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EFFECT OF SOURCE GAS CHEMISTRY ON TRIBOLOGICAL PERFORMANCE OF DIAMOND-LIKE CARBON FILMS*

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ABSTRACT

In this study, we investigated the effects of various source gases (i.e., methane, ethane, ethylene, acetylene and methane + hydrogen) on friction and wear performance of diamond-like carbon (DLC) films. Specifically, we described the anomalous nature and fundamental friction and wear mechanisms of DLC films derived from gas discharge plasmas with very low to very high hydrogen content. 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. The results of tribological tests revealed a close correlation between the friction and wear coefficients of the DLC films and the source gas chemistry. Specifically, films grown in source gases with higher hydrogen-to-carbon ratios had much lower friction coefficients and wear rates than the films derived from source gases with lower hydrogen-to-carbon ratios. The lowest friction coefficient (0.002) was achieved with a film derived from 25% methane - 75% hydrogen while the films derived from acetylene had a coefficient of 0.15. Similar correlations were observed on wear rates. Specifically, the films derived from hydrogen rich plasmas had the least wear while the films derived from pure acetylene suffered the highest wear. We used a combination of scanning and transmission electron microscopy and Raman spectroscopy to characterize the structural chemistry of the resultant DLC films.

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Key Words: diamondlike carbon, source gas chemistry, friction, wear.

INTRODUCTION

Diamondlike carbon (DLC) films represent a class of amorphous materials that combine high mechanical hardness and strength with exceptional tribological properties. They can afford both low friction and high wear resistance to sliding surfaces even without the use of any additional lubricants, thus are ideal for a wide range of tribological applications (such as, high-precision bearings, biomedical implants, mechanical seals, hard disks, microelectromechanical systems, molds, etc.) [1-3]. DLC films can be deposited at fairly low temperatures and at high deposition rates by a variety of methods, including ion-beam deposition, plasma source ion implantation, DC and RF magnetron sputtering, arc-physical vapor deposition (arc-PVD), plasma-enhanced chemical vapor deposition (PECVD), and laser ablation [4-10]. These films can be made highly hydrogenated (containing up to 50 at.% hydrogen) or essentially hydrogen free (i.e., less than 1% hydrogen) using appropriate deposition methods and/or carbon sources [1,3, 9,11]. They can also be doped by a variety of elements (e.g., nitrogen, fluorine, oxygen, silicon, tungsten, titanium, and niobium) to achieve better performance for specific applications [3,12-14].

The reported tribological data on DLC films differ substantially from one study to another. This is mainly due to the fact that the microstructure and chemistry of these films may vary substantially depending on the deposition conditions and source gases used. In general, it has been found that the tribological properties of these films are very sensitive to test conditions (such as environment, sliding speed, temperature, etc.) [13-19]. The presence of some dopants (e.g., silicon) in the structures of DLC films appears to make these films less sensitive to humidity [13]. The tribological performance of hydrogen-free DLC films is better in moist air, but hydrogenated DLCs provide much lower friction and wear in dry and inert test environments [18-23]. Most DLC films undergo permanent chemical and microstructural changes at high temperatures, and hence their friction and wear behavior degrades and their lifetimes shorten [17,24]. For example, above 300°C, hyrogenated DLC films graphitize and begin to wear out quickly [24]. Use of dopants (i.e., silicon, titanium, tungsten, boron) may retard the graphitization process and hence improve the durability of DLC films at elevated temperatures.

In this study, we explore the effects of various source gases on the friction and wear performance of DLC films produced in a plasma enhanced chemical vapor deposition (PECVD) system. We hope that the results of this study will lead to a better understanding of the effect of source gas composition on friction and wear and hence will enable the synthesis of novel DLC films with much-improved friction and wear performance.

