DLC Coatings on Spherical Elements of HIP Endoprostheses

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Abstract

Hard coatings are increasingly being used in medicine to protect metal endoprostheses The experimental process for the high-productive synthesis of high-quality diamond-like carbon (DLC) coatings with high hardness and a sufficiently high level of adhesion to the spherical shaped parts of the hip joint made from the stainless steel or cobalt-chrome alloy have been developed. DLC coating deposition was performed by vacuum-arc method from a high-productive source of the filtered vacuum-arc carbon plasma of rectilinear type with a "magnetic island". The high degree of thickness uniformity in the coating on the head of the hip joint with a high adhesion to the metal joint base was developed. Modernization of the vacuum arc plasma source allowed to accelerate the cathode spot motion, exclude substrate overheating and increase the diamond-like carbon hardness up to 30-40 GPa. The high adhesion level was achieved as a result of the high voltage pulsed of substrate bias potential use and multilayer architecture of DLC coating. The DLC coating

on the heads of hip endoprosthesis did not peel off when boiling endoprosthesis or when immersing it into the liquid nitrogen. [1]

Keywords: diamond-like carbon, head of hip joint, vacuum-arc, filtered plasma source, adhesion.

Introduction

Hip joint fracture has become one of the most problems of the old people in the world. Total hip replacement, in which the head of the femur and its socket are replaced, is the main procedure to re-establish the functions of fractured hips. The lifetime of the implants strongly depends on the design and quality of the used materials. The most used metal implants become loose and release toxic ions due to the wear between the moving surfaces and the corrosion in human fluids. This makes the implants fail within 20 years and revision is often required in old age. In order to reduce the ion release and extend the lifetime of the implant the different coatings and surface treatment of the hip joint have been developed. DLC thin films have been attracted due to its low coefficient of friction, high hardness, and excellent biocompatibility. But the main problem of DLC coating use is its poor adhesion to biomedical alloys due to the high internal stress of DLC coating because of the ion bombardment during deposition. Different methods were used for increasing the adhesion to the metal base of the hip joint: metal Ti, Cr interlayer, doping DLC films by metal (Ti, Cu, Zr, etc.) or Si, N impurities, diamond nanocrystals incorporation in the DLC films and so on. Vacuum arc deposition with using filtered from graphite macroparticles plasma is the most promising method for deposition of high-quality DLC films.

The purpose of this study is the development of a process for the high-productive synthesis of high-quality DLC coating with high hardness and a sufficiently high level of the adhesion to the spherical shaped parts of the hip joint made from the stainless steel and cobalt-chrome alloy.

Method and Results

DLC deposition was performed by the vacuum-arc method from a high-productive source of the filtered vacuum-arc carbon plasma of rectilinear type with a "magnetic island". The source was installed in a modernized installation of bulat-6 [1, 2]. The general view of the mounted source on the vacuum chamber of this installation is shown in Figure 1. The scheme of the modernized installation is shown in Figure 2.

