Lubricating coating prepared by PIIID on a forming tool

J F Martinatti[1], **L V Santos**[2], **S F Durrant**[1], **N C Cruz**[1] **and E C Rangel**[1]

[1]Paulista State University, Av. Três de Março, 511, 18087-180, Sorocaba, SP, Brazil
[2]Technological Institute of Aeronautics, São José dos Campos, SP, Brazil

E-mail: elidiane@sorocaba.unesp.br

Abstract. In this work, the performance of a-C:H films produced by the hybrid Plasma Immersion Ion Implantation and Deposition technique as lubricating layers for a steel forming tool has been investigated. Hardened steel (AISI M2, 64 HRC) plates coated with a commercial TiN layer were used as substrates and the films were deposited in a vacuum chamber fitted with two parallel-plate electrodes. The discharges were generated in atmospheres composed of 91% C_2H_2 and 9% Ar by the application of radiofrequency power (13.56 MHz, 100 W) to the upper electrode while the lower one, also used as the sample holder, was biased with high voltage negative pulses (3.6 kV, 30 μs, 300 Hz). A deposition time of 840 s was used. The effects of the gas pressure, p, on thickness, molecular structure, wettability, surface morphology and topography, hardness and friction coefficient of the films were investigated. Film thickness increased from 0.3 to 0.5 μm when p was increased from 2.7 to 16.5 Pa. Generally, the films were slightly hydrophilic, with contact angles of around 84°, and the deposition decreased the roughness of the steel. A polymer-like structure was detected in high pressure depositions and an amorphous carbon structure derived from the low pressure procedures. Hardness decreased from 8.2 to 7.0 GPa with increasing p. Improvement in tribological performance was indicated by the fall in the friction coefficient from 0.5 to 0.2 as the deposition pressure was reduced. Operating at the latter value (of μ) would lead to a significant reduction in wear and hence to significant economy in diverse industrial applications.

1. Introduction

Hydrogenated amorphous carbon films, a-C:H, are part of a class of organic materials with very attractive properties such as high hardness, optical transparency and low coefficient of friction. The characteristics of the a-C:H films are strongly dependent on chemical composition and the proportion of sp^3 hybridized carbon atoms. That is, the higher the fraction of tetrahedrally bonded carbon of sp^3 atoms the higher the mechanical resistance of such materials, whose hardness can reach values close to that of diamond. It is well known that the formation of sp^3 groups during the deposition is enhanced when the film grows under ion bombardment [1]. More specifically, when the energy per deposited carbon ion is around 150 eV, the energy transferred by the ion impact promotes the breakage of sp^2 bonds and enhances the formation of sp^3 groups. Therefore, by controlling the energy of the ions it is possible to modify the microstructure of the bombarded material. On the other hand, the higher the fraction of sp^3 bonds, the higher the internal stress, which may limit the physical stability of the material. When the forces associated with the internal stress overcome the cohesive forces between film and substrate, the coating peels off. Although a-C:H coatings show great potential in applications, these are still limited by high levels of internal stress [2]. Specific investigations have to be conducted

for each particular application to adjust the levels of internal stress (for each particular substrate) to provide good coating adhesion without deleterious effects on the desirable properties.

In this context, Plasma Immersion Ion Implantation and Deposition (PIIID) [3] is a very convenient technique. Similarly to the conventional Plasma Enhanced Chemical Vapor (PECVD) process [4,5], the deposition is enhanced by the plasma. In PIIID experiments, however, the substrate holder is biased with high voltage negative pulses which accelerate the positive ions towards the sample. Plasma immersion ion implantation and deposition is an environmentally friendly and cost effective technique that is able to eradicate the need for intermediary layers to improve the physical stability of the stressed a-C:H films.

Aiming at the improvement of physical resistance and the reduction of the friction coefficient, a-C:H films have been deposited by PIIID on AISI M2 and TiN coated AISI M2 steel forming tools. The influence of the plasma pressure on chemical composition, roughness, hardness, friction coefficient, morphology and topography of the coated tools has been studied.

