Acta Polytechnica CTU Proceedings **8**:20–23, 2017
doi:10.14311/APP.2017.8.0020

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MECHANICAL PROPERTIES OF Cr-DLC LAYERS PREPARED BY HYBRID LASER TECHNOLOGY

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Abstract. Diamond like carbon (DLC) layers have excellent biological properties for use in medicine for coating implants, but poor adhesion to biomedical alloys (titanium alloys, chromium alloys and stainless steel). The adhesion can be improved by doping the DLC layer by chromium, as described in this article. Chromium doped diamond like carbon layers (Cr DLC) were deposited by hybrid deposition system using KrF excimer laser (deposition diamond like carbon - graphite target) and magnetron sputtering (deposition chromium - chromium target). Carbon and chromium contents were determined by wavelength dispersive X-ray spectroscopy. Chromium content of Cr DLC layers was 0, 1, 2, 4-5 and 15 17 at.%. The topology and roughness of layers were studied using atomic force microscopy. Roughness of chromium doped DLC layers was measured on Si substrates about 0.2-0.7 nm and on metallic substrates about 1-6 nm. Mechanical properties were studied by nanoindentation. Hardness and reduced Young's modulus were reduced with rising the Cr content. Hardness and reduced Young's modulus reached from 15.0 GPa to 31.2 GPa and from 172.7 to 271.5 GPa, respectively. Films adhesion was determined by scratch test and reached 19 N for titanium substrates and for highest Cr concentration. Good adhesion to biomedical alloys and high DLC hardness will help to progress in the field of implantology.

1. Introduction

Tissue grows around and into all forms of carbon [1–3]. Diamond-like carbon (DLC) layers have potential applications in orthopaedics, cardiology, ophthalmology, nephrology, and other fields of medicine [1, 4–9]. DLC layers are ideal for coating stents, heart valves, because of its excellent haemocompatibility and reduced thrombus formation, and for joint implant protective films [10].

DLC have unique mechanical (high hardness $= 1 - 80\ GPa$), tribological (low friction coefficient $\approx 0.01 - 0.7$, high wear resistance), optical (transparency in IR and VIS), topological (nanosmooth), and biological (chemical inertness, no cytotoxicity, good biocompatibility and haemocompatibility) properties [1, 11–13]. These properties can be modified and adapted for specific medical applications by using doping.

Dopants in DLC layers produce changes in hardness, coefficient of friction, resistance to wear, surface roughness, adhesion, and even biocompatibility and biological properties [13, 14]. The scheme of typical dopants and supposed change of DLC properties is in Figure 1 [13].

The influence and properties of a lot of proposed elements was successfully tested and characterized till now. In our case, the doping of chromium was used to change the mechanical properties and increase the adhesion DLC layers to biomedical alloys.

2. Experimental

2.1. Depositions

Chromium doped diamond like carbon layers (Cr-DLC) were deposited by hybrid deposition system consists of pulsed laser deposition (PLD - KrF excimer laser) and magnetron sputtering (MS). PLD technique was used for the deposition of DLC and MS technique for doping chromium. Deposition parameters are summarized in Table 1. Figure 2 shows the schematic diagram of the deposition system used to prepare the Cr-DLC film samples. Silicon (100) wafers and biomedical alloy (Ti-6Al-4V) were used as substrates. Ti-6Al-4V substrate was polished before deposition (roughness was 7.7 ± 1.2 nm).

2.2. Characterization

Chromium content of Cr DLC layers was determined by a wavelength dispersive X-ray spectroscopy (WDS - JEOL 840). More information can be found in [12].

Adhesion - Macro scratch tester (REVETEST Scratch Tester - CSM co.) was used to determination of the adhesion [15]. Scratch test parameters are summarized in Table 2. An optical microscope was used to evaluate the critical force.

Hardness and reduced Young's modulus - Nanohardness was measured on the NanoTest system with

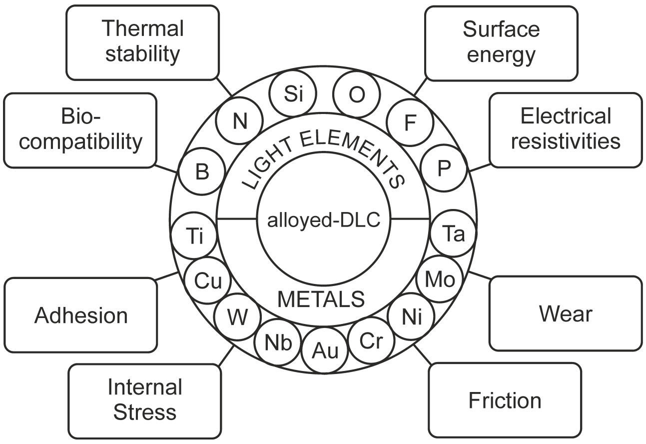

Figure 1. Scheme of proposed doping elements of DLC [13].

