Deposition and Investigation of Amorphous Hydrogenated Carbon Films from Acetylene Plasma[1]

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Abstract – The result of the researches of amorphous hydrogenated carbon (DLC) films deposition on metal samples are presented. The operating regimes for DLC films deposition on metal samples were obtained. It was found that for the formation of hard adhesive DLC films on a metal surface a high-voltage negative pulse bias (more than 5 kV) is required. It is shown that DLC film deposition on stainless steel results in increase of surface hardness from 4–5 to 9–11 GPa. At that the measured hardness H to modulus of elasticity E ratio, making about 0.1, is typical for diamond-like carbon films. For hardening the SS surface, nitriding or N^+ ion implantation from the surrounding bulk plasma can be used before deposition of DLC films. The nitriding (with negative dc or bipolar bias voltages) during 5 h leads to an increase in SS surface hardness from 4–5 to 16–17 GPa. The implantation of the specimens from the bulk nitrogen containing plasma during 1 h provides an increase in SS surface hardness from 4–5 to 13–15 GPa. The most significant increase in surface hardness is found for N-implanted HSS specimens with DLC films deposited at amplitudes of negative bias voltage of –10 and –15 kV. The specimens obtained in this mode display hardness greater than that of the initial specimens, of the DLC film deposited on the initial HSS surface, and of the N-implanted specimens without DLC coatings.

1. Introduction

Hard hydrogenated amorphous carbon (a-C:H films) or DLC (diamond-like carbon) films represent the technological interest for wear and corrosion resistant improvement of metal products [1, 2]. At present, a large attention is given to technology of DLC deposition for the medicine applications [3]. The problem of deposition of such films during one vacuum cycle on a workpieces with surface area up to few square meters is urgent for technology [4].

For generation of bulk hydrocarbon-containing plasma a discharge systems based on filament cathode [5] or different version of RF discharge are used [6, 7]. The filament cathode has low reliability however. At the same time the widely used systems based on RF discharge do not provide high plasma density in a large volume. This limits the technological possibilities of DLC deposition process. The use of discharge system with electron injection from constricted arc [8] for such process allows increasing the plasma density in order of magnitude. Furthermore, wide possibilities of independent adjustment of operating parameters allow selecting an optimal operating regime for DLC deposition.

2. Experimental setup and diagnostics

The experimental setup for DLC film deposition is shown schematically in Fig. 1.

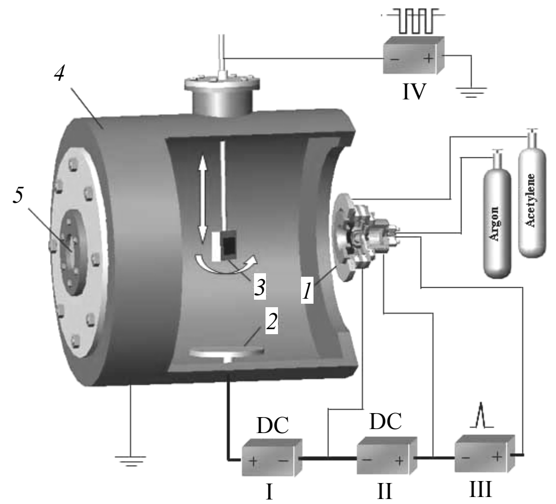

Fig. 1. Scheme of experimental setup: *1* – plasma generator; *2* – main discharge anode; *3* – moveable holder with specimen; *4* – vacuum chamber; *5* – window. Power supplies: I – main discharge; II – emitter discharge; III – trigger discharge; IV – pulse bias

Plasma generator *1* was located on the face of vacuum chamber *4* of volume 1 m^3. At the bottom of the vacuum chamber, there was stainless steel anode *2* of the main discharge. The area of anode *2* was 150 cm^2. Window *5* was used for visual observation and infrared measurement of the specimen temperature. DLC films were deposited on structural black steel, stainless steel, and high-speed steel. Before deposition, the specimen surface was mechanically polished with diamond

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paste and wiped with ethyl alcohol. The specimens were placed on movable holder *3* at the center of the chamber. The area of the specimens was 2÷4 cm^2 and that of the holder was ~100 cm^2. Voltage from power supply IV was applied to the specimens. Power supplies I–III were used to power the discharges. The plasma density was measured using a plane Langmuir probe with a guard ring and a collecting surface of area 5 cm^2. The probe was arranged 10 cm away from the specimen holder.

For increasing the lifetime of the cathode grid of the main discharge, the operating current of the emitter discharge was decreased down to 10÷15 A. The voltage of the main discharge was 100 V. The flow rate of argon to the cathode cavity of the plasma generator was 30÷35 sccm. The flow rate of acetylene to the chamber was varied between 10 and 30 sccm. Methane and a propane-butane mixture were also used as hydrocarbon gases, but preference was given to acetylene because it provides higher deposition rate, compared to that of the above gases.