[1] Original Article

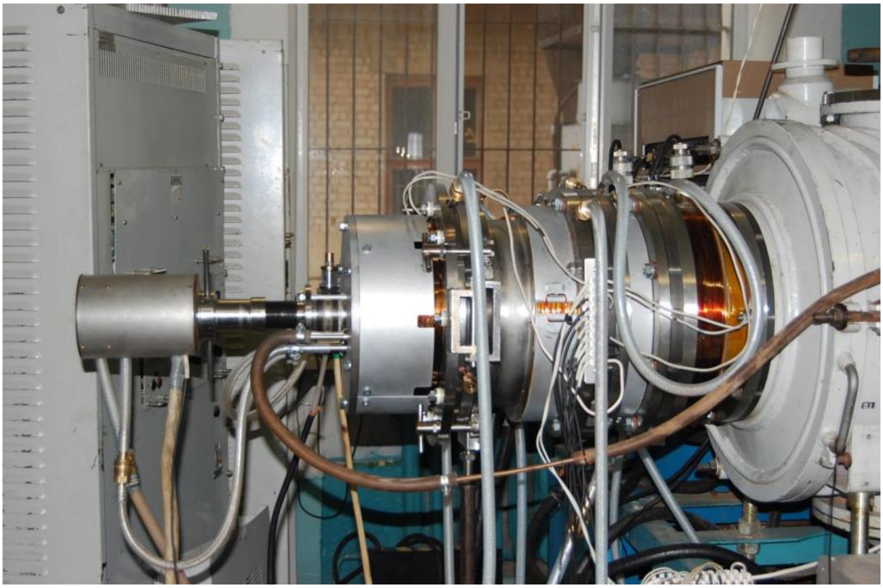


Fig.1. Photo of a high-productive source of the filtered vacuum-arc plasma mounted on the vacuum chamber.

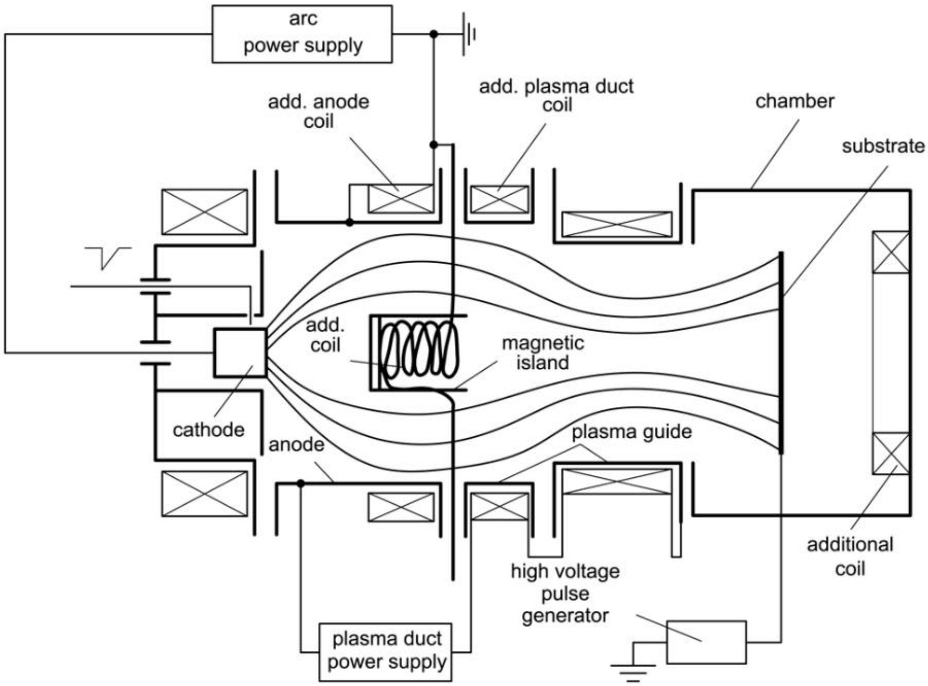


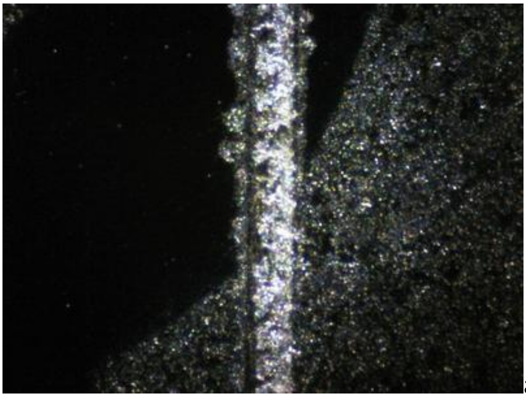
Fig.2. Diagram of a modernized vacuum-arc set up with a high-productive source of the filtered vacuum-arc plasma.

