

Optimisation of mechanical properties of plasma deposited graded multilayer diamond-like carbon coatings

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Multilayer amorphous diamond-like carbon films with graded silicon and oxygen content exhibiting hardness in the range from 16 to 24 GPa were deposited using low pressure PECVD. The films were optimised for deposition on steel substrates. To evaluate the impact resistance of graded amorphous carbon films in dynamic loading wear applications an impact test has been used. During testing the specimen was cyclically loaded by tungsten carbide ball that impacts against the coating surface. Results of these tests show usability of coatings in dynamic load and enable to optimize the design of the coating/substrate system for the particular use. The films with optimum structure exhibited very good resistance against delamination, high fracture toughness and low friction coefficient. The principal new finding concerns the fracture toughness of the film and the interfacial adhesion. Upon impact test the films remain attached to the substrate, even the impact load exceeding 200 N. The films can sustain compression strains without debonding or spalling.

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1. Introduction

For optimisation of performance of the coating it is necessary to optimise the following materials parameters: the elastic modulus, hardness, surface strength, film fracture toughness, film intrinsic stress, impact resistance and film-substrate adhesion. A rigid, hard coating reduces the maximum radial tensile strength in the substrate and this reduction increases with the modulus and thickness of the coating. However, it is accompanied by a substantial increase of the maximum tensile stresses in the coating itself [1,2]. Moreover, the differences in property characteristics of coatings and the substrate may result in tangential stresses at the interface. Elastic contact between brittle film and indenting particles may lead to the formation of Hertzian cone cracks. These stresses arise from the radial tensile stresses around the contact area. The resulting strain is difficult to be relaxed and it builds up with increasing film thickness. When the elastic recovery force of the film exceeds a critical value, the stresses in the film are relaxed by cracking or wrinkling, which results in spontaneous delamination. Gradients in elastic properties of a coating can provide substantial improvements in the resistance to indentation. The variation in elastic properties can be achieved by composition change of the film simply adjusting the deposition conditions during the film growth. We developed nanocomposite DLC films with graded silicon

and oxygen content exhibiting enhanced fracture toughness, high surface hardness, low compressive stress and high thermomechanical stability. We proposed to protect the substrate surface with a multilayer coating with gradient in elastic modulus and hardness in order to suppress the indentation induced cracking and delamination. The films were optimised for deposition on steel substrates. To evaluate the impact resistance of graded amorphous carbon films in dynamic loading wear applications an impact test has been used [3,4]. During testing the specimen was cyclically loaded by tungsten carbide ball that impacts against the coating surface.

2. Experimental

The modified DLC films were prepared in r.f. capacitive discharges at low pressures (8-20 Pa). The reactor was a glass cylinder with two, inner parallel plate electrodes, made of graphite. The bottom electrode, with the diameter of 150 mm, was capacitively coupled to the r.f. generator (13.56 MHz) via a blocking capacitor. The substrates, for deposition were placed on the r.f. electrode, the r.f. voltage of which was superimposed with a negative d.c. self-bias. The r.f. power was 50 W. The corresponding self-bias voltage varied from -250 V to -300 V depending on the gas mixture and deposition pressure. The modified DLC films were prepared from a

mixture of methane, hydrogen and HMDSO (hexamethyldisiloxane - $\text{Si}_2\text{OC}_6\text{H}_{18}$). The flow rate of hydrogen was 0.35 sccm and the CH_4 flow rate was 1.4 sccm. The HMDSO flow rate Q_{HMDSO} varied from 0 to 0.87 sccm. The graded DLC film was deposited on several types of substrates (silicon wafers, glass, steel) with graded decrease of the HMDSO content in the deposition mixture keeping the flow rates of methane and hydrogen at 1.4 sccm and 0.35 sccm, respectively.

The indentation resistance of the modified DLC films was studied using the instrumented indentation test based on analysis of the loading/unloading hysteresis. The tests were carried out by means of Fischercope H100 tester equipped with a Vickers four-sided diamond pyramid. The applied load was registered as a function of indentation depth during loading/unloading cycles. The instrumented indentation technique enables to determine the elastic and plastic part of the indentation work (W_e and W_{pl}), the effective elastic modulus ($Y = E/(1-\nu^2)$, where E is the Young's modulus and ν is the Poisson's ratio of the films) and the hardness of the film. In the case of the indentation testing of thin films, the measured properties depend on the indentation depth due to combined response of the coating and the substrate. Therefore, the measured elastic modulus and hardness values were corrected for the substrate influence. The morphology of the indentation prints was studied by optical microscopy (SEM), scanning electron microscopy and atomic force microscopy (AFM).