EXPERIMENTAL PROCEDURES

In this study, we used a PECVD method to deposit DLC films on the polished surfaces of AISI M50 balls and H13 steel substrates. The films were about 1 μm thick and were derived from pure methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), ethylene (C_2H_4), and CH_4 + hydrogen (H_2) gases. Note that the hydrogen-to-carbon (H/C) ratio for the pure source gases is between 1 (for C_2H_2) and 4 (for CH_4). For hydrogen rich CH_4 plasmas, the H/C ratio will be much higher.

The procedure for forming DLC films on steel substrates by PECVD involved sputter-cleaning of the substrates in an Ar plasma for 30 min by applying a 1200-1700V bias. The substrates were then coated with a 50 - 70 nm thick silicon bond layer by switching to a sputtering mode and sputtering silicon from a target. In some cases, silane (SiH_4) gas was also used to form a bond layer on steel substrates. Finally, carbon-bearing source gases were bled into the chamber and the deposition of DLC on the substrates was started. The gas pressure varied between 10 and 13 mtorr and the RF bias was maintained at 1600 V. Further details of the deposition process can be found in Ref. 25.

The friction and wear testing of DLC coated samples were carried out in a ball-on-disk tribometer, in a dry nitrogen environment under a 10 N load (which created a peak Hertz pressure of 1.04 GPa) and at a velocity of 0.5 m/s for a distance of 5 km. To measure the true friction coefficients of the DLC films, coated AISI M50 steel balls (9.5 mm in diameter) were rubbed against the coated H13 steel disks. The Vickers hardness of the substrates and balls was ~8 GPa and their surface roughness was better than 0.05 μm centerline average (CLA). Each coating was tested twice in dry nitrogen (0% humidity) and the average friction and wear values were reported in appropriate charts. 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 various source gases revealed broad peaks centered at ~1560 cm^{-1} and shouldered peaks at ~1350 cm^{-1}. The shouldered peaks were somewhat less pronounced on films produced in pure gas plasmas. In general, the films produced in this study displayed Raman features typical of DLC films and were consistent with the Raman spectra presented elsewhere [1,26,27]. SEM and TEM micrographs in Figure 1 show the structural morphology of a film derived from 25% CH_4 and 75% H_2. The structural morphology of other films was essentially similar to that shown in these figures. Based on the features displayed in both micrographs, it can be concluded that these films are structurally amorphous, free of volume defects, and have good bonding to their substrates.

Figure 2 shows the friction and wear performance of DLC films derived from pure source gases (i.e., CH_4, C_2H_2, C_2H_6, and C_2H_4). The friction values in this figure are based on the average of the steady-state portion of the actual friction traces. As is clear, the friction coefficient of the films grown in pure C_2H_2 plasma was the highest and the friction trace of this test pair was also very erratic and unsteady. Other DLC films grown in CH_4, C_2H_6, and C_2H_4 exhibited much lower friction coefficients at steady states (i.e., 0.015, 0.04, and 0.08, respectively). Note that one major difference in these source gases is the ratio between hydrogen and carbon. The H/C ratio is one for C_2H_2 and 4 for CH_4. The friction trace of the CH_4-grown film was the smoothest of all. When tested under the same conditions, the friction coefficient of an uncoated M50 ball against the uncoated H13 steel disk was ~0.8.

The wear rates of DLC-coated M50 balls during sliding against DLC-coated H13 disks in dry nitrogen follow a similar trend to that of the friction results as shown in Fig. 2. Specifically, test data show that balls coated with C_2H_2-grown films suffer the most wear (i.e., 7.5×10^{-7} $mm^3/N.m$), whereas those balls coated with CH_4-grown films suffer the least amount of wear (i.e., 9×10^{-9} $mm^3/N.m$). The wear rate of an uncoated M50 ball against the uncoated H13 disk under the same test condition was 4.6×10^{-6} $mm^3/N.m$. The wear rates of balls coated with C_2H_6 and C_2H_4 grown DLC films were moderate, but still significantly higher than those of the balls coated with a CH_4-grown DLC film.