2. Experiment

Heat treated AISI M2 steel samples with and without a 9 μm- thick TiN top layer were obtained from forming tools used in the automotive part stamping process. Prior to the depositions the samples not coated by the TiN film were mirror polished and all the samples were sonicated in detergent, distilled water and isopropyl alcohol baths and then dried using a hot air gun. The samples were further cleaned by the exposure for 600 s to plasmas generated in atmospheres composed of 50% Ar and 50% H_2 at a total pressure of 4.1 Pa. The plasmas were excited by the application of radiofrequency power (13.56 MHz, 150 W) to two parallel plate electrodes fitted inside a cylindrical stainless steel vacuum chamber fully described elsewhere [6]. After the cleaning procedure, without exposing the samples to air, the atmosphere was changed to 91% C_2H_2 and 9% Ar for PIIID experiments. In all the experiments, the background pressure was 2.8 Pa while the total pressure owing to the gas feed ranged from 2.7 to 16.5 Pa. The radiofrequency power was kept at 100 W and for ion implantation the substrates were biased with -3600 V pulses at a repetition rate of 300 Hz and pulse length of 30 μs. The chemical composition of the films has been investigated by Infrared Reflectance Absorbance Spectroscopy (IRRAS) using a Jasco FTIR-410 spectrometer. The thickness and the roughness of the coatings have been determined by profilometry using a Veeco Dektak D150 while the morphology has been assessed by scanning electron microscopy with a Quanta Inspect S – FEI Company microscope. Surface wettability was evaluated by measuring the water contact angle using a Ramé-Hart 100-00 goniometer. Contact angle and thickness measurements have been performed using glass substrates to avoid any artifact associated with tool roughness. A Hysitron TriboIndenter was used to evaluate film hardness through nanoindentation experiments with a Berkovich tip and a CETR-UMT micro tribometer was employed for the tribological characterizations.

3. Results and discussions

The film thickness, h, as function of the total pressure, p, is shown in figure 1. In the range of pressures investigated, a continuous growth of h as p was increased was observed. This tendency can be understood considering that the higher the pressure the higher the availability of film precursor species.

Figure 2 shows the mean roughness, R_a, of the samples prepared directly on polished M2 steel and on TiN-M2 steel as a function of the pressure of the gases. It is observed that when the substrate has a high roughness (TiN-M2 steel), film deposition leads to a reduction in R_a, independently of the pressure employed. When the substrate has a low surface roughness (M2 steel) the deposition of the film tends initially to an increase in R_a with an increase in pressure up to 5.5 Pa. For depositions made at greater pressures, there is a tendency for R_a to fall. According to a study by Salvadori [7], the roughness tends to increase beyond its initial value owing to the greater deposition rate on peaks than in valleys. In agreement with the BD model [8], with an increase in film thickness, the roughness

decreases owing to the filling of the valleys by the lateral growth of the film surface. For both of the substrates, the lower roughnesses were obtained using plasmas at greater pressures.
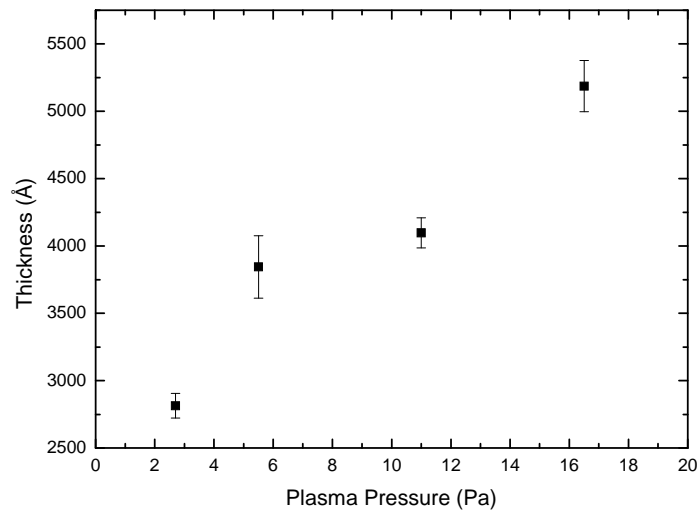