The instrumented indentation test enables also the determination of the fracture toughness of the coating/substrate system. The fracture toughness of films and film/substrate interface could be estimated from the analysis of the energy dissipated during the indentation according to Malzbender [5, 6]. The area between the loading and unloading curves gives the total amount of irreversible dissipated indentation work W_{irr} . The fracture of the coating/substrate interface appears immediately as a jump on the loading curve. From the loading/unloading hysteresis we can obtain the indentation work W_{fr} needed for creation of delaminated area with radius c . The interfacial energy release rate G_{int} can be obtained on the basis of W_{fr} . The interfacial fracture toughness K_{int} may be calculated according to following formulae:

$$G_{\text{int}} = \frac{\Delta W_{\text{fr}}}{\pi c^2}, \quad K_{\text{int}} = \sqrt{G_{\text{int}} E_{\text{int}}}, \quad (1)$$

$$\frac{1}{E_{\text{int}}} = \frac{1}{2} \left(\frac{1}{E_f} + \frac{1}{E_s} \right) \quad (2)$$

Here E_{int} is the so called interfacial elastic modulus defined by Hutchinson and Suo [7]. E_f is the film elastic modulus and E_s the substrate elastic modulus.

The atomic composition of the prepared films was studied with combined RBS and ERD analysis.

The internal stress was determined by silicon wafer curvature measurements. The modification in radius of

curvature after film deposition is linked to the stress in the film via the Stoney equation:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \cdot \frac{t_s^2}{t_f} \cdot \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (3)$$

Where E_s and ν_s are the Young's Modulus and the Poisson's ratio of the substrate, t_s and t_f are the thicknesses of the substrate and the deposited film, respectively, R_0 and R are the radius of the system (substrate + film) before and after the deposition.

Dynamic impact wear tester [4] developed in Institute of Scientific Instruments ASCR in collaboration with Brno University of Technology was used to evaluate the wear resistance of the graded multilayer diamond-like carbon films. Setting of the impact tester: the impact force can be adjusted from 150 N to 600 N. The tungsten carbide ball 5.0 mm in diameter with guaranteed geometry and surface roughness was used for impact testing. After each the test, wear scars were evaluated by means of profilometer Talystep (Taylor-Hobson) and confocal microscope LEXT OLS 3100 (Olympus).

3. Results and discussion

Diamond-like carbon thin films with various silicon and oxygen content were prepared using methane, hydrogen and hexamethyldisiloxane ($\text{Si}_2\text{OC}_6\text{H}_{18}$, HMDSO) mixtures. In order to evaluate the effect of HMDSO admixture on mechanical properties of prepared films, complex study on their indentation and wear resistance was done. The summarisation of the results is given in Tab. 1.

Table 1. Summarisation of the results on mechanical properties of films prepared with various HMDSO flow rates Q_{HMDSO} . H – indentation hardness, E – elastic modulus, K_{int} – interfacial fracture toughness, σ – intrinsic stress.

i	Q_{HMDSO} [sccm]	H [GPa]	E [GPa]	K_{int} [MPam ^{0.5}]	σ [GPa]
1	0	23 ± 2	150 ± 5	0.08 ± 0.03	-1.73
2	0.11	22 ± 1	125 ± 5	0.10 ± 0.04	-1.65
3	0.12	20 ± 2	130 ± 5	0.12 ± 0.05	-1.67
4	0.25	20 ± 1	123 ± 5	0.45 ± 0.05	-1.35
5	0.38	19 ± 1	117 ± 5	1.15 ± 0.05	-0.35
6	0.40	18 ± 2	115 ± 2	0.97 ± 0.05	-0.43
7	0.46	17 ± 2	108 ± 2	1.08 ± 0.04	-0.37
8	0.51	16 ± 1	95 ± 2	0.88 ± 0.07	-0.27
9	0.53	15 ± 1	93 ± 5	0.93 ± 0.05	-0.15
10	0.89	14 ± 2	73 ± 5	0.15 ± 0.03	-0.04

In order to evaluate the true mechanical properties of the coatings, it was important to separate the substrate

contribution from the experimental load-displacement data. The film hardness values listed in Tab.1 were obtained from the total coating-substrate indentation response using the semi-empirical approach proposed by Bhattacharya and Nix [8].

