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The analysis of microhardness measurement approach for characterization of hard coatings

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Abstract

The analysis of problems concerning thin film (1–5 μ) microhardness measurement by means of different techniques is conducted in case of diamond-like carbon coatings. It is shown experimentally that the extrapolation of the $\lg(H_m - H_s)$ vs. d dependence to zero d values, where H_s is microhardness of the film substrate, H_m is formal microhardness of the substrate with coating and d is Berkovich pyramid depth, leads to reliable coating microhardness values H_f independent on substrate properties and characterizing the properties of the coating itself. This approach is used to obtain the average H_f values of multilayer coatings. It is found that the surface roughness of the coatings impedes the correct determination of the coating microhardness by means of nano-indentor techniques. The coating surface smoothening (mechanical or by ion etching) provides the conditions for correct microhardness measurement. It is concluded that the real H_f values of diamond-like carbon coatings obtained by pulse arc graphite sputtering exceeds 100 GPa.

Keywords: Thin film; Carbon coating; Microhardness

1. Introduction

Microhardness is often used to characterize the strength of solid materials and strengthening coatings, since it is the property which is easy to measure. However, a common way of microhardness (H) measurement (by measuring the imprint size of diamond pyramid at loads commonly exceeding 200 mN) in the case of thin (approx. 1–5 μm) hard coatings usually gives only an effective value H_m [1], which differs from the microhardness of coating (H_f) itself, because at such loads the coating during measurement is deformed together with the underlying substrate material. This leads to the dependence of the effective value H_m on the load (Fig. 1) [2]. In this case, the dependence of the indentor depth (d) upon load (P) can be used for determining the actual value of H_f. The recent progress in nano-techniques [3], allows significantly reducing the load values (≤ 20 mN) and thus the ability of direct microhardness measurement for hard coatings. In the present paper, a comparison of both approaches (common and nano-) for the determination of H_f values in case of diamond-like carbon coatings (DLC) and multilayer Ti–C films has been performed in three runs and discussed.

2. Results and discussion

DLCs were obtained in a vacuum facility equipped with three sources (gas ion source for etching, electric arc source for non-magnetic metal sputtering and pulse arc carbon source for DLC deposition) by pulse sputtering of graphite target with different frequencies ($f \sim 1$–30 Hz). For a given design of a sample holder variation in f provides different substrate temperature (T_s): for $f = (1–5)$ Hz, $T_s \sim (70–120)$ °C, $f = 20$ Hz, $T_s \sim 300$ °C.

The substrates with different initial microhardness values H_s ranging from 2 GPa (carbon steel) to 18 GPa (WCC) Co alloy were used. To obtain a good adhesion, the intermediate TiC layer [4] was deposited. The adhesion quality was checked by a visual microscope inspection of standard Rockwell imprints.

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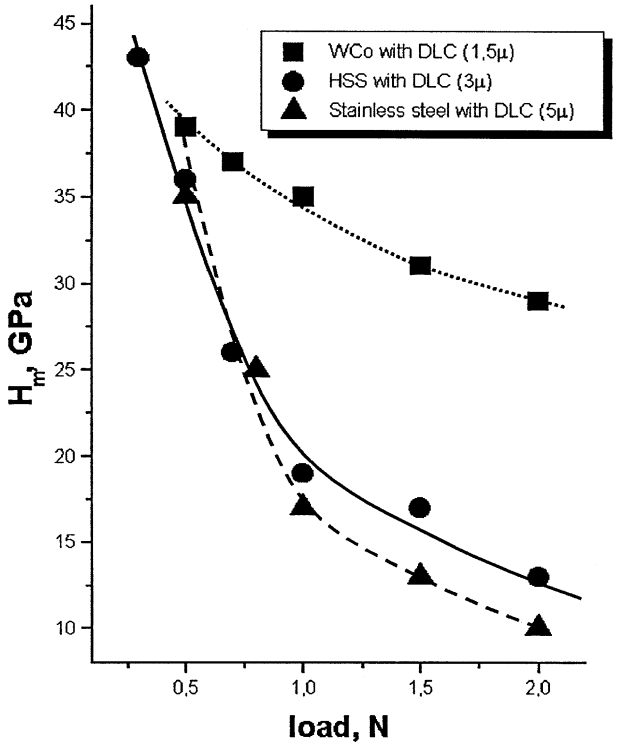

Fig. 1. Dependencies of microhardness H_m on the Vickers pyramid load P for DLCs deposited on different substrates.

