PROPERTIES OF DLC COATINGS DEPOSITED BY DC AND DC WITH SUPERIMPOSED PULSED VACUUM ARC

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Comparative studies of the structure, mechanical and tribological properties of DLC coatings deposited in DC and DC with superimposed high current pulse modes of operation vacuum-arc plasma source with the graphite cathode are presented. Imposition the pulses of high current on DC vacuum-arc discharge allows both increase the deposition rate of DLC coating and reduce the residual compressive stress in the coatings what promotes substantial improvement the adhesion to the substrate. Effect of vacuum arc plasma filtration with Venetian blind filter on the deposition rate and tribological characteristics of the coatings analyzed.

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INTRODUCTION

Carbon DLC (diamond-like carbon) coatings possess unique properties: high hardness and strength, low coefficient of friction, transparency, high thermal conductivity, erosion, chemical and thermal stability, biocompatibility. This leads to wide possibilities of their application in mechanical engineering, optics, electronics, medicine and other fields. Cathodic vacuum-arc discharge generating a stream of highly ionized carbon plasma is an efficient tool for deposition the DLC coatings for various purposes [1]. However, one disadvantage of the method is the presence of macroparticles in the plasma flow and, consequently, significant content of particulates (droplet fraction emitted from the cathode) in the condensate.

The most radical means of suppressing the droplet fraction are magnetoelectric filters [2]. But the higher the desired degree of purification, the lower output ion current of the filter and so lower the deposition rate. At the same time, in many practical cases there is no need in "ultra cleaning" of plasma. Removing the large-scale fraction of the particulates from the bulk of the plasma may be enough to make the film be available for practical use.

For example, the presence of the droplets with a particle size less than 1 micron is quite acceptable in wear-resistant anti-friction nanostructured coatings on working parts of friction surfaces and instruments. In this regard, a significant practical interest the alternative methods for particulates suppression attract which, although not provide perfect cleaning of the plasma, but are more simple and cheap compared to the methods that require use of filters. One of the ways in reducing the particulates emission is decreasing the residence time of the cathode spot in the same place, which is achieved in pulsed arc [1, 2]. Also DC vacuum arc method with superimposed high-current arc pulses [3] give good results.

The aim of the present work is comparative study of the structure, mechanical and tribological properties of DLC coatings fabricated using filtered and unfiltered vacuum arc plasma in the vacuum arc source operating both in DC mode, and DC with the imposition of high-current pulses.

1. EXPERIMENTAL TECHNIQUES

DLC coating deposition was carried out on a modernized industrial vacuum arc installation C55CT made by the INOVAP GmbH. Two vacuum arc sources with the graphite cathodes and the vacuum arc source with the cathode of high-purity chromium, all of diameter of 70 mm are used in the installation. Upgrade of the setup included use of the water-cooled linear Venetian blind filters placed in the vacuum chamber in front of the sources of metal and carbon plasma, as well as the montage of water-cooled electrodes for AEGD process mode. The design of the filter has been optimized for the best quality of filtration [3].

Samples of high-speed steel (HSS) with the dimensions of Ø32×3 mm polished to a roughness of R_a = 0.02 µm were used as substrates. They were washed in acetone and alcohol in an ultrasonic bath, and finally the samples were fixed in the chamber on the drum type substrate holder. The rotation speed of the substrate holder during deposition of carbon coating was 5 turn/min. The vacuum chamber was preliminary pumped to 1×10^{-3} Pa. Argon gas (99.999 % purity) was used to improve operation stability of the used vacuum arc plasma sources. After preliminary cleaning of the samples surface by Ar ions in the AEGD (Arc-Enhanced Glow Discharge), the ion cleaning of the surface was carried out by the accelerated Cr ions and then the underlayer of chromium for improving adhesion was deposited.

All stages of the process in the present experiments were identical and differed only by the modes of operation of the vacuum-arc sources.

Deposition modes used:

1 – nonfiltered DC vacuum-arc with arc current of 50 A with superimposed high-current arc pulses;

2 – filtered DC vacuum-arc with arc current of 50 A with superimposed high-current arc pulses;

3 – filtered DC vacuum-arc with arc current of 50 A.

Pulse parameters for 1 and 2 pulsed modes: amplitude of arc current pulses – 1400 A; pulse duration – 300 µs; repetition frequency – 100 Hz.

Since the planetary substrate holder had no additional cooling, and the temperature is one of the key parameter which determines the DLC properties [4], in the experiments the substrate was cooled through the breaks of the process after the phase of adhesive metal sublayer deposition. During the stage of amorphous carbon DLC coating deposition the substrate temperature limit of 45°C was set. Temperature was simultaneously measured by an industrial PT-100 thermocouple mounted in the center of the chamber.