The fracture toughness was calculated according to Malzbender from formulas (1) and (2).

On the basis of above described investigation coatings with graded change in mechanical properties from polymer-like to diamond-like character were prepared. The graded change was achieved decreasing the HMDSO content in the gas mixture from 25% to zero. The layers, which were used for composition of the graded coating are listed in Tab. 1. The thicknesses of the composing layers were set proportionally to their fracture toughness (see Tab.1.). The film composition and the thicknesses of particular layers d_i were chosen on the basis of the following expressions

$$d_i = 0.2K_{int}(10-i) \text{ and } d_{tot} = \sum_{i=1}^9 d_i \quad (4)$$

where d_{tot} is the total film thickness in micrometers, i refers to the succession of the layers from the interface, $K_{int}(10-i)$ is the fracture toughness of the layer with number of order $N=10-i$ according to Table 1.

The dynamic impact wear tester has been used to evaluate the impact resistance of the graded composite coatings deposited on steel substrate. After each the test, wear scars were evaluated by means of confocal microscope and profilometer and the volume of the created craters was calculated.

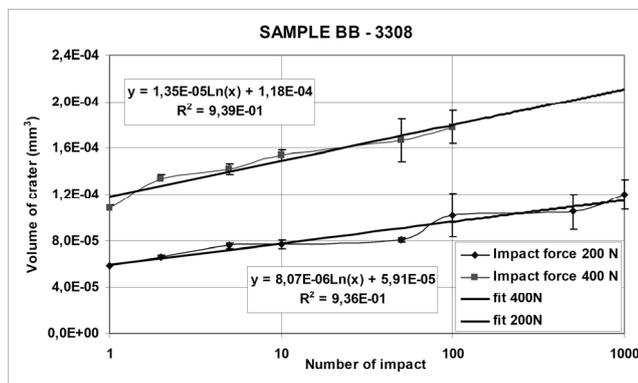


Fig. 1. Mean values of crater volume versus impact force 200 N and 400 N.

In Fig. 1 the dependences of the crater volumes created during testing of the coated sample on the number of impacts obtained at impact force 200 N and 400 N are compared. Each measurement was five times repeated at the given number of impacts and at the given impact force. The deviation from the mean values was indicated in graph by error bars. The mean part of the dependence represents the usable area of the tested coating/substrate system, in particular the dynamical load [4] regime, which is given first of all by the impact force, the size and the material properties of the indenter. This part we can fit

using linear regression (in semi-logarithmic coordinate). The corresponding values of coefficients of determination R^2 are given in Fig. 1. The slope of the straight line is then directly proportional to the wear of the tested system, thus indirectly proportional to its dynamic resistance at given conditions. Plastic-elastic deformation in the region from one to five impacts corresponds primarily to the plastic deformation of the substrate.

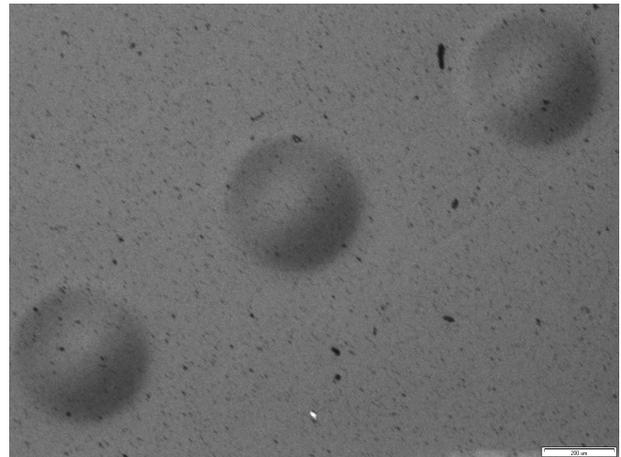


Fig. 2. The optical image of craters created with impact force of 200N obtained by means of optical microscopy in Nomarski contrast. The marker in the bottom right corner of the image indicates 200μm.

In Fig. 2 the optical image of craters obtained in Nomarski contrast are shown. This image demonstrates that the creation of the crater at loads of 200 N did not cause delamination or cracking of the coating around the crater even after long time storage.