The first microhardness measurement run was conducted by means of the PMT-3 ($P=0.2-2$ N) and 'Akashi' ($P=0.05-1$ N) microhardnessmeters. According to the obtained effective microhardness values (H_m) the dependencies $f(d)=\lg(H_m-H_s)$ [1] were plotted. The H_f values were obtained by extrapolation of $f(d)$ dependencies to zero d value. The standard correlation $d=D/7$, where D is the Berkovich pyramid imprint size, which has been used.

The typical $f(d)=\lg(H_m-H_s)$ dependencies for DLCs and multilayer films on different substrates (each coating type was obtained in one deposition cycle) are depicted in Fig. 2. The numerical values are presented in Table 1. As seen, the H_f values for the same type of coatings deposited in one cycle on substrates having different H_s coincide within 10%. Thus, one can conclude that the obtained H_f values reflect mainly the properties of coatings themselves and are almost independent on a substrate type.

By means of this approach it becomes possible to analyze directly the effect of deposition conditions on the properties of coatings. It turns out that the DLCs deposited at low substrate temperature ($f=1$ Hz, $T_s\sim 70$ °C; samples 6, 7 in Table 1) have markedly higher H_f values than those obtained at higher substrate temperature ($f=20$ Hz, $T_s\sim 300$ °C; samples 8,9 in Table 1). The increase of Ti content in each layer of multilayer films (samples 4, 5, 11 in Table 1) leads to reduction in H_f. The use of various gas environments in DLC deposition cycle also leads to reduction in H_f, especially in case of Ar (Table 2).

The second microhardness measurement run was performed by means of two different nano-hardnessmeters with varying load in Lanzhou Institute of Physics, China (P up to 20 mN) and in Institute of Superhard Materials, Ukraine (P up to 10 mN), for 2 μm thick DLCs on hard speed steel (HSS). A special attention was paid on the following measuring conditions:

1. The same temperature of a sample and nano-indentor,
2. The suppression of device vibrations,

Table 1
Microhardness of DLC's and multilayer Ti–C films deposited on different substrates

Sample number	Type of substrate	*Hs* (GPa)	*f* (Hz)	DLC thickness (μm)	*H* (GPa)	
					PMT-3	AKASHI
DLC coatings deposited in one vacuum cycle						
1	HSS	9.5	5	~3	95	–
2	ShX15	8.5	5	~3	90	–
3	Carbon steel	2	5	~7	95	–
Multilayer films (20 nm Ti+480 nm C) for samples deposited in one vacuum cycle						
4	WCo	18	5	3	55	–
5	HSS	9.5	5	3	50	–
DLCs deposited at different frequency of graphite target sputtering						
6	HSS	9.5	1	~1	80	80
7	HSS	9.5	1	~1,4	100	90
8	HSS	9,5	20	~1	55	60
9	HSS	9.5	20	~1	60	60
10	WCo	18	5	1.5	110	–
Multilayer film (20 nm Ti+4800 nm C)						
11	HSS	9.5	5	4	70	–