The results in Fig. 2 reveal a close correlation between H/C ratio of source gases and tribological performance. In general, the higher the ratio the better the friction and wear performance. In an effort to further demonstrate the beneficial effect of hydrogen on the friction and wear behavior of DLC films, we ran a series of sliding tests on films that were grown in gas discharge plasmas that consisted of pure CH_4, 75% CH_4 + 25% H_2, 50% CH_4 + 50% H_2, and 75% CH_4 and 25% H_2. Figure 3 summarizes the results of these tests. It is clear that the close correlation between C/H ratio and tribological performance becomes even more pronounced when the DLC films are grown in H_2 rich gas discharge plasmas. Specifically, the higher the amount of H_2 in the gas discharge plasma the lower the friction coefficient of the resultant films. Note that the friction coefficient of the film grown in pure CH_4 plasma is the highest (i.e., 0.015) in Fig. 3 and that of the film grown in 25% CH_4 + 75% H_2 is the lowest (i.e., 0.002). Figure 4 compares the actual friction coefficient traces of the CH_4 grown film with that of a

50% CH_4 +50% H_2-grown film. As is clear, the DLC films grown in 50% CH_4 + 50% H_2 exhibits much lower friction coefficients at steady states than the film grown in pure CH_4. The frictional trace of the film grown in 50% CH_4+50% H_2 grown film is much smoother than that of the pure CH_4-grown film.

The wear rates of DLC-coated M50 balls during sliding against DLC-coated H13 disks in dry nitrogen are shown in Fig. 3. Except for the film grown in 50%CH_4 + 50%H_2, these rates show a similar trend to that of the friction results presented in the same Fig. Specifically, test data show that balls coated with pure CH_4-grown films suffer the most wear (i.e., 9 x 10^{-9} $mm^3/N.m$), whereas those balls coated with 25%CH_4 + 75% H_2 -grown films suffer the least wear (i.e., 4.6 x 10^{-10} mm^3/Nm). Again, the wear rate of an uncoated M50 ball against the uncoated H13 disk was 4.6 x 10^{-6} mm^3/Nm when tested under the same conditions.

DISCUSSION

In general, DLC films are known for their high hardness and mechanical strength which are thought to be essential for their high wear resistance and durability. However, the results of our study indicate that high hardness alone will not insure high wear resistance or long wear life; low friction is also needed. The C_2H_2 grown films of this study had the highest hardness (i.e., 30 GPa) but exhibited the poorest wear performance. Whereas, the films grown in pure CH_4 and 25% CH_4 + 75% H_2 plasmas had hardness values of 20.8 and 14 GPa, respectively; but the wear rates of these two films were two to three orders of magnitude lower than that of the films grown in pure C_2H_2 (see Figs. 2 and 3). The most striking difference between these films is their friction coefficients and the source gases from which they were derived. Specifically, the films grown in C_2H_2, CH_4 and 25% CH_4 + 75% had corresponding friction coefficients of 0.15, 0.015, and 0.002. In short, it looks that lower friction in DLC films results in lower wear, higher hardness alone cannot assure better wear resistance or durability.

The results of this study further confirmed that DLC films were self-lubricating and able to provide very low friction coefficients to sliding surfaces. However, the most striking finding was that the DLC films produced in highly hydrogenated plasmas attained super low friction coefficients (i.e., 0.002 for films grown in 25% CH_4 and 75% H_2). The films grown in pure C_2H_2 and CH_4 had friction values of 0.15 and 0.015, respectively. In the past, several mechanisms were proposed to explain the generally low friction nature of DLC and diamond films. It has been speculated that these films are chemically inert, hence, they exert very little adhesive force during sliding against other materials and thus provide low friction. Other mechanisms, such as micrographitization [28-30] and formation of transfer layers [19,22,31] on mating surfaces, have also been proposed to explain the low friction nature of DLC films.