The hardness and the elastic modulus of the DLC film surface layer were studied with a NanoTest 600 nanoindenter (MicroMaterials, Great Britain). The maximum load on the Berkowich diamond indenter (a trihedral pyramid) was 200 mN. The final hardness and elastic modulus were found by averaging the results of ten measurements. The penetration depth of the indenter into the coating versus the applied force was analyzed by the Oliver and Phar method [9].

The friction coefficient of the DLC films was measured with a high-temperature tribometer (CSEM Instruments, Switzerland). Since high-speed steel is difficult to shape for tribological tests, SS specimens were used to measure the friction coefficients of the films. The surface of all specimens was polished in one cycle. A ∅3 mm tribological ball (tungsten carbide) traveled around a circle of radius 5 mm with a linear velocity of 10 cm/s under 1 N load. The total track was 100 m long.

The microrelief of DLC film surfaces was examined using a Solver P47 atomic-force microscope (NT-MDT, Russia). Images of the surfaces were taken in the contact mode with the use of a CSC12 silicon cantilever (NT-MDT).

Before film deposition, the specimen surface was subjected to ion cleaning in the Ar plasma. In so doing, a negative dc bias voltage of –(200÷500) V was applied to the specimen for 5÷15 min.

The surface irregularity is attributable to sputtering of the films due to ion focusing in the near-electrode layer. Actually, with a negative bias voltage of –(200÷500) V, the ion layer thickness for the above plasma density is no greater than 1 cm, i.e., much smaller than the holder diameter, whereas with negative bias voltage of –(10÷20) kV, the layer thickness becomes comparable with the diameter of the specimen holder. Since the expanding layer tends to assume a spherical shape and, at $1 \cdot 10^{-3}$ Torr, the layer can be considered collisionless, regions of more intense ion bombardment where sputtering dominates over deposition appear at the holder center and rounding edges. This supposition is indirectly supported by the distinct diminution of the inhomogeneous region with increasing the operating pressure, e.g., to $5 \cdot 10^{-3}$ Torr. In this case, the free path of ions (~2÷3 cm) becomes smaller than the near-electrode layer thickness ~7÷12 cm.

To eliminate the effect, a ring protruding 2 cm above the holder level was arranged at the holder periphery. In further experiments, such design of the holder allowed uniform DLC film deposition on the specimens region.

3. Experimental results and discussion

The plots (Fig. 2) suggest that the DLC film deposition leads to at least a double decrease in the friction coefficient of the SS specimen. Furthermore increasing the amplitude of negative bias voltage decreases the friction coefficient.

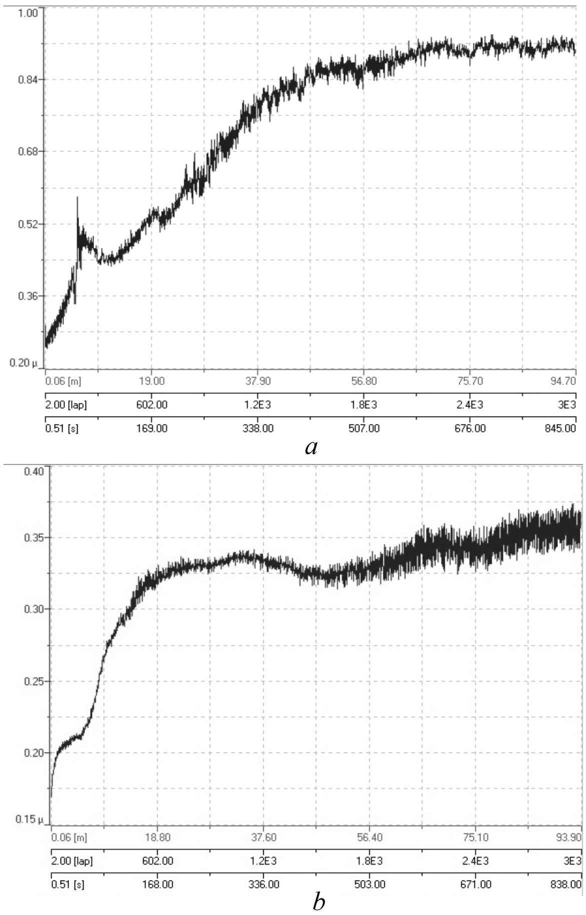
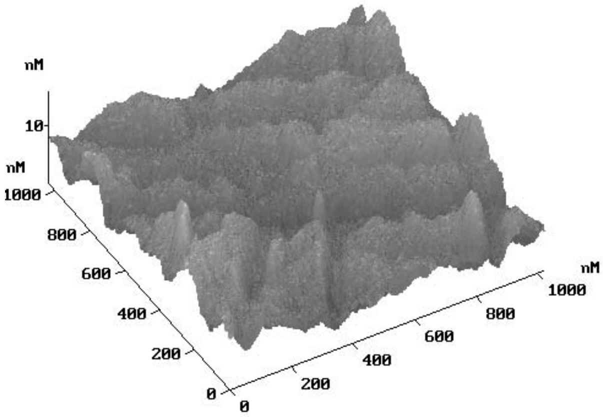


