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DLC/TI THIN FILMS PROPERTIES PREPARED BY HYBRID LASER TECHNOLOGIES

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Abstract. Layers of diamond-like carbon are usable in many fields of industry as well as in medicine. Many scientific groups have worked with different types of deposition techniques to prepare DLC layers with improved or unique properties. The DLC properties could be improved by various dopations. In this study, we focused on DLC layers doped by titanium, prepared by hybrid laser depositions. Two techniques were used: Dual pulse laser deposition (DualPLD) and pulse laser deposition in combination with magnetron sputtering (PLD/MS). Preliminary tests for morphology, wettability, adhesion, hardness, corrosion, friction and wearability were examined. DLC samples were prepared on Si(100) wafer and on Ti6Al4V alloy substrates with titanium concentration from pure up to 25 at.%. Friction of the prepared layers ranged from 0.09 to 0.18. The films exhibited very low wear for loads 1 N and 2 N. The tested pin wear grew with decreasing titanium dopation. The measurements of the contact angle and determination of surface free energy were done for water, diiodomethane and ethylene glycol. Hardness and Young's modulus decreased with higher titanium dopation, on the other hand adhesion improved with increasing amount of titanium in film.

Keywords: PLD, DLC, titanium, surface properties, laser deposition, magnetron sputtering.

1. Introduction

In this study, we focused on the changes in the mechanical and corrosion behavior with various amount of titanium in DLC/Ti thin films. Two techniques for dopation of titanium were used [1–3]. The first technique was based on pulsed laser deposition (excimer laser, KrF, $\lambda = 248$ nm) combined with DC magnetron sputtering. The second technique was dualPLD. Laser fluency was 8 J/cm^2 for DLC deposition and 5 J/cm^2 for metal dopant. Power of magnetron was from 40 W to 300 W for metal dopant.

We studied behavior of layers for Ti concentration from 1 at.% to 25 at.%. Si(100) and Ti6Al4V alloy were used as substrates. Prepared films were characterized with focus on their basic physical properties, such as crystallinity by XRD, morphology by AFM and mechanical profilometry, chemical bonding nature by WDX, surface free energy by contact angle. Hardness and Young's modulus were studied by nanoindentation. Macro adhesion was studied up to 30 N. Wearability and tribological properties were studied as well. The content of sp^3 bonding was studied by XPS. Special focus was given on tribological properties. Corrosion rates were measured as function of Ti concentration.

2. Experimental

Wearability test was performed by tribometer (Anton Paar) with linear movement. Chromium steel testing ball with 6 mm diameter was used. Speed of the testing ball was 5 cm/s, total testing length 10 m, used loads during tests were 1 N and 2 N. The tests were performed as dry. The friction was determined from the test records.

Nanoindentation tests were performed on all samples for determination of hardness and elastic modulus. All measurements were implemented on layers with thickness 500 nm and the indentation depth was less than 10 % of the layers thickness. For more details, see [4].

Adhesion of the films was tested for samples on Ti6Al4V substrates. We tested samples by progressive load from 1 N to 30 N. Three types of critical forces were evaluated. At least two scratches for each layer were tested. For more details, see [4].

Wettability was measured by three liquids: distilled water, diiodomethane and ethylene glycol, by contact angle measurement system (DSA100, Krüss Company). Surface free energy was determined by Drop shape analysis software with Fowkes method. The volume of droplets was (0.4 ± 0.1) ml. The measurement technique was sessile droplet and static contact angle. Each sample was tested at least on three

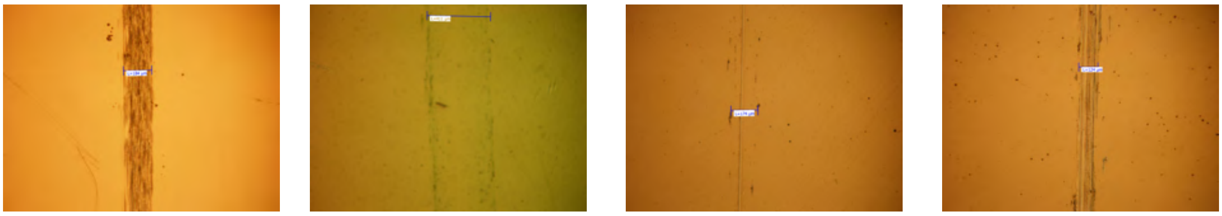

Figure 1. From left wearability of the Ti6Al4V substrate and samples Ti:DLC7(pure DLC), Ti:DLC10 (5 at.% Ti) and Ti:DLC12(25 at.% Ti). The figures are captured at magnification 200x.

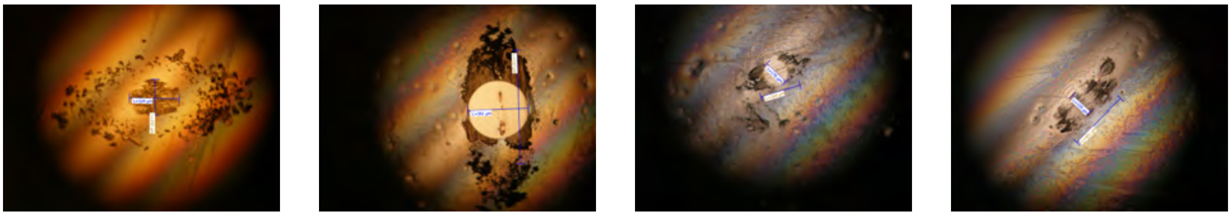

Figure 2. Wearability of the testing ball after tests for Ti6Al4V substrate and for samples Ti:DLC7(pure DLC), Ti:DLC10 (5 at.% Ti) and Ti:DLC12(25 at.% Ti). The figures are captured at magnification 200x.