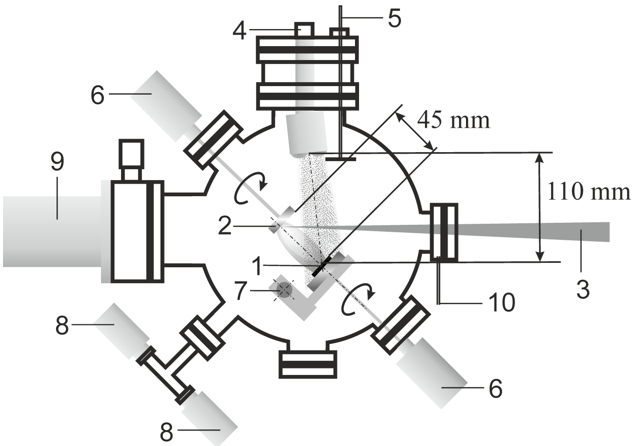

Figure 2. The scheme of hybrid deposition system: 1 - Substrate, 2 - Carbon target, 3 - Laser beam, 4 - Magnetron with Cr target, 5 - Magnetron stopper, 6 - Rotation, 7 - RF, 8 - Vacuum gauge, 9 - TBM, 10 - Gas flow (Ar).

	Laser repetition rate [Hz]	Laser energy density [J·cm^{-2}]	Magnetron power [W]	WDS Cr content [at. %]	Hardness [GPa]	Reduced Young's modulus [GPa]
Cr-DLC-0	20	8	0	0	31.2 ± 1.4	271.5 ± 16.8
Cr-DLC-1	40	8	40	1	24.8 ± 1.1	236.3 ± 11.4
Cr-DLC-2	20	8	40	2	21.8 ± 0.8	217.7 ± 4.4
Cr-DLC-3	10	8	40	4 - 5	17.5 ± 0.9	183.9 ± 9.5
Cr-DLC-4	3	8	40	15 - 17	15.0 ± 0.6	172.7 ± 3.4

Table 1. Deposition parameters, chromium content and mechanical properties of DLC and Cr doped DLC layers.

Indenter parameters	Diamond type, Rockwell, radius: 200 μm
Normal load	Linearly ramped - minimum 1 N and maximum 30 N
Scratch length	8 mm
Scratch speed	10 N·min^{-1}
Critical loads Lc_2	Edge spallation
Critical loads Lc_3	Spallation inside the groove

Table 2. Scratch test parameters.

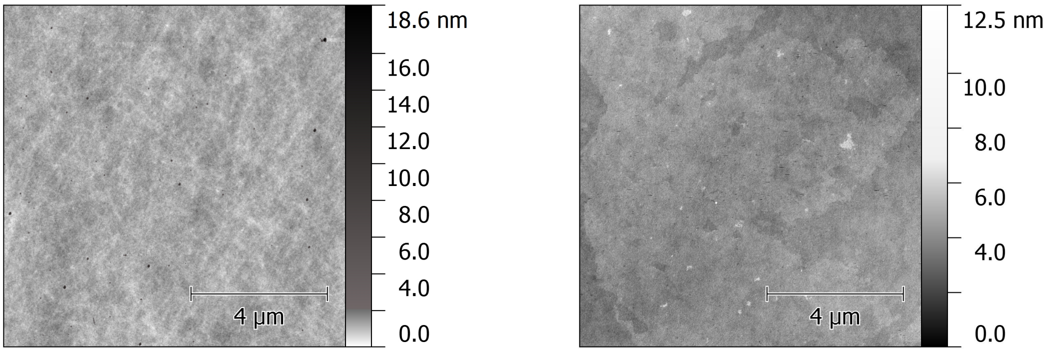

Figure 3. AFM scans of the surfaces. Samples with various concentrations of chromium: AFM of pure DLC (left), DLC with 15-17 at. % of Cr (right).