The thickness of the synthesized amorphous carbon DLC thin films was determined according to the data published by T.J. Moravec [5]. This method is based on a comparison of the coating interference color with standard colors for a diamond-like carbon coating with a known refractive index. Furthermore, the thickness was monitored using calotest method.

Quantity estimation of the surface defects emerged during the synthesis of carbon coatings was made according to the method described in [3]. A HOMMEL-ETAMIC T8000 stylus profilometer was used to measure surface roughness of DLC thin films deposited onto HSS substrate. Also profilometer was used to determine the film stress by using the radius of curvature technique that compares the curvatures of bare silicon substrates Si (100) cut-out from 0.5 mm thick plate and substrates covered with a thin film. Stoney's equation was used to calculate the stress [6].

Measurements of hardness and Young's modulus were performed using the nanohardness testing instrument Fischerscope HM 2000 and DCM Nano Indenter® XP produced by the company MTS with Berkovich pyramid indenter. Adhesive properties were measured using the scratch tester REVETEST® produced by the company CSM, as well as by Daimler-Benz method, according to VDI 3198 standard, using Rockwell indenter.

Tribological tests of the coatings were performed on T10 device in accordance with the method of ball-on-disc. Ceramic Al_2O_3 ball (Ø10 mm) was used as the counter-body. Following test parameters were used: the normal load L = 20 N, sliding speed V=0.2 m/s; radius of the friction track R = 10 mm. Tribological tests were performed in ambient air with a relative humidity of 40…50 %. To measure the dimensions of the wear track HOMMEL-ETAMIC T8000 stylus profilometer was used.

2. RESULTS AND DISCUSSION

Table presents the thickness of the DLC coatings fabricated in various modes, their structural characteristics, as well as the test results of the samples. It can be seen that the thickness of the coatings is strongly dependent on the used mode of deposition. Since the duration of the processes in the experiments was fixed, it indicates a different deposition rate. As might be expected, the maximum deposition rate observed in the mode 1 (unfiltered vacuum arc plasma, DC + high current pulses). In this case the coating thickness reached 0.9 µm.

According to optical microscopy, defects in form of the droplets occupy about 30 % of the coating surface in case deposition from the unfiltered plasma. However, use of a high current pulsed vacuum arc mode promotes deposition with droplets of a small size. The droplet size distribution is presented in Fig. 1. Size almost 85 % of the droplets does not exceed 1.4 microns. According profilometer data, the surface roughness R_a of the coating is of 0.14 microns. Using the filter during coating deposition in a pulsed (mode 2) allows improve the quality of the surface, but at the same time the deposition rate drops 4 times.

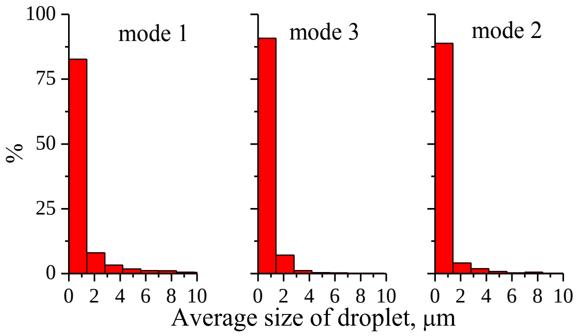


Fig. 1. Droplets size distributions on the surface of the DLC coatings deposited in different modes

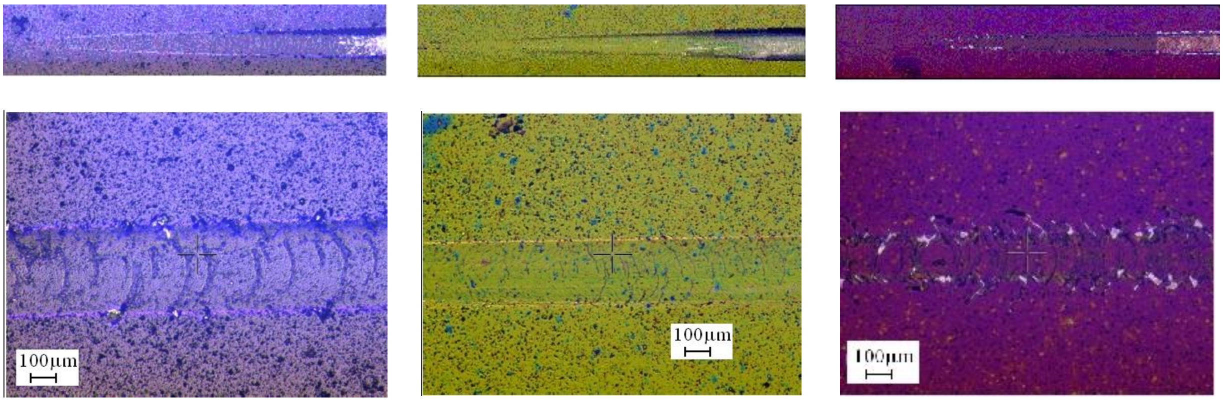
Characteristics of the DLC coatings deposited in different modes

