NANOHARDNESS OF WC/C COATING AS A FUNCTION OF PREPARATION CONDITIONS

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1. Introduction

Amorphous hydrogenated carbon (a-C:H) coatings, including diamond-like coatings (DLC), which are rich in sp^3 content, exhibit very high hardness, low friction and other properties, which make them attractive for hard protective and wear resistant films, coatings on magnetic storage devices, micro-electromechanical systems and others[1,2]. The amorphous carbon films can be deposited by variety of methods including ion-beam deposition, sputtering technique, plasma enhanced chemical vapor deposition (PECVD), pulsed laser deposition and the magnetron sputtering. Magnetron sputtering is possibly the most common and in that case, Ar^+ ion bombardment of a carbon target is used and a bias voltage is applied to the substrate. However, one of the problems of such coatings is a poor adhesion of the sputtered carbon films due to high intrinsic compressive stresses. Several approaches have been developed to reduce the stresses: post-deposition annealing, formation of the multilayer films consisting of sequential rich in sp^2 and sp^3 content layers[3,4]. Metal doped carbon coatings are also an interesting group which can be tailored into nanocomposite structure with special properties. Although DLC and various metal-doped DLC nanocomposite coatings have been extensively studied, W-doped diamond-like carbon films have received comparatively little attention. WC exhibits relatively high hardness and its combination with the properties of amorphous carbon in the nanocomposite structure results in a coating with low friction coefficient and good wear resistance[5]. However, similarly as pure DLC, W based-carbon coatings some drawbacks, including a poor adhesion with common substrate materials[6], low fracture toughness (35 J m^{-2}, ref.[7]) and the effect of hydrogen in the structure on the friction behavior of sp^2 rich coating. There are only a few studies on carbon based coatings without the influence of hydrogen. Some aspects of the tribological behavior of such non-hydrogenated metal containing DLC coating studied here by Camino[8], Yang[9,10], Zeng[11] and Konca[12]. The hardness values ranging from 1600 HV to 3300 HV were obtained despite relatively high sp^2 content by increasing bias voltage from 20 V to 90 V (ref.[9]) due to nanocomposite structure[10]. Thus, the purpose of the work is to investigate the process of the deposition conditions on the formation and nanohardness of non-hydrogenated WC/C coatings.

2. Experimental procedure

The studied WC/C films were deposited on the polished high speed steel (HSS) and Si (100) substrates using combined PVD-PECVD techniques. The substrates were cleaned by the Ar ions prior to the deposition. In some cases, a Ti sublayer was deposited using an electron gun. Then, the vapors of the W and C from a precursor were introduced into the main chamber, they were ionized and accelerated toward the substrate with the negative bias. The main deposition parameters were total gas pressure in the chamber, bias voltage applied to the substrate and current density at the substrate surface. Four series of coatings were prepared varying these parameters to optimize the conditions. Thin Ti interlayer has been deposited on the substrate in at the beginning in several cases to achieve better adhesion with the substrate. Later, Ti layer was excluded and the WC/C film was deposited directly on the substrate. Phase composition was investigated using X-ray diffraction. Film thickness was measured and the surface morphology and structure were studied in SEM on the broken cross sections. The elastic properties of the films were conducted using a nano-indenter UMIS 2000. The hardness and the reduced elastic modulus of the films were measured with a Berkovich tip, which was forced into the coating using a coil and magnet assembly. The maximum load was up to 1 mN or 5 mN in 20 steps followed by a 5 sec dwell and unloading in 10 steps. Nanohardness was determined from the penetration depth at the maximum load and the reduced elastic modulus from the unloading part of the curve according the method of Oliver and Pharr. At least 15 indentations were performed automatically for each coating and the average values were calculated.

3. Results and discussion

The variation in the deposition conditions and the coating thicknesses are summarized in Tab. I. At the beginning (sample designated as #13), Ar carrier gas was used which resulted in the total pressure up to 4 Pa. Ti sublayer was also deposited in this case. However, the coating delaminated from the substrate in small chips, which covered significant parts of the substrate. The repetition without Ti sublayer and without Ar revealed slightly better adhesion. Thus, subsequent coat-

Table I
Deposition condition for the studied WC/C coatings

Sample	Total pressure [Pa]	Bias [kV]	Beam current [mA cm^{-2}]	Thickness [nm]
#13, Ar	4	3.8	1	300
#20	1	5	1	200
#24	2	5	0.8	700
#21	0.8	4.5	1.2	200

ings were produced without Ar and Ti at under total pressure in the range from 0.8–2 Pa. Bias voltage was in the range from 3.8 up to 5 kV and the beam current varied from 0.8 up to 1.2 mA cm^{-2}.

The reduction of the pressure and bias increase (#20) did not solve the delamination problem, therefore we varied the beam current and the thickness (i.e. longer deposition time) of the coating. Though not fully optimized, the best results from the viewpoint of coating stability were obtained in the case of sample #21 under the lowest total pressure and highest beam current. X-ray diffraction indicated the presence of broad diffuse peaks and indentified WC which suggests that the produced coatings are nanocomposites. The morphology of this coating #21 is illustrated in Fig. 1. In contrast to all other coatings it is very smooth and almost featureless. Preliminary AFM study showed surface relief of less than 10 nm on Si wafer and up to 25 nm on the polished steel substrate. The cross section at the broken edge of the coating in Fig. 1 shows globular features with the size of 10–20 nm, which also supports the presence of nanocomposite structure. However, more detail TEM study is necessary to reveal the structure of the coating unambiguously.

