graphitic nature (Fig. 5). Thus, limited graphitization of sliding surfaces (under the influence of high contact stresses and some frictional heating) may have been responsible for the wear. Similar observations were made on DLC films produced and tested by other investigators [26-29].

The large disparity in the friction and wear performance of films listed in Table 1 may be caused by several factors. The most logical one is that the films produced in a methane plasma are much poorer in hydrogen than films produced in a highly hydrogenated plasma. Briefly, we believe that the excellent friction and wear behavior of films derived from highly hydrogenated plasmas are due to the fact that they contain more hydrogen in their structures than the pure methane-grown films. Briefly, we believe that hydrogen plays an important role in the frictional behavior of DLC films. Films grown in methane + hydrogen plasmas contained more hydrogen in their microstructures than films grown in pure methane, so these films were more saturated with a species that pacifies the dangling bonds of carbon atoms that can otherwise cause high adhesion or friction during sliding.

CONCLUSIONS

From the friction and wear data presented in this study, it is clear that a significant difference exists in the tribological properties of DLC films derived from methane and methane + hydrogen plasmas. The methane-produced DLC films exhibited significantly higher friction coefficients and wear rates (except for the film produced in 50% methane + 50% hydrogen) than the films produced in methane + hydrogen plasmas. We think that these differences in friction and wear are most likely due to the much higher hydrogen to carbon ratios in the source gases from which the DLC films were derived. It is logical that the films produced in highly hydrogenated plasmas contained higher amounts of hydrogen in their structures, and thus further confirming that hydrogen plays an important role in the friction and wear performance of DLC films.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38.

REFERENCES

1. B. Bhushan, *Diam. Rel. Mater.*, 8 (1999)985.
2. A. Grill, *Surf. Coat. Technol.* 94/95(1997)507.
3. A. Matthews and S. S. Eskildsen, *Diamond and Rel. Mat.* 3(1994)902.
4. S. Neuville and A. Matthews, *MRS Bull.*, 22 (9)1(997) 22
5. K. Miyoshi, J. J. Pouch, and S. A. Alterovitz, *Mater. Sci. Forum*, 52/53 (1989)645.
6. A. A. Voevodin, M. S. Donley, and J. S. Zabinski, *Surf. Coat. Technol.*, 92(1997)42.
7. H. Ronkainen, J. Koskinen, A. Anttila, K. Holmberg, and J.-P Hirvinen, *Diamond and Rel. Mat.*, 1(1992)639.
8. H. Dimgen and C. P. Klages, *Surf. Coat. Technol.*, 49(1991)543.