The high efficiency of the plasma source is ensured by the realization in it the original method of transporting the vacuum-arc plasma when it is filtered from particulates, due to a substantial decrease in the plasma losses on the structural elements of the filtering system. The essence of this method is to reduce the loss of plasma fluxes on the walls of the anode and the magnetic island, the plasma flows are influenced by a magnetic field generated by two electromagnetic coils located outside the anode and inside the "magnetic island" (Figure 2). These coils are included in the arc discharge circuit. If the plasma jet approaches to the anode or magnetic island, the current through the corresponding coil increases and an additional magnetic field is created which repels the plasma jet from the surface of the anode or magnetic island. As a result, the plasma losses inside the filtering system are substantially reduced [2,3]. In addition to the new plasma source, the unit is also equipped with an original inverter power source for the vacuum arc [4] and a high-voltage pulse generator for feeding an impulse negative bias potential to the substrate. The pulse generator provides the following pulse parameters: amplitude of 0.5-2 kV, pulse duration of 6-20 μs, repetition frequency of 1.2-12 kHz. To stabilize the operation of the plasma source, argon is introduced into the vacuum chamber to a pressure of 1×10^{-2} Pa. The thickness of the deposited DLC coating was ranged from 1.3 μm up to 2.7 μm; the thickness measurements were carried out using the MII-4 interference microscope. The adhesion to the substrate was evaluated on the base of scratch testing. The diamond indentor (with a tip of spherical shape, with a radius of curvature of 0.5 mm) moved along the surface at a speed of 0.57 mm/s at a constant load in the range of 5-40 N. The hardness of the coatings was measured by the G-200 nanoindentor using the continuous stiffness measurement (CSM) mode. DLC films have been deposited on two types of substrates made from stainless steel and cobalt-chrome alloy using in hip joints. To ensure the required level of DLC coating adhesion to the stainless steel or cobalt-chrome alloy surfaces without using a metal sublayer of a carbide-forming metal, the PIIID method (deposition from the plasma with simultaneous implantation) was used [5].

The surface uniformity and coating thickness controlled with the help of scanning electron microscopy method on PEM Mira 3 LMU (Tescan). Elementary analyze performed using energy dispersive spectrometer Oxford X-Max80 (Oxford Instruments). Study parameters, such as magnification, visible field and detector used (BSE - elastically reflected electron detector, SE - secondary electron detector), accelerating voltage, focal length and scale mark are shown in each image. After the first study, carbon inclusions were detected on the surface, so the sample was cleaned in an ultrasonic disperser (Elma Ultrasonic S30H) in an ethanol environment.

Results and Discussion

The method provides an improvement in adhesion characteristics due to a reduction in internal compressive stresses in the coating and forming the mixed interlayer between substrate material and coating at the expense of supply to the substrate high-voltage pulses of a potential of negative polarity during deposition. In the course of carrying out the experimental studies, the optimal parameters of the pulses of bias potential were selected for the deposition of multilayered DLC coating. These parameters ensure as in the case of two-layered and three-layer DLC coating a sufficiently good adhesion of DLC coating with the thickness from 1.3 to 2.7 μm to the stainless steel and cobalt-chrome alloy. The results of scratch testing of DLC coating showed that under loadings on the indenter up to 40 N there are no noticeable delaminations of these coatings from the substrate (Figure 3a). However, at a load of 40 N, penetration of the indenter into the coating body was observed, that was evidence of its insufficient hardness.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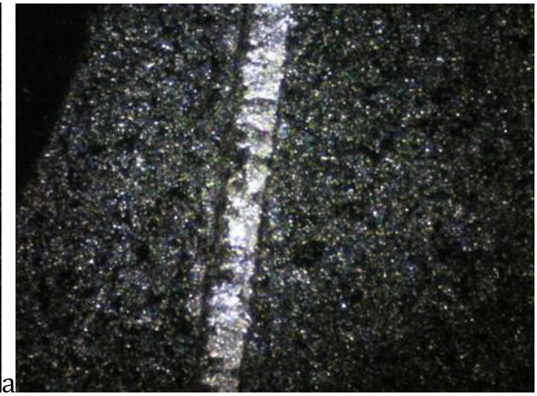
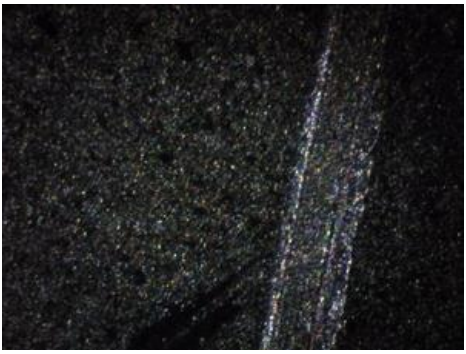