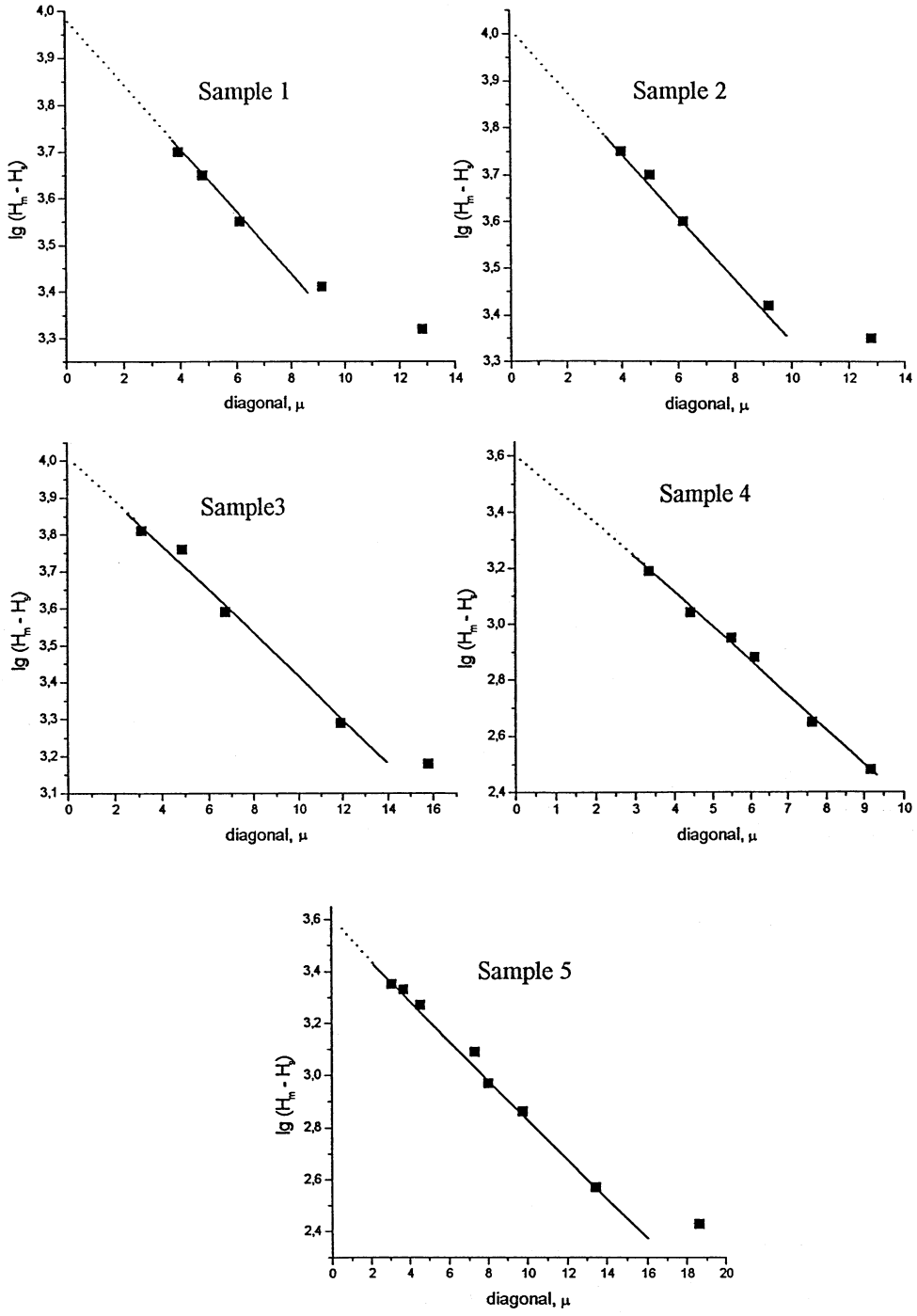

Fig. 2. Lg($H_m - H_s$) vs. Vickers pyramid trace diagonal size. The characteristics of samples 1–5 are depicted in Table 1.

Table 2
DLC microhardness deposited at different assistant gases

Sample number	Substrate material	Assistant gas	P (Pa)	Film thickness (μm)	H_s (GPa)	H_f (GPa)
1	HSS	–	$(3-5)\times10^{-3}$	3	9.5	90
2	Carbon steel	Ar	$(1.5-1.8)\times10^{-2}$	4.5	2	65
3	Carbon steel	N	$(1.5-1.8)\times10^{-2}$	5	2	85
4	Stainless steel	N	$(1.5-1.8)\times10^{-2}$	5	2.7	85

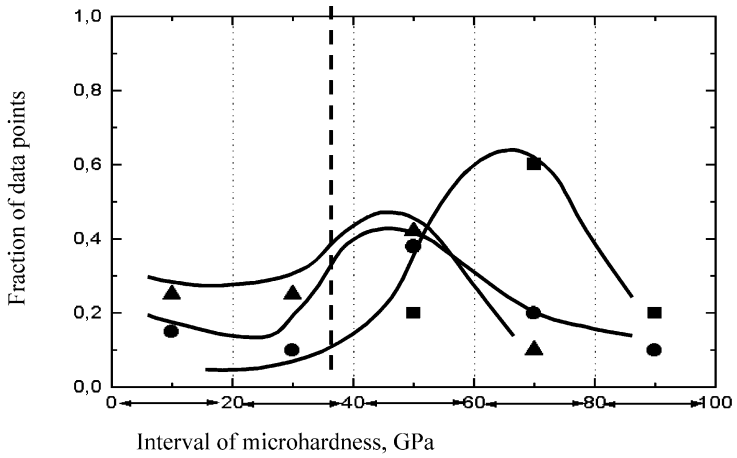

Fig. 3. Fraction of microhardness data points detected within the microhardness specified intervals under the random choice of measuring points on the surface of DLC coating: (a) insert of abnormal diagram P vs. d;)b) insert of normal diagram P vs. d.