Figure 1. Film thickness as a function of the total gas pressure.
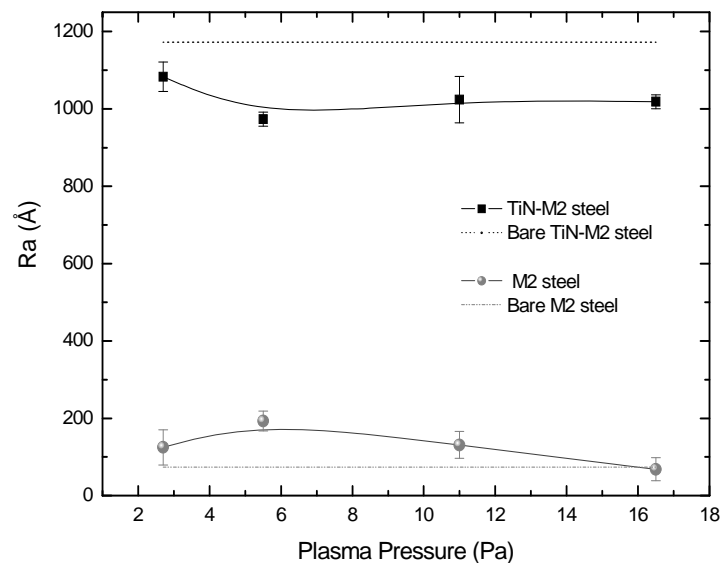
Figure 2. Average roughness of the films as a function of the plasma pressure. Dotted lines represent the R_a values for the uncoated substrates.

Figure 3(a) shows a topographic image of the TiN-M2 steel surface, obtained by AFM, where the peaks and valleys owing to the surface treatment (hard turning) before the application of the TiN layer are evident. Figure 3(b) shows the surface topography of the system containing the film deposited at 2.7 Pa, where the pattern produced by the working of the surface is still clearly observable. Figure 3(c) shows the topography of the sample that received the film from a plasma at $p = 5.5$ Pa. Comparing this image with the previous one, it can be seen that the valleys have been filled-in by the film, resulting in a more regular surface with a reduced surface roughness. Figures 3(d, e) show the topography of surfaces prepared at 11.0 and 16.5 Pa plasmas, respectively. Triangular structures are observed, which

indicate pointed defects in the surface and the continuous disappearance of the marks left by the machining of these samples by the film coverage. Holes are also identified more frequently in the last two images.
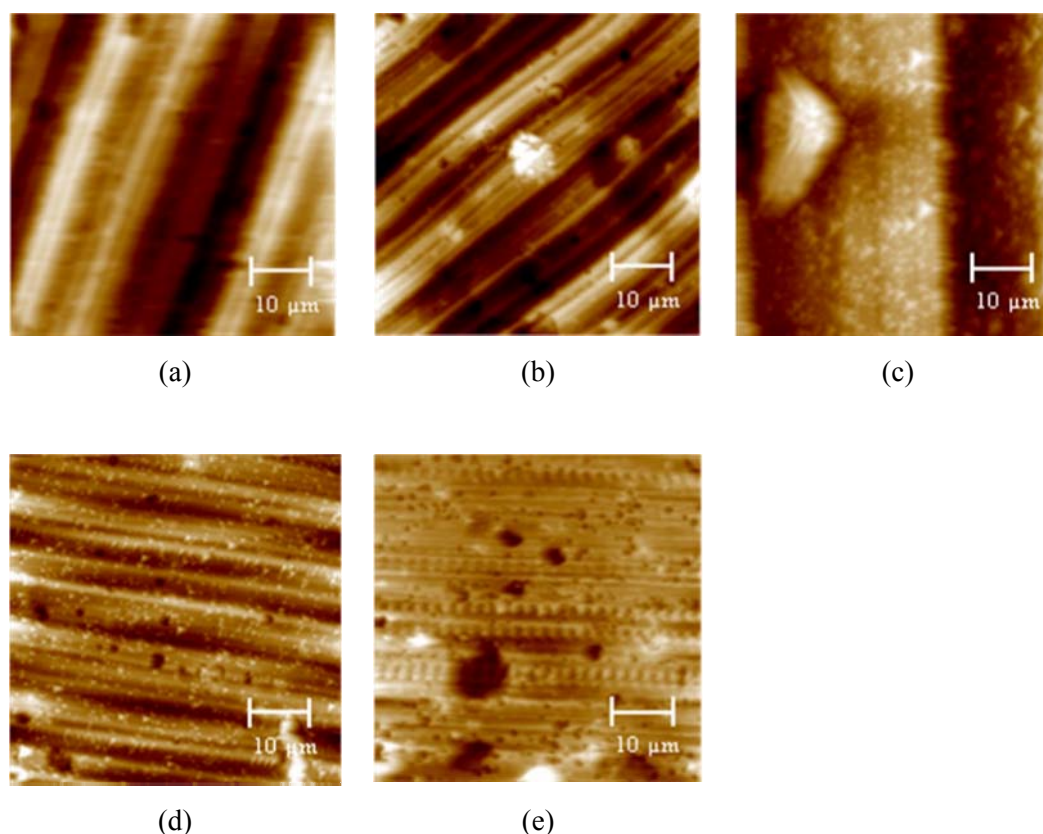