From a tribological standpoint, one can argue that the extent of friction between two sliding surfaces is largely governed the physical condition of the contacting interface and the extent of chemical interactions between the sliding interfaces and with surrounding environment. Physically, rougher surfaces can create higher ploughing, and hence higher friction, whereas chemical interactions between two sliding surfaces control the extent of adhesive bonding across their interface. In short, making and breaking of chemical bonds at the sliding interfaces determine the extent of friction. In our study, the most apparent difference between films that exhibited dramatic difference in friction and wear performance was the difference in the amounts of hydrogen in the source gases. The test results in Figs. 2 and 3 suggest that the DLC films produced in source gases with higher amounts of hydrogen exhibit superior friction and wear performance. Specifically, it is clear that DLC films grown in a 25% methane+75% hydrogen plasma provided the lowest friction coefficient (0.002 at steady-state), whereas films grown in a pure acetylene plasma provided the highest friction coefficient (see Figs. 2 and 3). The films grown in increasingly higher amounts of hydrogen containing plasma fell between acetylene- and methane+75% hydrogen in terms of their frictional characteristics (Figs. 2 and 3). These observations suggests that hydrogen is essential for achieving low friction and high wear resistance on DLC films.

It is know that hydrogen can easily attach and passivate the dangling surface bonds of carbon atoms in diamond and related materials [32-35]. Apparently, when the dangling surface bonds are passivated, the adhesion component of friction is drastically reduced. In fact, the low-friction mechanism of diamond in ambient air is largely attributed to the highly passive nature of its sliding surface [33-35]. When hydrogen is desorbed or removed from the sliding surfaces of DLC films or 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 carbon atoms and the counterface materials [33-37].

In short, we believe that hydrogen plays a key role in the extent of chemical interactions and hence friction of the DLC films. Films grown in hydrogen rich plasmas are more likely to contain more hydrogen in their microstructures than the films grown in pure C_2H_2 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

The friction and wear results presented in this study demonstrate that a significant difference exists in the tribological properties of DLC films derived from different source gases. The C_2H_2 grown DLC films exhibited the highest friction coefficients and wear rates. Among the pure source gases, the films produced in CH_4 plasmas exhibited the best friction and wear performance. The performance of films of C_2H_6 and C_2H_4 fell between C_2H_2 and CH_4. The best friction and wear performance was afforded by the films grown in hydrogen rich CH_4 plasmas. We propose that these differences in friction and wear are due to the difference in hydrogen contents the gas discharge plasmas 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 strucutures, and thus they were chemically more passive and unable to establish strong bonds across the sliding interface.