9. S. J. Harris, A. M. Weiner, and W.-J. Meng, *Wear*, 211(1997)208.
10. A. K. Gangopadhyay, P. A. Wolernmet, M. A. Tamor, and W. C. Wassell, *Tribol. Int.*, 30(1997)9.
11. A. Erdemir, M. Switala, R. Wei, and P. Wilbur, *Surf. Coat. Technol.*, 50(1991)17.
12. C. Donnet and A. Grill, *Surf. Coat. Technol.*, 94-95(1997)456.
13. A. Erdemir, C. Bindal, G. R. Fenske, P. Wilbur, *Tribol. Trans.*, 39(1996)735.
14. J. J. Cuomo, J. P. Doyle, J. Bruley, and J. C. Liu, *Appl. Phys. Lett.*, 58(1991)1.
15. R. Wei, P. J. Wilbur, A. Erdemir, F. M. Kustas, *Surf. Coat. Technol.*, 51(1992)139
16. T. Michler, M. Grishke, I. Traus, K. Bewilogua, H. Dimigen, *Diam. Relat. Mater.*, 7(1998)459.
17. C. Donnet, M. Belin, J. C. Martin, J. M. Martin, A. Grill, and V. Patel, *Surf. Coat. Technol.*, 68-69(1994)626.
18. C. Donnet, T. Le Mogne, L. Ponsonnet, M. Belin, A. Grill, V. Patel, *Tribology Letters*, 4 (1998) 259 - 265.
19. D. S. Kim, T. E. Fischer, and B. Gallois, *Surf. Coat. Technol.*, 49(1991)537.
20. K. Holmberg, J. Koskinen, H. Ronkainen, J. Vihersalo, J. P. Hirvonen, and J. Likonen, *Diamond Films and Technol.*, 4(1994)113.
21. A. Erdemir and G. R. Fenske, *Tribol. Trans.*, 39 (1996) 787.
22. A. Erdemir, G. R. Fenske, J. Terry, P. Wilbur, *Surf. Coat. Technol.*, 94-95(1997)525.
23. A. Erdemir, I. B. Nilufer, O. L. Eryilmaz, M. Beschliesser, and G. R. Fenske, *Surf. Coat. Technol.*, 121(1999).589.
24. D. S. Knight and W. B. White, *J. Mater. Res.*, 4 (1989) 385.
25. J. Robertson, *Advan. Phys.*, 35 (1986) 317.
26. Y. Liu, A. Erdemir, and E. I. Meletis, *Surf. Coat. Technol.*, 82 (1996) 48-56.
27. Y. Liu, A. Erdemir, and E. I. Meletis, *Surf. Coat. Technol.*, 86/87(1996)564.
28. A. Erdemir, C. Bindal, and C. Zuiker, *Surf. Coat. Technol.*, 86/87(1996)692.
29. A. Erdemir, F. A. Nichols, X. Z. Pan, R. Wei, and P. Wilbur, *Diamond and Rel. Mat.*, 3 (1993) 119.
30. S. V. Pepper, *J. Vac. Sci. Technol.*, 20 (1982) 643.
31. F. P. Bowden and J. E. Young, *Proc. Roy. Soc., London*, 208 (1951) 444.
32. F. P. Bowden and A. E. Hanwell, *Proc. Roy. Soc., London*, A295 (1966) 233.
33. D. Dugger, E. Peebles, and L. E. Pope, in *Surface Science Investigations in Tribology, Experimental Approaches*, Eds. Chung, Y.-W., Homolo, A. M., and Street, G. B., ACS Symposium Series 485, pp. 72-102, American Chemical Society, Washington D.C. (1992),
34. M. N. Gardos and B. L. Soriano, *J. Mater. Res.*, 5 (1990) 2599.

Table 1. Effect of plasma gas composition on steady-state friction coefficients and wear rates of resultant DLC films. Test conditions: Load: 10 N, Speed, 0.5 m/s; Temperature, 22-23°C; test environment: dry N₂.

Carbon Films Grown in	Friction Coefficients	Ball Wear Rates (mm ³ /N.m)	Hardness (GPa)	Elastic Modulus (GPa)
100% CH ₄	0.015 ±0.002	9.0x10 ⁻⁰⁹ ±2.1x10 ⁻⁹	20.82±1.13	122 ±3.4
25% H ₂ + 75% CH ₄	0.01 ±0.001	7.36x10 ⁻⁰⁹ ±1.8x10 ⁻⁹	17.1 ±0.66	96.6 ±2
50% H ₂ + 50% CH ₄	0.004 ±0.002	1.23x10 ⁻⁰⁸ ±0.5x10 ⁻⁸	15.7 ±0.45	85.9 ±1.5
75% H ₂ + 25% CH ₄	0.003 ±0.0005	4.60x10 ⁻¹⁰ ±1.5x10 ⁻¹⁰	14.0 ±0.33	60.6 ±0.9
90% H ₂ + 10% CH ₄	0.004 ±0.001	2.8x10 ⁻¹⁰ ±1.2x10 ⁻¹⁰	7.66 ±0.18	47.2 ±0.78
100% C ₂ H ₂	0.27	7.5X10 ⁻⁷	30.1 ±0.77	200.5 ±2.9
Hydrogen Free DLC	0.65 (0.25*)	2.8x10 ⁻⁷	-	-

* The friction coefficient was very erratic and high (fluctuating between 0.6 and 0.7) until the coating was worn out on the ball side, then decreased to values between 0.2 and 0.3 while sliding against the coating on the disk side.

FIGURE CAPTIONS

Figure 1. Raman spectra of DLC films derived from increasingly hydrogenated CH_4 gas discharge plasmas.

Figure 2. SEM cross-sectional photomicrograph of a DLC film derived from 25% CH_4 + 75% H_2 .

Figure 3. Variation of hardness and elastic modulus of DLC films with hydrogen in plasma.

Figure 4. Friction coefficients of DLC films derived from pure CH_4 and 25% CH_4 + 75% H_2 gas discharge plasmas.