Figure 3. Atomic force microscopy images of the bare TiN-M2 substrate (a) and of the same material after exposure to plasma immersion ion implantation and deposition at 2.7 Pa (b), 5.5 Pa (c), 11.0 Pa (d) and 16.5 Pa (e). Image area: 50 X 50 μm^2.

Figure 4 shows a line profile of the surface of the TiN-M2 steel sample after the deposition of the a-C:H film at a total gas pressure of 2.7 Pa. It is clearly observed that the profile produced by machining of the surface is not completely covered by the deposition of the a-C:H film.

Figure 5 shows the infrared spectra of films deposited on polished M2 steel for various values of p. The spectra of the films deposited at lower gas pressures (2.7 and 5.5 Pa) do not present bands characteristic of plasma-deposited organic films. There is a slight indication that OH groups are present, namely the absorption at around 3620 cm^{-1}. Film thickness cannot be the only factor to be considered here since spectra characteristic of polymer-like films were obtained from even thinner films in a previous study [9]. For films deposited at higher values of p, there are bands related to the stretching and the deformation of C-H groups (2920 and 1434 cm^{-1}, respectively) and the stretching of C=C groups (1615 cm^{-1}). These alterations in the spectra may be ascribed to the diminution in the energy delivered to the material per unit of area, since the deposition rate grows, shifting the a-C:H to a polymer-like structure.

From the above results it is clear that the film characteristics depend on the plasma pressure employed for deposition. A structure typical of hydrogenated amorphous carbon, which is transparent in the infrared part of the electromagnetic spectrum, is obtained at lower pressures while a polymeric structure is obtained when the pressure is increased [10].
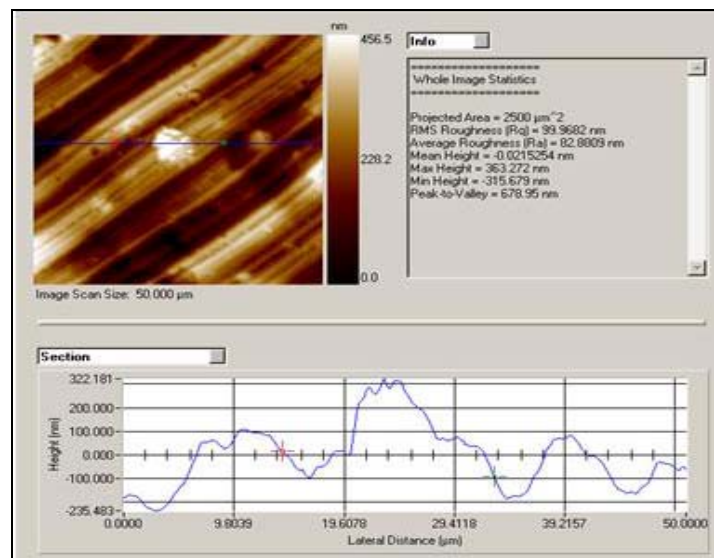
Figure 4. Line profile in the surface of the steel sample AISI M2 with TiN layer after deposition of the a-C:H film using a total gas pressure of 2.7 Pa.
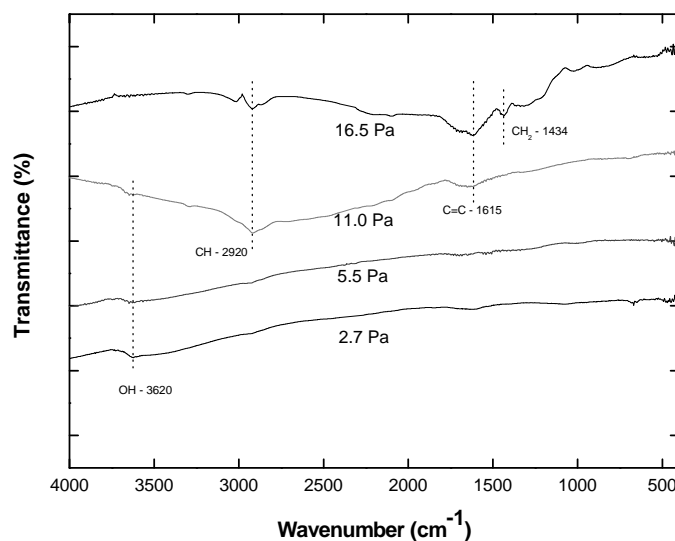