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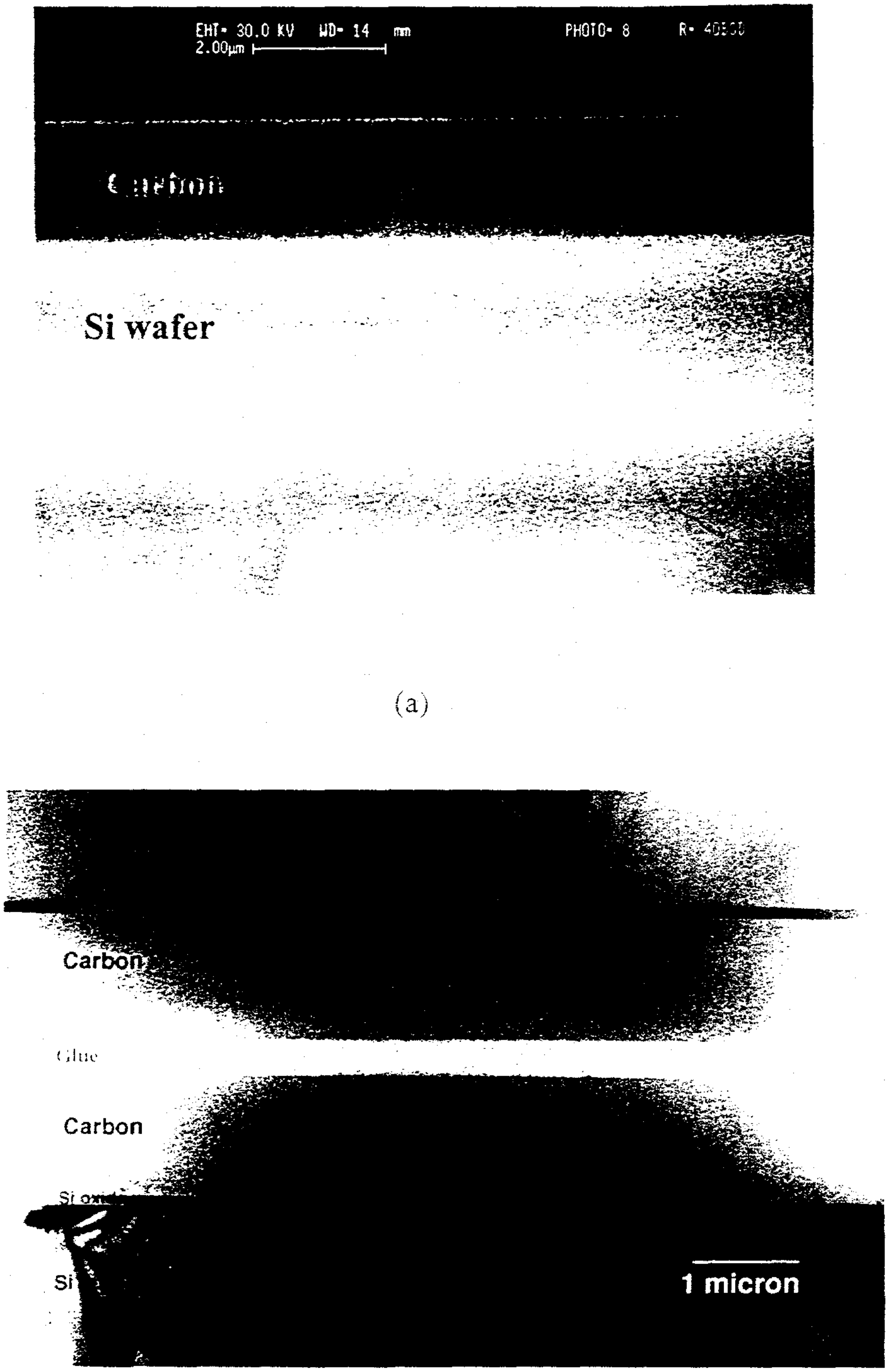
FIGURE CAPTIONS

Figure 1. (a) SEM and (b) TEM cross-section micrographs of a DLC film produced in a 25% CH_4 +75% H_2 plasma.

Figure 2. Friction and wear performance of DLC-coated M50 balls sliding against DLC-coated H13 steel disks in dry nitrogen.

Fig. 3. Friction and wear performance of DLC films grown in pure CH_4 and hydrogen rich CH_4 plasmas.

Fig. 4. Comparison of the friction coefficients of DLC films derived from pure CH_4 and 50% CH_4 + 50% H_2 plasmas.


EHT= 30.0 KV WD= 14 mm
2.00µm
PHOTO= 8
Carbon
Si wafer
Carbon
Glue
Carbon
Si oxide
Si
1 micron

(a)

(b)