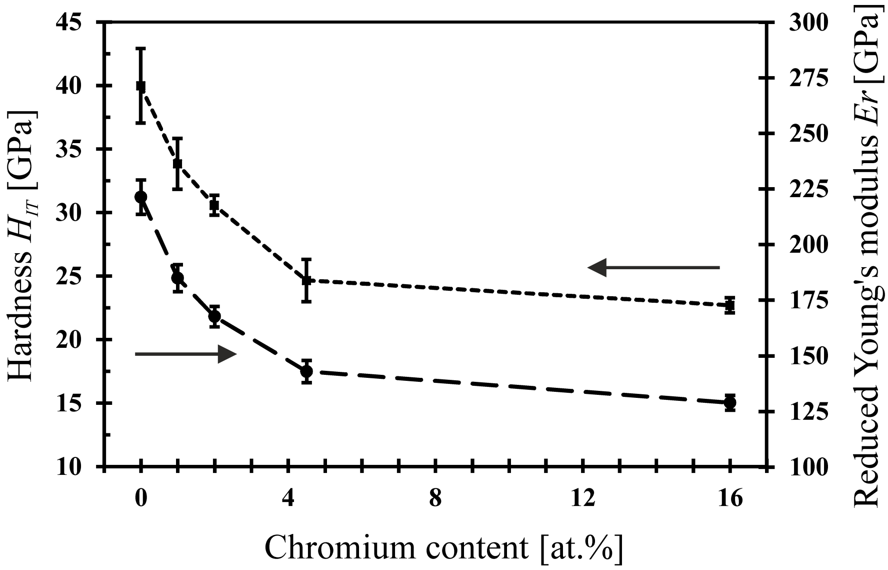

Figure 4. Hardness and reduced Young's modulus of the DLC and Cr-DLC films with various Cr contents.

a Berkovich diamond tip. Maximum indentation depth of the indenter was 10 % (about 60 nm), to minimize the effect of substrate on the resulting hardness. The presented values are averages of 20 measurements. Hardness and reduced Young's modulus was calculated according to [16].

3. Results and discussion

Cr DLC films were synthesized using hybrid system (magnetron sputtering and pulsed laser deposition) of carbon and chromium target. In dependence with deposition conditions the Cr content moved from 1 at. % to ~ 17 at. % (WDS), and the thickness was 800 ± 100 nm on titanium substrate and 100 ± 30 nm on silicon substrate. AFM showed that the layers were smooth, but with small amounts of random droplets - see Figure 3. Roughness (R_a) were calculated from 10×10 μm area (software NOVA P9) [15]. R_a of our layers was measured on Si substrates about 0.2-0.7 nm and on metallic substrates about 1-6 nm.

Adhesion - Diamond like carbon have poor adhesion to metal alloys [1]. Baragetti [17] presented that diamond like carbon on aluminium alloy had critical load (Lc_3) about 3.5 N. Two scratches were made in each layer and the adhesion was evaluated using a CCD micrograph. Due to the substrate roughness caused by polishing, the character of load trace was not monotonous. This fact complicated the determination of critical load parameters. The first spallation presence was used as the critical load value. Results of scratch tests measurement showed that the critical load (Lc_3) for the pure DLC films was about 14 N and for Cr DLC films ranged from 15.3 N (1 at. %) to 19 N (15-17 at. %). The same trend was observed in [15]. The higher value of adhesion for pure DLC layers (compared to Baragetti group) can be due to the application of the RF cleaning before the deposition and a further increase was reached by chromium doping.

Hardness and reduced Young's modulus - The applied maximum load for the film was observed at the depth of 60 nm. Nanoindentation also makes it possible to specify the modulus of elasticity. The determination of the reduced Young's modulus for the instrumentally performed hardness test is based on the inclusion of the elastic strain of the given material and also of the testing indenter. The hardness and reduced Young's modulus values for the diamond-like carbon film were determined to be ∼ 31.2 and ∼ 271.5 GPa, respectively - see Table 1 and Figure 4. Hardness of Cr-DLC layers prepared by PLD+MS decreased from 24.8 GPa (1 at. %) to 15.0 GPa (15-17 at. %), as the Cr content increased, as well as reduced Young's modulus of 236.3 GPa (1 at. %) to 172.7 GPa (15-17 at. %) - see Table 1 and Figure 4.

4. Conclusion

This paper focuses on doped DLC films (Cr-DLC films on silicon and titanium alloy). The layers were prepared using hybrid laser technology (PLD+MS). The Cr content moved from 1 at. % to ∼ 17 at. %. AFM showed that the layers were smooth, but with small amounts of random droplets. With the Cr content rise, both the hardness and Young's modulus were reduced from 31.2 GPa to 15.0 GPa and 271.5 GPa to 172.7 GPa, respectively. Scratch test showed that critical load Lc_3 rose with Cr content and that the maximum critical load Lc_3 was 19 N. Good adhesion on biomedical alloys and high hardness DLC will help to progress in the field of implantology.

Acknowledgements

This work has been supported by the Grant Agency of the Czech Technical University in Prague (grant No. SGS16/111/OHK4/1T/17 and SGS16/190/OHK4/2T/17), the Grant Agency of the Czech Republic (grant No. GA15 05864S) and the Ministry of Education, Youth and Sports of the Czech Republic (grant No. LO1409).

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