Figure 5. Raman spectroscopy of wear debris particles found around the edges of wear scars and tracks.

Figure 6. Long-duration friction and wear performance of a DLC film derived from 25% CH_4 + 75% H_2 plasma.

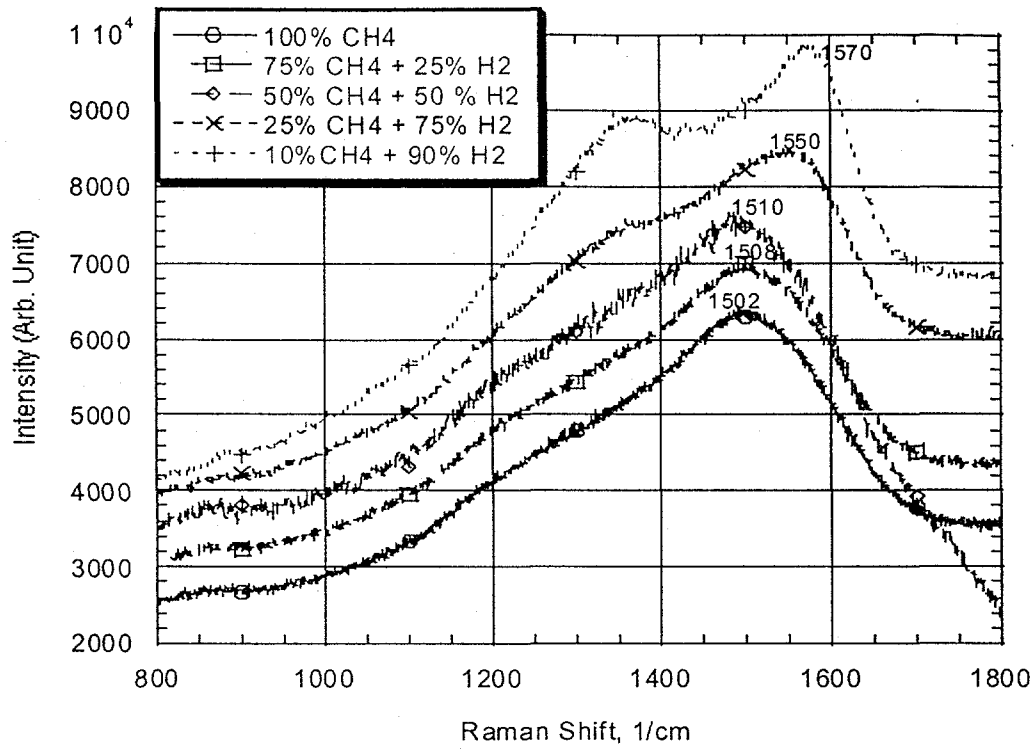


Fig. 1

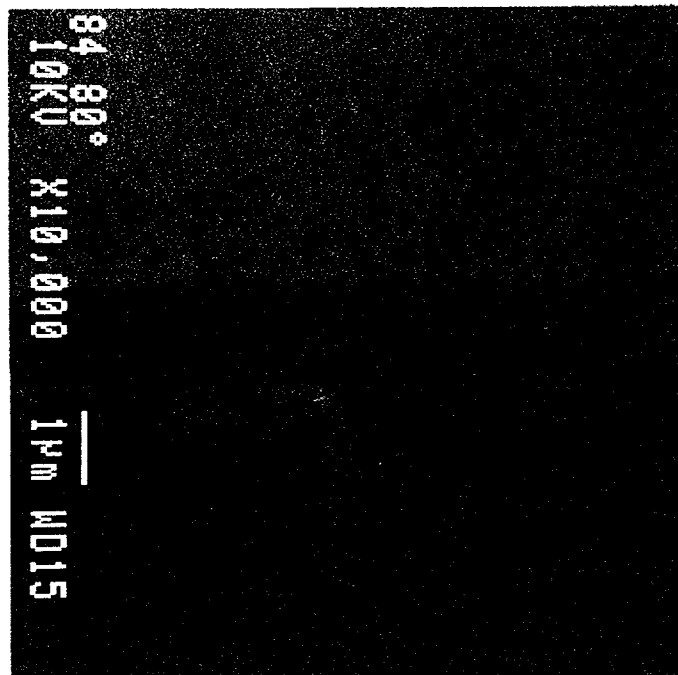


Fig. 2.