№ mode	Mode characterization	Thickness, µm	Surface occupied by defects, %	Hardness, GPa	Young's modulus, GPa	Stress, GPa	R_a, µm	Scratch testing: Lc1, N	Scratch testing: Lc2, N	Scratch testing: Friction coefficient	Wear testing: Test duration, hour	Wear testing: Wear track depth, µm	Wear testing: Wear track width, µm	Wear testing: Friction coefficient
1	nonfiltered DC+ pulses	0.90	30	15	131	3.6	0.14	16	52	<0.12	2	0.31	0.65	<0.18
2	filtered DC+ pulses	0.25	10	48.2	441	8.6	0.02	22	45	<0.05	1	0.12	0.23	<0.17
3	filtered DC	0.10	6	51.1	415	15.6	0.01	6	18	<0.05	-	-	-	-

Number of droplets on the surface of the coating reduced to 10 %, the content of the drops smaller than 1.4 micron size increases to almost 90 %, and the surface roughness is reduced to 0.02 microns. Surface of the coating deposited from the filtered plasma in the mode 3 (DC arc current) is visually identical to that in the pulse mode. Drops occupy only 6 % of the surface area of the coating, and their size distribution is almost identical to that of the mode 2. Surface roughness is of 0.01 microns. However, the deposition rate of the coating is the lowest, 2.5 times lower than when using the pulsed mode, and nearly 10 times lower than at the deposition without filter.

It is known that the wear resistance of the coatings is influenced by many interrelated factors: the hardness parameter H/E, the level of residual stress, surface roughness, the adhesion to the substrate. DLC coatings deposited from the filtered plasma, characterized by a hardness of about 50 GPa, indicating high content of sp^3-bonds. The hardness of the coating deposited from the unfiltered plasma is much lower, about 15 GPa. Decrease in hardness is due to decrease in the content of the sp^3 bonds associated with high content of the graphite drop component with sp^2 bonds. In this case, all coatings have similar values of the parameter H/E in the range 0.11…0.12.

An important characteristic of coatings is also the quality of the adhesion to the substrate. One of the methods for estimating the adhesion of the films is Daimler-Benz method (Rockwell indenter test). The coatings at the edges of the prints do not break down and not peel off from the substrate, showing a fairly good adhesion. At higher magnification only small cracks in the coating at the edge of the print are shown.



a *b* *c*

Fig. 2. Scratch marks obtained on tested DLC coatings: a – mode 1; b – mode 2; c – mode 3

More information gives a scratch test. Photographs of the scratch tracks on the surface of the DLC coatings are presented in Fig. 2. Load values L_{C1}, when starting the coating cracking and load L_{C2}, at which the coating begins to delaminate from the substrate, and the friction coefficient are shown in Table. It can be seen that the coating formed from the filtered plasma at DC arc mode (mode 3) exhibits inferior adhesion. The value of the load L_{C1}, when seen the first crack in the scratches, is 6 N and L_{C2} = 18 N. Then there are significant chips of the coating material on the edges of the scratch track. Coatings deposited in pulse modes show a much better adhesion to the substrate. Load values L_{C1} and L_{C2} for mode 2 are of 22 N and 45 N, and for the mode 1 is 16 N and 52 N, respectively. There are no chips on the edges of the scratches.

Presumably, the differences in the nature of coating damage during scratch testing are determined by the difference in the level of compressive residual stresses that are generated in the coating during deposition. Cracking observed in the coating deposited from the filtered plasma in a DC mode where the stress level is extremely high – 15.6 GPa. At pulsed arc mode deposition the level of residual stresses reduced to 8.6 GPa. Perhaps the processes that allow reduce stress, similar to those that occur when the stress relaxation occurs in the coatings deposited at a high-voltage pulsed substrate bias potential [7]. In the coatings deposited in a pulsed mode without plasma filtration the stress level is even lower – 3.6 GPa. This may be due to a compensatory role of defects in form of droplets which occupy a considerable part of the volume of the coating. By reducing stress, coatings deposited in pulse mode not break off on scratch testing.