Fig. 1

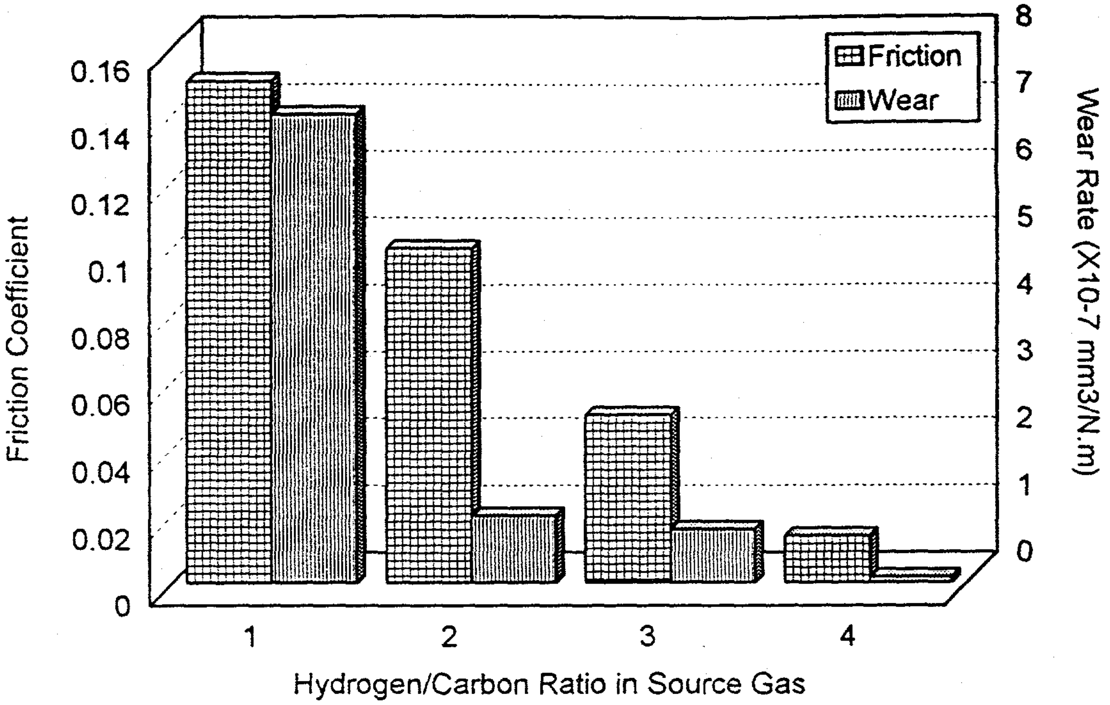

Friction
Wear
Friction Coefficient
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Wear Rate (X10-7 mm3/N.m)
8
7
6
5
4
3
2
1
0
1
2
3
4
Hydrogen/Carbon Ratio in Source Gas