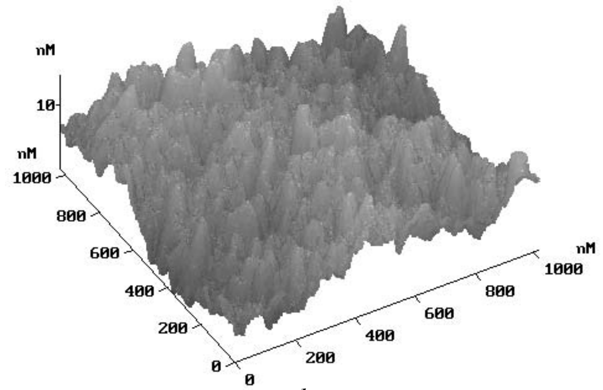
Fig. 2. Friction coefficient of the SS specimen without (*a*) and with DLC films (*b*)

The examination of microrelief shows that the root-mean-square values of surface roughness for –15 and –20 kV (2.5 and 2.6 nm, respectively) are only moderately greater than those for the initial specimen

(2.4 nm). At the same time, the specimens display lower friction coefficients due to the presence of the DLC film on the surface. Comparison of three specimens with DLC films shows that the coating obtained at U_{bias} = –10 kV features not only the greatest roughness (6.2), but also the highest friction coefficient (0.55).



a



b

Fig. 3. AFM image of the SS surface without DLC film (*a*) (R_a = 1.9 nm, R_q = 2.4 nm) and with DLC film (*b*) (U_{bias} = –15 kV) (R_a = 2.0 nm, R_q = 2.5 nm)

For hardening the SS surface, nitriding or N^+ ion implantation from the surrounding bulk plasma can be used before deposition of DLC films. Nitriding (with negative dc or bipolar bias voltages) for 5 h leads to an increase in SS surface hardness from 4÷5 to 16÷19 GPa. Implantation of the specimens from the bulk nitrogen-containing plasma for 1 h provides an increase in SS surface hardness from 4÷5 to 13÷15 GPa.

It follows from the dependences that the most significant increase in HSS specimens hardness is found in the case where DLC film is deposited on the preliminary N^+ implanted surface at the amplitude of negative bias voltage of –10 and –15 kV. The specimens obtained in this mode display a hardness of 16÷17 GPa which is a greater than the hardness of the initial specimen, of the DLC film on the initial specimen surface, and of the N-implanted specimen without DLC film.

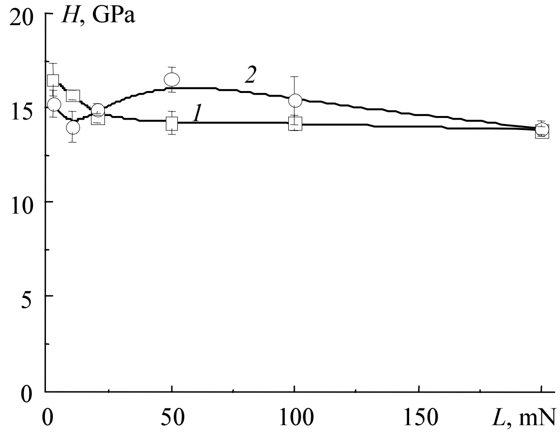


Fig. 4. Hardness versus nanoindenter load for the implanted specimens with DLC films. Amplitude of negative bias voltage in DLC film deposition: *1* – 10; *2* – 15 kV

The adhesion of each specimen was measured at three or four points. The average values at which the contact plate was broken away from the specimen surface were 150–180 kg/cm^2.

In all cases, the separation occurred at the “contact plate-film” interface, and never at the “film – metal surface” interface. The separation of the contact plate at small ultimate loads is presumably associated with low adhesion of the contact adhesive to the DLC film surface.

It should be noted that corrosion of the DLC film by the contact adhesive escaped detection also. The obtained adhesion together with the low friction coefficients and high hardness allows using these films as protective coatings on drills for machining metals such as copper and aluminum [11].

Deposition of DLC films allows a three-fivefold increase in corrosion resistance of the materials, compared to that of the initial specimens without DLC coatings.

The effect by hydrochloric and sulfuric acids for 30 min does not cause any appreciable changes of the specimen surface with DLC coatings, whereas that of the specimens without coatings does. After 15 min of attack by a mixture of hydrochloric and nitric acids ($3HCl + HNO_3$), erosion of the film was observed mainly in periphery regions of the specimen at the “film – metal interface” and where cracks were found.

4. Conclusion

The hard adhesive DLC films on the surface of SS and HSS specimens was obtained. For DLC formation high voltage negative pulse bias (up to 20 kV) was used.

Deposition of DLC films causes an increase in surface hardness from 4÷5 up to 16÷17 GPa and a decrease in friction coefficient from 0.92 to 0.35. The root-mean-square values of surface roughness for specimens with DLC films are only moderately greater than those for the initial specimens. Deposition of DLC films allows a three-fivefold increase in corrosion resistance of the materials, compared to that of the initial specimens without DLC coatings. The adhesion test at the ultimate load up to 180 kg/cm^2 shows that separations of DLC film from the specimens surface are not observed also.

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