b

Fig.3. A trace of the indenter on the surface of the test specimen with two-layer DLC coating, h = 1.3 μm. The edges of the track are partly ragged, there is exfoliation and penetration into the DLC coating - a. Penetration to the substrate is absent - b.

The results of measurements of the DLC coating hardness showed that it does not exceed 20 GPa. It was suggested that this is due to an increase in the content of the graphite phase in the DLC coating as a result of overheating of the substrate surface during deposition at the site of its contact with the plasma jet because of its slow movement along the surface of the substrate holder. The reason for the slow movement of the plasma jet along the surface of the substrate is, accordingly, the slow movement of the cathode spot (CP) of the vacuum arc along the working surface of the graphite cathode of the plasma source. Visual observations have shown that the average time for which the CP of the arc performs a complete revolution around the cathode axis is about 30 minutes. Such a slow motion of the CP was an obstacle not only to achieve the high hardness of the DLC coating but also to ensure the uniformity of the thickness of the coating along the circumference of the head of hip endoprostheses for a deposition time of fewer than 30 minutes. To resolve this problem, the vacuum-arc evaporator of the vacuum arc filter source was modernized, which allowed reducing the average time of one revolution of the cathode arc spot around the cathode axis from 30 minutes to 2 minutes. This made it possible to deposit DLC layers of equal thickness in a shorter period of time, which made it possible to create DLC multilayer of different structures by correspondingly adjusting the amplitude of the negative bias potential on the substrate for each layer. An increase in the speed of the moving of the CP, as shown by the experiments on the deposition of DLC coating on the heads, made it possible to increase the hardness of the DLC coating from 20 GPa to 40 GPa under other equal conditions. In this case, the adhesion of the coating to the substrate has remained at a sufficiently high level according to the results of scratch testing (Figure 4) (there were no coating peelings at normal load on the indenter up to 40 N).



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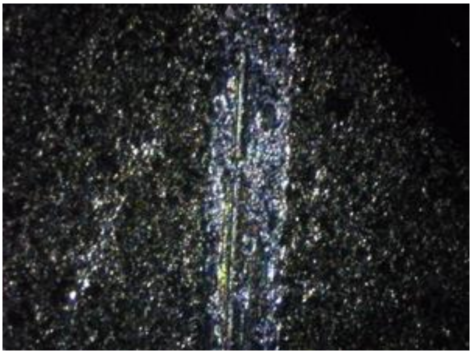

b

Fig.4. A trace of an indenter of a scratch tester on the surface of a test specimen with a two-layer DLC coating, h = 1.67 μm, H = 30 GPa (a) and three-layer DLC coating, h = 2.14 μm, H = 40 GPa (b) deposition using the improved evaporator.

We developed an experimental process of high-productive deposition of DLC coating on heads of hip endoprostheses (Figure 5). Such coatings are increasingly being used in medicine to protect metal endoprostheses installed inside the human body, both from electrochemical dissolution and from wearing the friction surfaces of prosthetic elements of various joints.

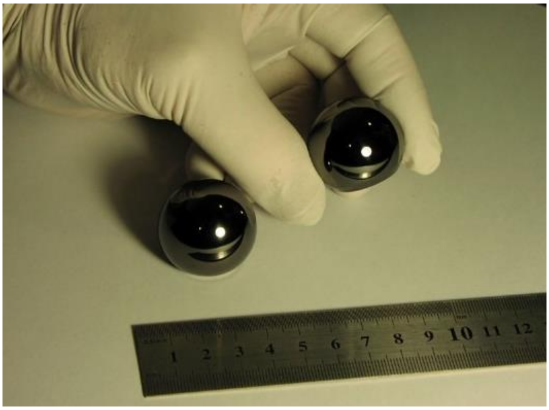

Fig. 5. The heads of hip joint endoprosthesis with DLC coatings.