Dual PLD	0 at.% Ti	1 at.% Ti	3 at.% Ti	5 at.% Ti	10 at.% Ti	25 at.% Ti
	0.12	0.14	0.13	0.12	0.11	0.09
PLD/MS	0 at.% Ti	1 at.% Ti	3 at.% Ti	5 at.% Ti	10 at.% Ti	25 at.% Ti
	0.13	0.15	0.14	0.18	0.15	0.16

Table 1. Friction on the layers of Ti:DLC prepared by dualPLD and PLD/MS methods.

different places. For each liquid, a new sample was used. From each droplet, series of 15 pictures were evaluated. Laplace profile fitting was used. Tested samples were on Si (100) and thickness of the films was around 100 nm.

We finished preliminary tests of the corrosion behavior as function of the amount of the titanium dopant in the DLC layers. We used potentiodynamic measurement and Tafel plots for I_{corr} determination and then for corrosion rate determination.

3. Results

Contents of the titanium dopant in the DLC layers were determined by WDX and confirmed by XPS. Prepared samples concentrations were 0, 1, 3, 5, 10 and 25 at.% of titanium. DualPLD technique was better to reach the desired dopants concentration. The XRD tests confirmed that all the samples were amorphous with detection of Ti and TiC phases for the highest Ti concentration (10 and 25 at.% Ti). Thickness of the prepared layers were approximately 500 nm, for layers on Ti6Al4V substrates and 100 nm for layers on Si (100). AFM was used for morphology determination. Both methods produced smooth layers around 1 nm, just for dualPLD method roughness increased for 10 and 25 at.% Ti up to 5 resp. 15 nm.

Wearability tests have been done for loads 1 N and 2 N. For these loads, there were no damage observed on samples. The wearability of the ball decreased with increased amount of titanium in layers. Examples are on the figures 1 and 2. From comparison of the coated and uncoated materials, the uncoated materials were seriously damaged. The friction for pure DLC layers was 0.125 ± 0.05. For dual PLD method we observed slight increase in friction for lower concentration up to 0.14 and then decrease to 0.09. For PLD/MS method we observed slight increase for dopated layers but without clear trend, for more detail see table 1.

The hardness for pure DLC layers starts at (31 ± 1) GPa and was decreasing with increasing of the titanium content to 12 ± 2 GPa for 25 at.% of titanium. The decrease was slightly quicker for PLD/MS technique. The same behavior we observed for elastic modulus with the highest values around 250 GPa for pure DLC and decrease to 150 GPa for 25 at.% Ti content of titanium practically same for both methods.

The adhesion values seemed to increase with content of the titanium with exception for highest concentration of titanium for PLD/MS method. Critical force FC3 started at 5.6 N for pure DLC and increased to 18.4 N for dualPLD technique for 25 at.% Ti. For PLD/MS technique critical force was increasing up to 20.2 N for 10 at.% Ti but for 25 at.% Ti it reduced to 9.2 N. This could be connected with lower hardness of titanium.

The contact angle for water was in range from 57.7° to 71.5° for dual PLD method and from 53.8° to 70.0° for PLD/MS method. CA for ethylene glycol was in range from 34.5° to 42.8° resp. from 30.1° to 44.0° and for diiodomethane the range was from

34.9° to 38.3° resp. 32.0° to 36.4° for dual PLD resp. PLD/MS method. The results showed no trends in CA in correlation with titanium content in layers. From the free surface energy calculation we can conclude that all the tested layers are dominantly disperse.

From the corrosion tests, the high concentration of the titanium dopants seemed to improve corrosion resistivity against the pure DLC. For various concentrations there were no clear trends observed and further tests should be performed before any conclusions could be made.

4. Conclusion

We prepared diamond-like carbon samples doped by titanium in concentration up to 25 at.% by two deposition techniques dual PLD and PLD/MS. We made standard testing as XRD, WDX, XPS, AFM, profilometry measurements etc. The main focus was put on mechanical and tribology testing.

For both techniques, the hardness and elastic modulus were decreasing with higher content of the titanium, as we expected. There were no significant changes based on used methods. We observed better adhesion related to increasing titanium concentration in films. This is connected with lower compression stress due dopation. On the other hand, for the highest concentration for PLD/MS there was lower adhesion observed, which could be connected with lower hardness. Wearability test showed no damage to the coatings at load 1 N or 2 N (no matter on Ti concentration) but wear of the testing ball was significantly higher for lower Ti concentration in films. This is probably connected to higher layer hardness. Tests will be continued with higher loads. For corrosion behavior, only preliminary tests are available. Corrosion resistance was better for higher titanium amounts, when the highest concentration had up to three times better Icorr parameter. For wettability, there are no clear trends based on titanium content. All layers are dominantly disperse.

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