3. The high accuracy of indentor vertical positioning upon load and
4. The high accuracy of imprint position ($\pm$400 nm).

In each measuring point the diagram P vs. d has been recorded and typical diagrams are shown in the insets in Fig. 3. The points are selected randomly and the strong scattering in H_f data is observed (Fig. 3). At the points where the abnormally low H_f values ($<$40 GPa) were obtained, also the abnormal diagrams had been observed. At the same time, in the measuring points with $H_f>40$ GPa, the normal diagrams were found. It might be thought that such scattering in the obtained data is caused by morphology of a DLC surface (Fig. 4). It is seen that the average relief roughness is approximately 100 nm with separate peaks up to 1000 nm and the relief roughness values are comparable with nano-indentor depth. It is obvious that, in the majority of cases the condition of a correct microhardness measurement (hard indentor—ideal plane) is not valid. It is hard to find, especially for low load values, the place where the imprint size corresponds to the actual microhardness of the coating, since the load during imprinting can be concentrated only on the relief peaks thus leading to the increase of imprint size and underestimated H_f values. Only in the minority cases, the condition of a correct microhardness measurement occurs to be valid and therefore, the rare values of $H_f\sim100$ GPa might be the most reliable. Thus, it could be thought that for the correct microhardness measurement either the smooth parts of the surface have to be found or the surface has to be smoothened.

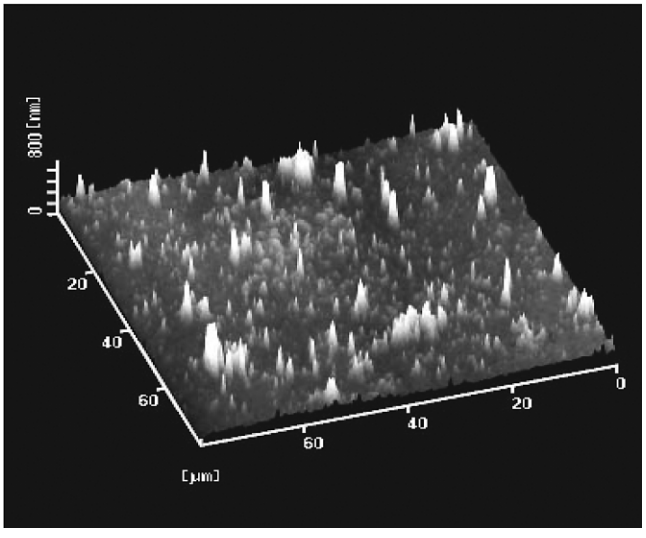

Fig. 4. AFM image of DLC surface, scan dimension is (80×80) μm.

To confirm this assumption, the third microhardness measurement run for the smoothened surface relief roughness DLCs were conducted (Table 3). The smoothening was conducted both by mechanical polishing with 1 μ diamond paste or by argon or oxygen ion etching (different parts of the same samples) to the depth approximately 100 nm. The measurements for mechanically polished samples performed by nano-technique with aid of 'Diavat Ltd.' (Israel) (Table 3) demonstrate the increased averaged microhardness values that actually are close to 100 GPa, a value estimated as a real H_f based upon the previous run data analysis.

The use of samples with smoothened surface turns out to be useful also for common microhardness measurements. In this case, the imprints can be measured with higher accuracy and this permits performing measurements at lower loads. As a result, a quality of extrapolation to d zero value is better and obtained H_f values are also close to 100 GPa (Table 3). The data presented in Table 3 show that the reliable values of microhardness for DLCs without hydrogen are close to

Table 3
DLC microhardness after surface treatment

Substrate material	Treaitment of DLC surface	H_f (GPa)
HSS	DLC surface after deposition	80
	DLC surface after etching by oxygen (etching depth ~100 nm)	121
	DLC surface after etching by argon (etching depth ~100 nm)	140
ShX-15 steel	DLC surface after deposition	90
	Mechanical polishing by diamond paste	100

the microhardness of solid diamond $H_f \sim (140–160)$ GPa [5]. In this meaning, these coatings are really 'diamond-like'.

3. Summary

1. The extrapolation of logarithmic plot H_m vs. d to zero d values in case of common microhardness measurements gives correct values of thin (about several microns) film microhardness H_f values independent on substrate material properties.
2. The nano-indentor technique has to be used with a great care if surface relief roughness is comparable with a nano-indentor depth.
3. The surface relief smoothening either mechanically or by ion etching provides conditions for obtaining correct film microhardness values by means of a common technique (item 1) as nano-indentor one.

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