The developed process provides a high degree uniformity of the coating thickness, which was controlled at the initial stage of the coating deposition by the uniformity of the color of the interference reflection from the deposited film over the entire spherical surface of the article. The identical color of the deposited coating indicated a high degree of the coating thickness uniformity throughout its surface. For the DLC coating deposition the high-productive rectilinear vacuum-arc filtered plasma source was used as well as plasma flows control system, ensuring the uniformity of coating over the entire spherical surface. The applied diamond-like coatings had a high adhesion to the hip joint surface and a low level of internal stresses, the coatings did not peel off when boiling endoprostheses or when immersing it into the liquid nitrogen.

The nano-hardness of the coating is up to 40 GPa. The thickness of the DLC coating on the spherical element of hip endoprostheses was about 1 μm (Figure 6). The composition of the medical stainless steel is shown in the (Table 1) and on (Figure 7).

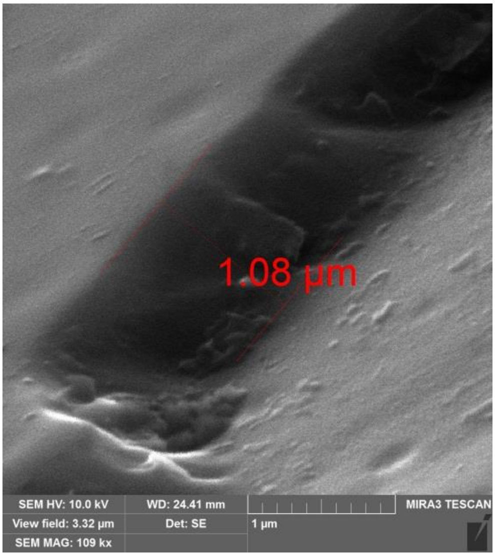

Fig. 6. Picture of hip head surface coated with DLC coating at the top left and uncoated at the right part of the drawing (Scanning electron microscopy:10.0kV).

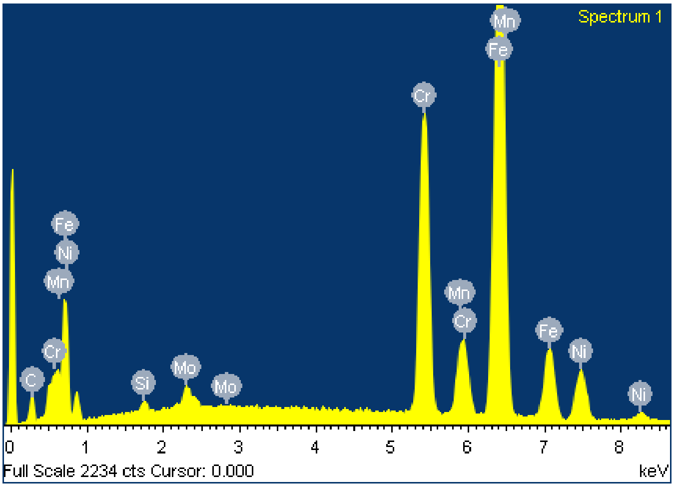

Fig. 7. EDS spectra of uncoated hip joint element surface.

Table 1. The composition of the medical stainless steel

The composition of the hip head of implant, %								
C	O	Si	Cr	Mn	Fe	Ni	Mo	Total
6,14	-	0,28	20,36	4,15	58.87	8,47	1,73	100