Nanohardness tests were initially performed with the maximum load of 1 mN to be within the limit 10% of the film thickness and to avoid substrate effects. However, the scatter among the obtained values exceeded 100% and it was reduced to acceptable level only when the load was increased to 5 mN. Typical penetration depth under those conditions was around 120 nm, which means that the obtained values are lower than they should be because of the influence of softer substrate. Fig. 2 shows several loading-unloading curves obtained on a coating #21. The scatter of the curves, though still significant, is acceptable. The absence of pop-ins indicates sufficient adhesion. The results of the measurements are summarized in Tab. II.

The average nanohardness of the studied coatings is within the range from 20 GPa to 24 GPa and the reduced elastic modulus in the range from 265 GPa up to 320 GPa with significant scatter (up to 50% in some cases).

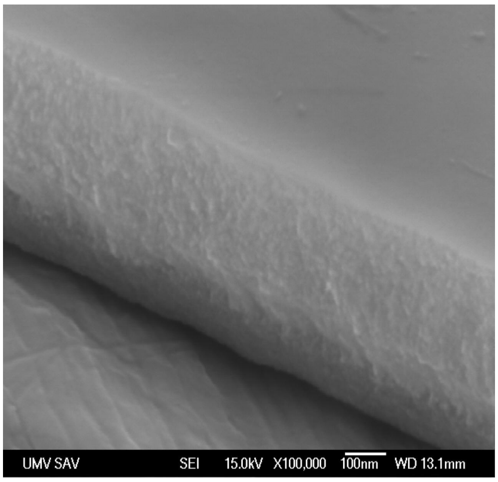

Fig. 1. **The morphology and the cross section of the WC/C coating on steel substrate (sample #21) by SEM**

Table II
Summary of the nanoindentation tests

Sample	Hardness [GPa] (min. – max.)	Elastic modulus [GPa] (min. – max.)
#13	24.1 ± 9.5 (16.9–45.8)	323 ± 96 (203–489)
#20	21.5 ± 3.1 (18.0–25.7)	318 ± 24 (297–355)
#24	19.9 ± 2.1 (17.7–22.9)	265 ± 12 (251–277)
#21	20.1 ± 11.9 (7.1–38.9)	266 ± 128 (106–350)

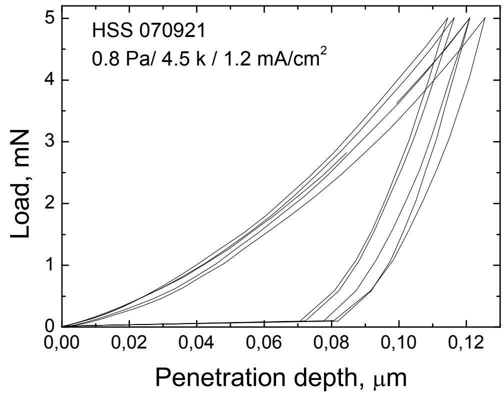

Fig. 2. **Indentation curves in sample #21**

Such a large scatter of the data seems to be the result of the compressive stresses developed during deposition in the layers and level of their relaxation.

The obtained hardness corresponds to the values for many other coatings and the true hardness of the studied coating can be increase when measured at smaller penetration depth and without the compressive stresses. The presence of such stresses is a principal problem for the nanoindentation measurements because the level of these stresses can be in the range from 1 GPa to 6 GPa (ref.[3,4]), which is in the same order of magnitude as the measured values. Obviously, additional investigations are the unbiased values of nanohardness from the studied coatings and to reduce the compressive stresses.

4. Conclusions

Current study on the nanohardness of WC/C coatings prepared by a PECVD method emphasizes the problems with delamination and nanohardness measurements resulting from the presence of large compressive stresses developed during deposition. These stresses can be slightly reduced via modification of the deposition conditions, especially total pressure and current density. Nearly optimized conditions for WC/C coating preparation were obtained and provided nanocomposite microstructure with the nanohardness of around 20 GPa and reduced elastic modulus of 266 GPa. However, additional TEM investigations are necessary to confirm the presence of nanoparticles in the coatings and further work on the reduction of the compressive stresses and improvement of coating adhesion.

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A set of thin WC/C coatings had been prepared by the PECVD technique from W and C precursors under different conditions on high speed steel and Si wafer substrates. The nanohardness and indentation modulus and microstructure of these films prepared were investigated in order to establish the correlations between the preparation conditions and mechanical properties. The main problem identified after deposition were high compressive stresses causing film delamination. The modification of the total pressure with slightly increased bias and beam current density resulted in the reduction of delamination. Very large variations in the indentation hardness and indentation modulus were also attributed to the presence of high local compressive stresses. The average hardness of the coating prepared under optimized condition was around 20 GPa and indentation modulus around 265 GPa.