Figure 5. Infrared spectra of films produced by PIIID using different plasma pressures. Spectra were acquired from films deposited onto polished stainless steel plates.

Figure 6 shows the water contact angle, θ, of the samples as a function of p. These measurements were undertaken on the same day as the deposition of samples prepared on glass substrates. Considering that the uncertainty in the measurements is about 4°, the contact angle remains almost constant ($\sim 85°$) as p varies; that is, the films are slightly hydrophilic. This result is very similar to that obtained in a previous study in which the pulsed polarization voltage was varied [9] and may be also interpreted in terms of oxygen incorporation in the film (figure 5).
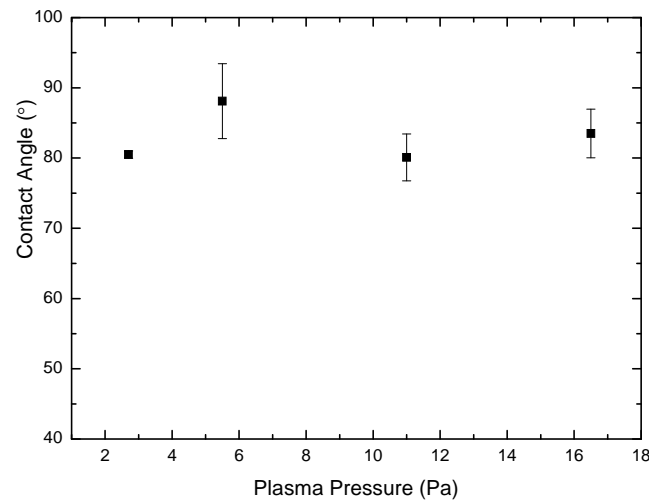
Figure 6. Contact angle of the films deposited onto glass substrates as a function of the plasma pressure.