Fig. 2

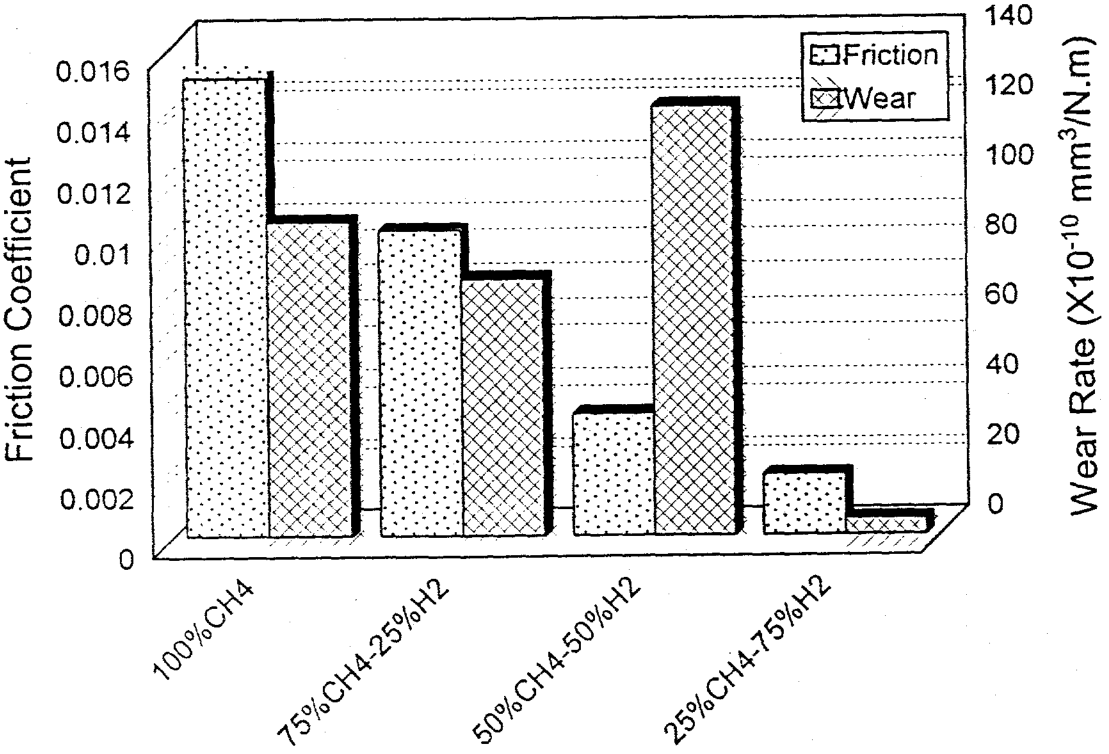

Friction
Wear
Friction Coefficient
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Wear Rate (X10-10 mm3/N.m)
140
120
100
80
60
40
20
0
100%CH4
75%CH4-25%H2
50%CH4-50%H2
25%CH4-75%H2

Fig. 3

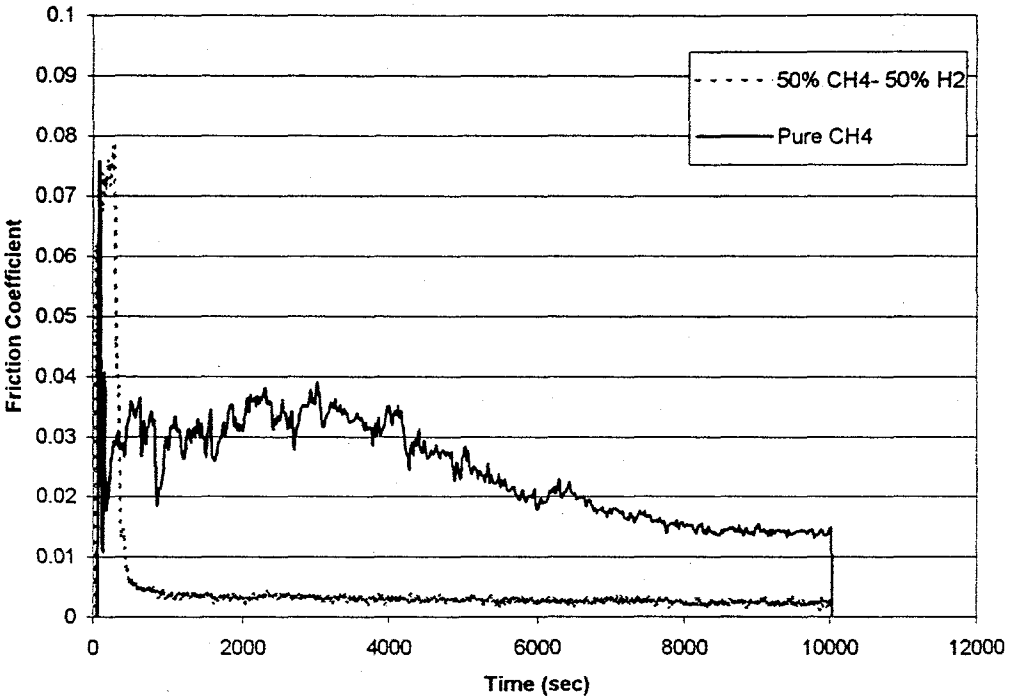

0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Friction Coefficient
0
2000
4000
6000
8000
10000
12000
Time (sec)
50% CH4- 50% H2
Pure CH4

Fig. 4