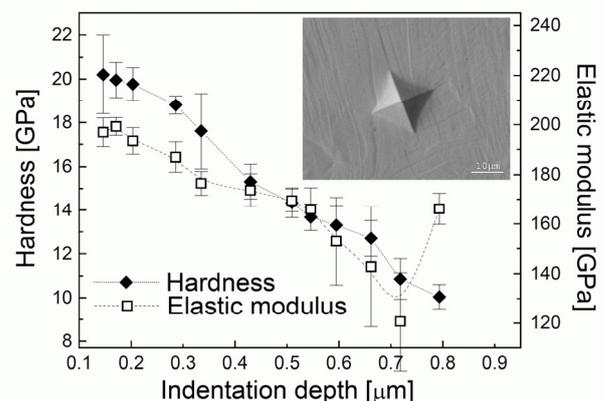


Fig. 3. The hardness and elastic modulus dependence on the indentation depth of the coating deposited on steel substrate with graded composition (4) together with the SEM image of the indentation print obtained at maximum indentation load of 1N.

The hardness and elastic modulus dependence on the indentation depth of the film deposited on steel substrate with graded composition (4) is given in Fig. 3 together

with the SEM image of the indentation print obtained at maximum indentation load of 1N. The hardness of the coating-substrate system had monotonically decreasing character due to decreasing hardness of the composing layers and due to the substrate influence at higher loads.

The depth dependence of the composite elastic modulus of the coating-substrate system had more complicated character. First it decreased monotonically with decreasing elastic moduli of the composing layers. Approaching the coating-substrate interface it increased because of the substrate influence. The elastic modulus of the substrate was higher than the elastic modulus of the composing layers at the interface. This had a beneficial effect on the good adhesion and impact resistance of the prepared graded coating.

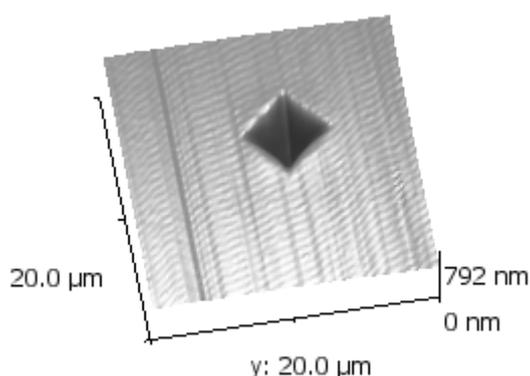


Fig. 4. The AFM image of the indentation print with indentation depth of 792 nm.

The fracture toughness of the film was excellent. The film could stand indentations with maximum loads of 1N without creation of cracks at the corners of the indentation prints or in the inner part of the imprint as it is demonstrated on the SEM image in Fig. 3 or in AFM image in Fig. 4. The AFM image of the indentation print in Fig. 4. demonstrates the high fracture toughness of the prepared coating. For plastic indentation depth of 792 nm (the maximum indentation depth was higher due to contribution of the elastic deformation) it was not possible to observe creation of cracks around the indenter, nor even in the inner part of the imprint.

4. Conclusion

Multilayer amorphous diamond-like coatings were prepared with graded silicon and oxygen content in order to optimize the coating performance to the steel substrates. The wear rate of the studied coating had a very low value for the impact force of 200 N, so the dynamic resistance of the prepared system is relatively high. This finding corresponds with the results of nanoindentation measurements. The small spread of measured values and the shapes of the craters correspond to the small wear rate, in particular at impact forces lower than 400N. Interfacial cracking for higher loads is the predominant damage mode. Upon indentation test the films remain attached to the substrate, even the impression load exceeding 1N. The films can sustain high compression strains without debonding or spalling.

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References

- [1] A. E. Giannakopoulos, International Journals of Solids and Structures **39**, 2495 (2002).
- [2] A.E. Giannakopoulos Thin Solid Films **332** (1-2), 172 (1998)
- [3] O. Knotek, B. Bosserhoff, A. Schrey, T. Leyendecker, O. Lemmer, S. Esser: Surface and Coatings Technology **54/55**, 102 (1992).
- [4] Engel P.A. et al.: Impact wear of multilayered electrical contacts, Wear, **181-183**, 730 (1995).
- [5] J. Malzbender, G. de With, Surface Coating and Technology, **135**, 60 (2000).
- [6] J. Malzbender, J. M. J. den Toonder, A. R. Balkenende, G. de With, Materials Science and Engineering R **36**, 47 (2002).
- [7] Z. Suo, J. W. Hutchinson International Journal of Fracture **43** (1), pp. 1-18
- [8] A. K. Bhattacharya, W. D. Nix, International Journal of Solids and Structures **24**(12), 1287 (1988) p.

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