Figure 7 shows the hardness, H, as a function of depth for films deposited on polished M2 steel, at pressures ranging from 2.7 and 16.5 Pa. The hardness of the as-received substrate and of quartz, the standard used for calibration of the indenter tip area, are also shown. It is important to note that, the hardness measurements were realized on the film prepared directly on M2 steel since the results obtained from samples prepared on TiN-M2 steel are influenced by the greater surface irregularities presented by these.
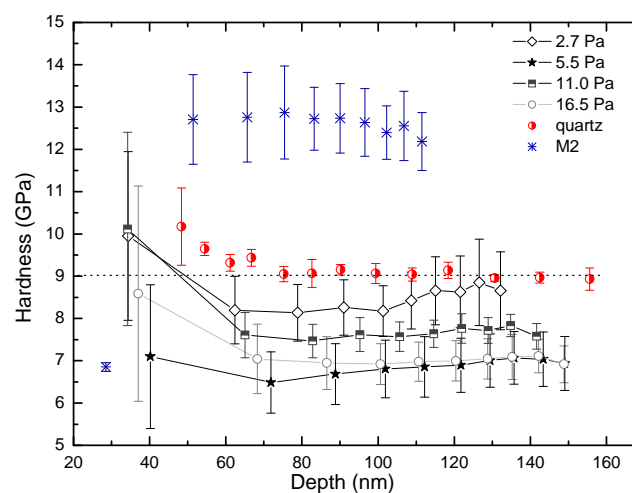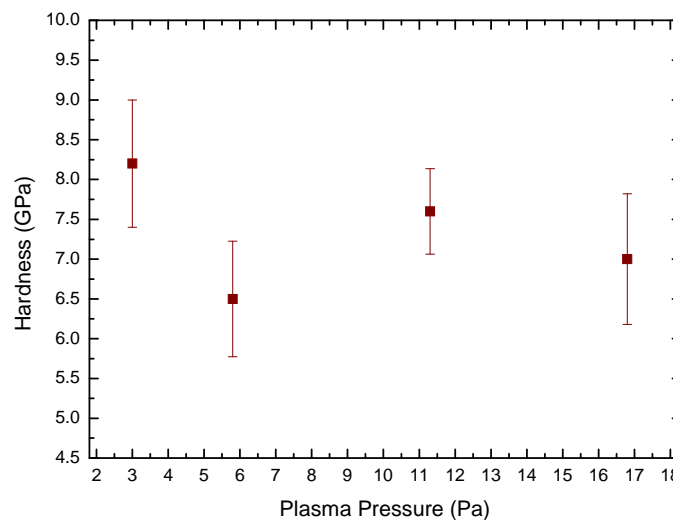

Figure 7. Hardness of the films as a function of depth for the samples prepared on M2 steel in plasmas of different pressures.

For depths greater than 60 nm, for which the hardness of quartz stabilizes at ~ 9 GPa, the hardest film was that deposited at the lowest pressure (2.7 Pa). It is interesting to note that for the samples deposited at the lowest pressures (2.7 and 5.5 Pa), there is an increase in hardness at increasing tip penetration, indicating the growing interference of the mechanical properties of the substrate with the

measurements. For the remaining films this effect is not observed owing to the greater film thicknesses. All the films are softer than the substrate.

Figure 8 shows the hardness of the films as a function of p, determined from the data in figure 7, in regions that correspond to 13 until 22% of the total film thickness. Generally, there is a fall in H for higher p, the lowest hardness being obtained at a pressure of 5.5 Pa. The film with the greatest mechanical resistance was that prepared at the lowest pressure. This result is consistent with an increase in the mean energy of the plasma species when the pressure is reduced. The increase in the mean free path of the ions with a reduction in pressure results in an increase in the energy supplied to the growing layer by ion bombardment. Both phenomena may favor the precipitation of sp^3 nuclei in the structure, thus increasing the hardness. The higher H values for the samples prepared at 11.0 and 16.5 Pa (compared to that prepared at 5.5 Pa) may be a consequence of the interference of the mechanical properties of the substrate since in these samples hardness was taken at a depth greater than 15% of the film thickness. It is believed from Raman analyses (not shown), that the hardness values for such samples are even lower than 7.0 GPa.

Figure 8. Hardness of the films as a function of the plasma pressure at a constant depth.