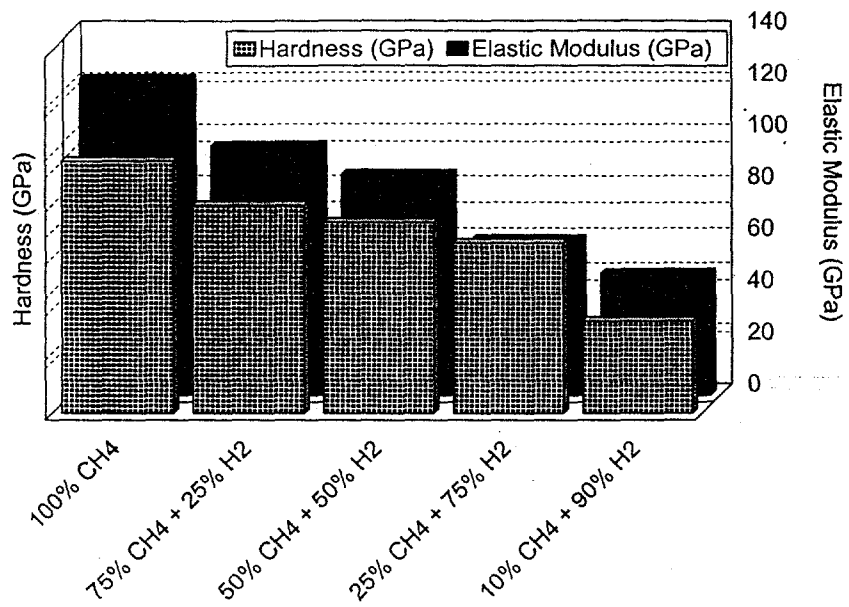


Fig. 3

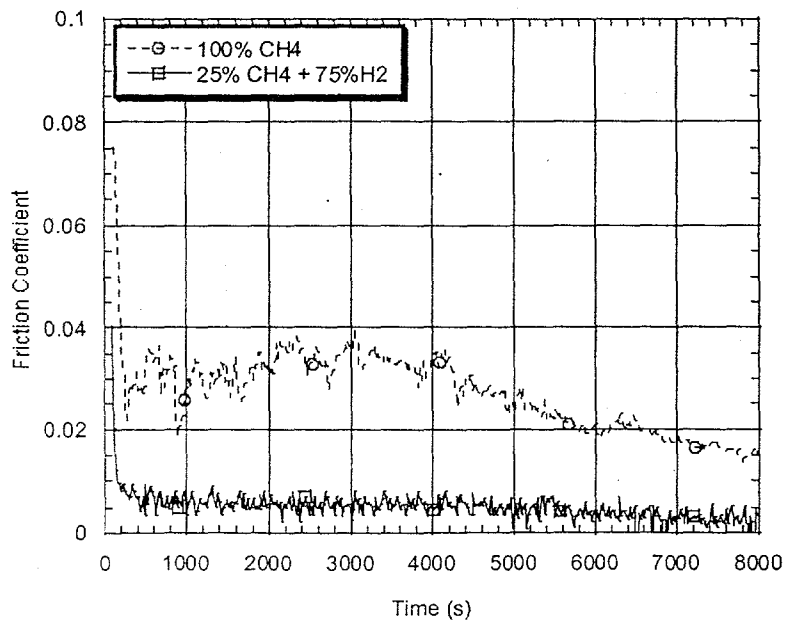


Fig. 4