Conclusions

Process of DLC coating deposition without the use of the metallic sub-layer on surfaces of the heads from stainless steel and cobalt-chrome alloy for hip endoprosthesis was developed. The required level of DLC coatings adhesion to the substrate material is provided by supplying a high-voltage impulse bias potential to the substrate during deposition. Due to the modernization of the source of the vacuum arc plasma, the speed of the movement of cathode spot of the vacuum arc along the cathode surface is significantly increased, which avoids overheating of the substrate and allows achieving a DLC coating hardness of 30-40 GPa. The high degree thickness uniformity of the coating on the heads of hip endoprosthesis with the high adhesion to the metal joint base was developed. Multilayer DLC coatings were obtained whose structure and mechanical characteristics can be controlled by specifying the amplitude of the bias potential and the deposition time of each layer. The parameters of the synthesis process were established, which provide a significant improvement in the characteristics of multilayer coatings, as compared to single-layer coatings. The best adhesion (when the indentor is loaded up to 40 N) two- and three-layer DLC coating with a hardness of 30-40 GPa are characterized. The applied diamond-like coatings had the high adhesion to the head surface of the hip endoprosthesis and a low level of internal stresses. The DLC coatings on the heads of the hip endoprosthesisdid not peel off when boiling endoprostheses or when immersing it into the liquid nitrogen. Further tribological studies will provide an answer to the promising use of the developed DLC coating for heads of the hip joint endoprosthesis.

Conflict of Interest

The authors of this paper have no financial or personal relationships with other people or organizations that could inappropriately influence our study.

References

[1] Bilek, M.M., McKenzie, D.R., Tarrant, R.N., Lim, S.H.M, McCulloch D.G. (2002).Plasma-based ion implantation utilizing a cathodic arc plasma. Surface and Coatings Technology. Vol. 156, 136-142.

[2] Kumar, A., Singh, D., & Kumar, S. (2022). "Adhesion enhancement mechanisms of DLC coatings on medical-grade stainless steel: Current status and future prospects." Diamond and Related Materials, 123, 108889.

[3] Liu, X., Chen, Y., & Wang, H. (2022). "Recent advances in vacuum arc deposition techniques for biomedical coatings." Surface and Coatings Technology, 441, 128540.

[4] Martinez-Martinez, D., & De Hosson, J. T. M. (2021). "On the evolution of mechanical properties of DLC coatings for medical implants: A systematic review." Acta Biomaterialia, 128, 48-67.

[5] Park, S., Kim, H., & Lee, J. (2022). "Long-term performance evaluation of DLC-coated hip prostheses: A 10-year follow-up study." Journal of Biomedical Materials Research Part B: Applied Biomaterials, 110(6), 1202-1215.

[6] Robertson, J., & Zhang, S. (2023). "Diamond-like carbon coatings for biomedical applications: A comprehensive review." Progress in Materials Science, 134, 101017.

[7] USA Patent # US 9,035,552 B2, Method and Device for Transporting Vacuum Arc Plasma // Vasylyev V. V., Strel'nitskij V. E.; assignee: National Science Center «Kharkov Institute of Physics and Technology» – No. PCT/UA2011/000105; Date: 04.08. 2013; Date of Patent: 05.19.2015.

[8] Vasylyev, V.V., Luchaninov, A.A., Strel'nitskij,V.E. High-productive source of the cathodic vacuum-arc plasma with linear filter(2014). Problems of Atomic Science and Technology,"Vacuum, pure materials, superconductors».89(1), 1-4.

[9] Vasylyev, V.V., Strel'nitskij,V.E. Features of the morphology of coating surfaces deposited from a filtered vacuum-arc cathode plasma to ferromagnetic substrates(2012) Physical surface engineering.Vol.10 (2), 162-172(in Russian).

[10] Vasylyev, V.V.,Luchaninov, A.A.,Strel’nitskij,V.E. Deposition of the diamond-like coatings on the surfaces of the ring-shaped dry gaseous seals made of SiC for use in high pressure compressors(2018).Problems of Atomic Science and Technology,. “Vacuum, purematerials, superconductors», 111(1), 88-92. (In Russian).

[11] Wang, R., Yang, Z., & Zhang, T. (2023). "Novel approaches in filtered vacuum arc plasma deposition for biomedical DLC coatings: A technical review." Surface Engineering, 39(4), 481-497.

[12] Zhang, W., Li, Y., & Chen, J. (2023). "Multilayer DLC coating architectures for improved tribological performance in hip joint replacements." Tribology International, 177, 107986.