Figure 9 shows the friction coefficient, μ, as a function of the friction time, t, for samples prepared directly onto M2 steel at different pressures. The results obtained for the bare substrate are also included for comparison. In the sample prepared with p = 2.7 Pa, the curve begins at 0.22 but rises continually with increasing test duration, reaching around 0.7 at 300 s. The initial μ value was as high as that of the film that was deposited in 5.5 Pa plasmas. Moreover, its growth is faster indicating an earlier failure in this case. For the films prepared at the highest pressure plasmas (11.0 and 16.5 Pa), the loss of protection occurs in the first stages of the tribological test. This behavior is ascribed to the rise in the deposition rate with increasing p, since this affects the film structure in two different ways: it enhances the internal stress as a consequence of the higher proportion of defects incorporated into the structure and reduces the implantation of carbon ions on the steel surface, a process that has a beneficial effect on the connection of amorphous carbon to steel substrates via carbide formation [5,6]. Carbon ion implantation also reduces structural mismatches between film and substrate, reducing the interfacial stress and improving connectivity [11]. The ion bombardment process is also decisive in influencing the mechanical resistance of the layers.
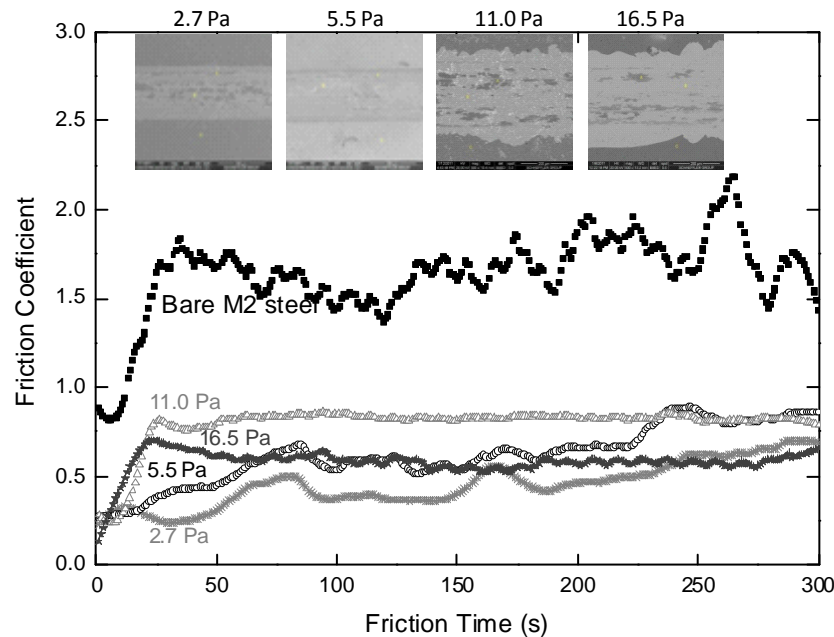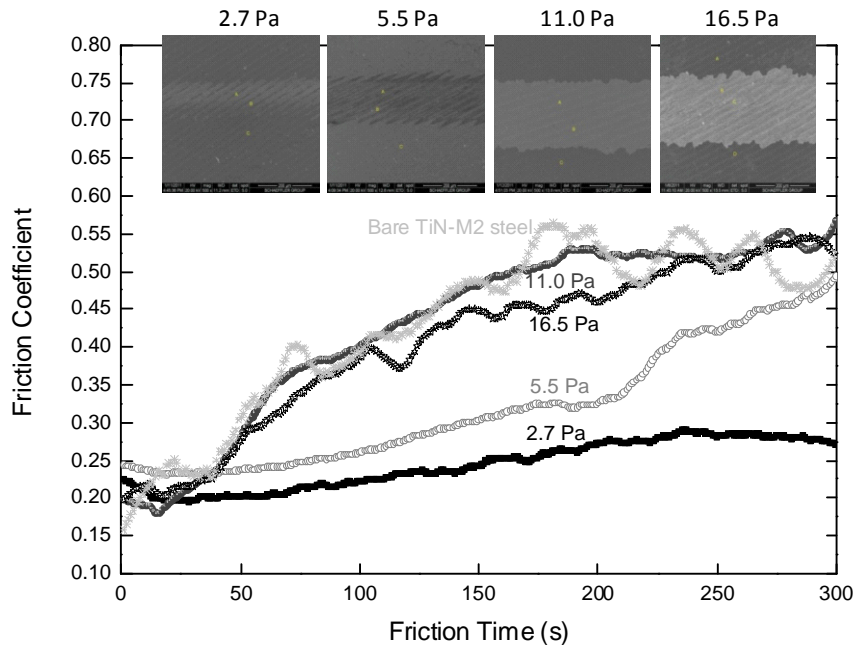
Figure 9. Friction coefficient as a function of the experiment time for the pair AISI 404 steel sphere and samples prepared on M2 steel by PIIDI with pressure varying from 2.7 to 16.5 Pa. Friction coefficient for the pair sphere-bare M2 steel is also presented. Micrographs of the tracks formed during the friction measurements are presented as insets. The bar scale in the pictures corresponds to 200 μm.