Thus, the vacuum-arc method of producing DLC coatings when the DC vacuum arc superimposed with high-current pulses has several advantages over a simple DC method: higher deposition rate, relatively low level of residual stress, high adhesion to the substrate. The pulsed DLC coating also showed good tribological characteristics in tests. At the initial stage of the test a process of the "run-in" asperities on the coatings surface takes place. The coefficient of friction is sufficiently high. For coatings with low surface roughness deposited from the filtered plasma (mode 2), it reaches a value of 0.3 and unfiltered (mode 1) – 0.45. After 100…150 s testing the coefficient of friction in both cases dramatically decreases and during total test time does not exceed 0.17 (Table).

Despite the significant differences in structural and mechanical properties of the coatings the mean rate of groove wear growth is not fundamentally different. So, after one hour test of the coating deposited from filtered plasma, depth and width of the groove wear is 0.12 microns and 0.23 microns, respectively. For the coating deposited from the unfiltered plasma, after two hour testing duration these values were 0.31 microns and 0.65 microns. Thus, the wear of the coating with a high content of droplets and lower hardness is only 1.3 times faster than that of more “clean” and hard one.

CONCLUSIONS

A comparative study of the surface morphology, mechanical and tribological properties of DLC coatings produced using vacuum arc plasma in the arc DC mode with superposition of high-current pulses and in their absence were carried out.

It was established that the method of vacuum-arc deposition DC with superimposed pulses of high current arc in the C55CT INOVAP installation allows 2.5-fold increase in the deposition rate of DLC coating, reduces the residual compressive stresses in the coatings, substantially improves the adhesion to the substrate and simultaneously provides good friction characteristics.

DLC coatings deposited by this method from the filtered plasma characterized by high hardness 48 GPa, a low amount of defects in form of droplets and the surface roughness close to the substrate surface roughness of 0.02 microns. In case deposition from the unfiltered plasma the coating hardness is reduced to 15 GPa, and the roughness increased by an order as a result of increasing the number of defects. The size of most of the defects remains practically unchanged and does not exceed 1.4 μm. The coatings produced in both modes show good tribological properties. After a short coatings break-friction, the coefficient of friction does not exceed 0.17.

When the coating should be deposited on the parts and components that do not require high-end surface finish, deposition from the unfiltered DC arc plasma in superposition with high-current pulses can be recommend, which provides the deposition rate four times higher than that of the filtered one using electromagnetic linear Venetian blind filter. Deposition DLC coatings on the high-precision components requires use deposition mode with filtration of plasma.

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СВОЙСТВА АЛМАЗОПОДОБНЫХ ПОКРЫТИЙ (АПП), НАНЕСЕННЫХ ПРИ ПОМОЩИ ВАКУУМНОЙ ДУГИ ПОСТОЯННОГО ТОКА И ПОСТОЯННОГО ТОКА С НАЛОЖЕНИЕМ ИМПУЛЬСОВ

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Представлены результаты сравнительных исследований структуры, механических и трибологических свойств алмазоподобных покрытий (АПП), осажденных методами разряда постоянного тока и постоянного тока с наложением дополнительных импульсов при использовании вакуумно-дугового источника плазмы с графитовым катодом. Установлено, что метод вакуумно-дугового осаждения постоянного тока с наложенными импульсами сильноточной дуги позволяет увеличить скорость осаждения АПП, снижает уровень остаточных напряжений сжатия в покрытиях, существенно улучшает адгезию к подложке и одновременно обеспечивает хорошие характеристики трения. Анализируется влияние фильтрации вакуумно-дуговой плазмы на скорость осаждения и характеристики покрытий.

ВЛАСТИВОСТІ АЛМАЗОПОДІБНИХ ПОКРИТТІВ (АПП), НАНЕСЕНИХ ЗА ДОПОМОГОЮ ВАКУУМНОЇ ДУГИ ПОСТІЙНОГО СТРУМУ ТА ПОСТІЙНОГО СТРУМУ З НАКЛАДАННЯМ ІМПУЛЬСІВ

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Представлено результати порівняльних досліджень структури, механічних та трибологічних властивостей алмазоподібних покриттів (АПП), осаджених методами розряду постійного струму та постійного струму з накладанням додаткових імпульсів струму при використанні вакуумно-дугового джерела плазми з графітовим катодом. Встановлено, що метод вакуумно-дугового осадження постійного струму з додатковими імпульсами струму великої амплітуди дозволяє збільшити швидкість осадження АПП, знижує рівень залишкових напружень стиску в покриттях, значно поліпшує адгезію до підкладки та одночасно забезпечує добрі характеристики тертя. Аналізується вплив фільтрації вакуумно-дугової плазми на швидкість осадження та характеристики покриттів,