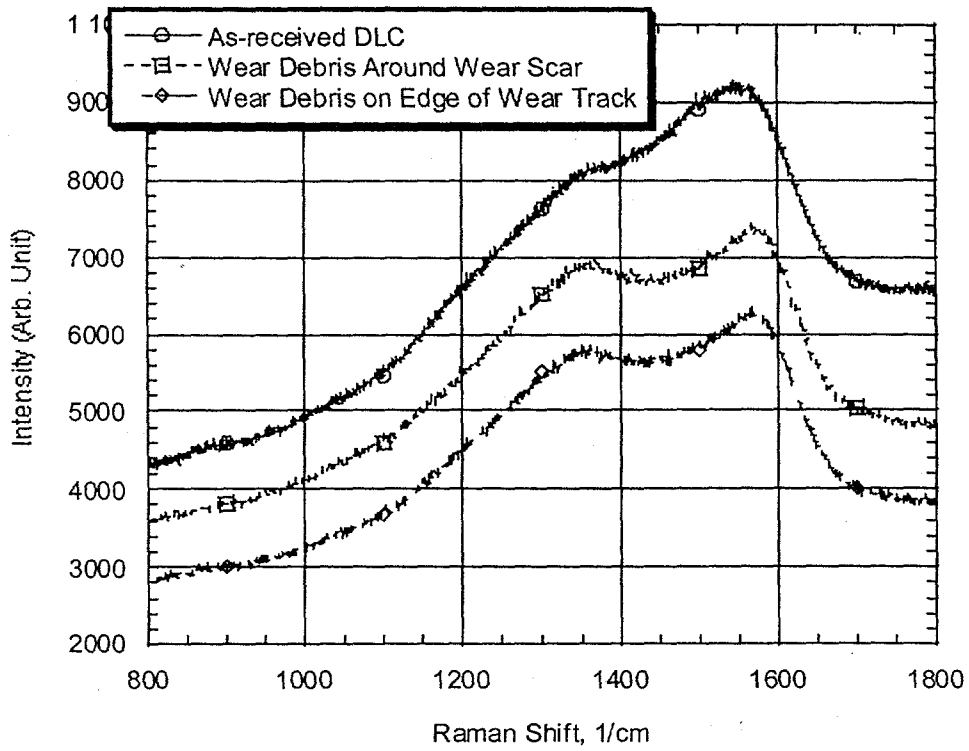


Fig. 5

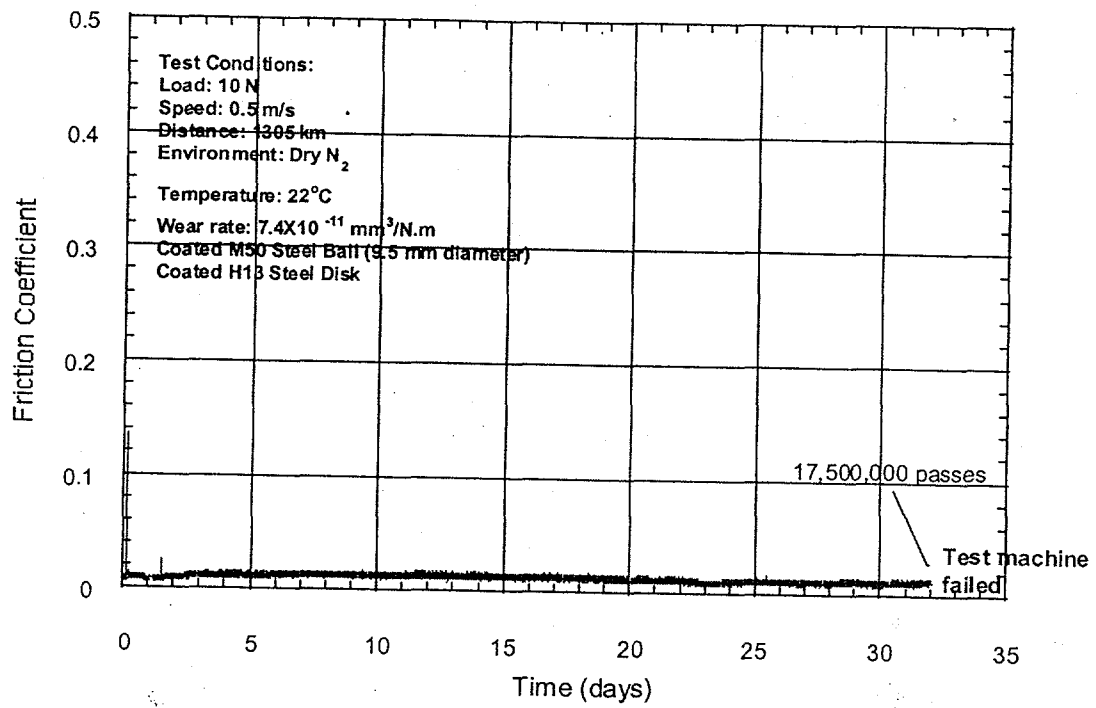


Fig.6