The insets in figure 9 are micrographs of the samples detailing the track regions. Wear tracks containing sparsely distributed tribolayers are clearly detected in all the samples but remarkable differences are noticed. First of all, the dimensions of the tracks generated in the samples treated at the lowest pressure plasmas (2.7 and 5.5 Pa) are considerably lower. Secondly, less film detachment occurred in the latter. Finally, the formation of a tribolayer was also more frequent for the steel treated at the lowest pressure. On the other hand, the film is completely removed from the track as depositions are conducted in plasmas of 11.0 and 16.5 Pa. In these cases the track dimensions are substantially higher, revealing a weaker connection between film and substrate. Therefore, the little damage produced in the coating deposited in 2.7 Pa plasmas is ascribed to an association of the low friction coefficient, stronger adhesion and superior mechanical resistance of this film.

Figure 10 shows the friction coefficient results for the samples prepared on TiN-M2 steel as well as for the bare TiN-M2 substrate. For deposition carried out in plasmas of 2.7 Pa, the curve initiates around 0.22 reaching 0.28 at the end of the experiment. Since the direct contact of the tribometer sphere with the TiN coating would result in friction coefficients of around 0.6 [12], the strong improvement provoked by this film on the system tribological performance is readily noticed. For the sample which received the film in plasmas of 5.5 Pa, the μ value starts around 0.24 and increases slowly during the test duration reaching 0.5 in 300 s. It is interesting to observe how μ reaches the 0.5 plateau in successively shorter times as one further increases *p* (11.0 and 16.5 Pa).

The characteristics of the tracks produced during the risk tests can be evaluated by the inset of figure 10. Just a slight mark is generated in the sample exposed to 2.7 Pa plasmas. The waviness of the substrate is also clearly detected. According to the micrographs and EDS (not shown) data, wear occurred just in the top regions with no tribolayer formation, while the depressions were kept unchanged. An increment in the track dimensions is the only modification observed as the test was conducted in the sample treated in 5.5 Pa plasmas. But upon further increasing *p*, there is complete

removal of the organic layer from the track. Evidence of tribolayer formation is obtained only for the highest pressure prepared sample (16.5 Pa).

Figure 10. Friction coefficient as a function of the experiment time for the pair AISI 404 steel sphere and samples prepared on TiN-M2 steel by PIIDI at different plasma pressures. The friction coefficient for the pair sphere-bare TiN-M2 steel is also presented. Micrographs of the tracks formed during the friction measurements are presented as insets. The bar scale in the pictures corresponds to 200 μm.

Therefore, considering the results presented here, it was possible to verify that the system tribological properties improve with decreasing deposition pressure, independently of the employed substrate. The higher proportion of carbon atoms incorporated into the surfaces by ion implantation is one of the responsible factors. Film hardness is also important. Despite being rougher, the samples prepared on TiN M2 steel presented a better result than that prepared on the smooth M2 steel. This fact confirms that adhesion and mechanical resistance are primordial aspects of the tribological performance of hydrogenated amorphous carbon.

4. Conclusions

It was observed that the pressure of the depositing plasma has a significant influence on the tribological response of hydrogenated amorphous carbon deposited on M2 and on TiN-M2 steel. The substrate chemical composition and topography are also decisive for the final film properties. Moreover, the mechanical resistance of the coating is an important factor since it is directly related to the film durability. New studies should be developed to investigate the effect of the film hardness on the tribological properties of these specific systems. It should be kept in mind, however, that extremely hard coatings may compromise the friction coefficient and wear rate since they may become brittle. Adhesion of the film to the substrate was observed to be another issue for the system tribological behavior. The formation of carbides, especially in the TiN substrate, substantially increased the connectivity of both materials. Lower deposition pressures also improved the film connectivity. The initial topography of the substrate was not the most important factor. The association of greater mechanical resistance, adhesion and lower friction coefficient is responsible for the lower wear rates produced in the optimized sample. Indeed, in this sample, the friction coefficient was reduced by more

than 50%, which can represent a significant cost reduction for a series of industrial applications. Finally it should be pointed out that the friction conditions employed here were severe considering the applied load. Certainly this compromised the film durability. New studies will be addressed to evaluating the tribological behavior of the same systems under milder friction conditions.

Acknowledgements

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