Correlation between Hardness, Internal Stresses and Elasticity Modulus in Diamond Like Coatings (DLCs)

I.Sh. Trakhtenberg[1], V.A. Yugov[1], A.B.Vladimirov[1], A.P. Rubstein[1], A.G. Gontar[2], C.N. Dub[2]

[1] *Institute of Metal Physics, Ural Branch Russian Academy of Sciences, S. Kovalevskoi St. 18, Ekaterinburg 620219, Russia, Phone: 343-378-38-66,e-mail: A.Vladimirov@imp.uran.ru*
[2] *Institute of Superhard Materials, Kiev, Ukraine*

Abstract – Thick (above 1 μm) DLCs are most perspective surface strengthening coatings for tools and friction pairs. For practical use it is important to have the simple and reliable methods for measuring and certification of films mechanical properties such as microhardness H_f, elasticity module E and internal stresses σ_0. The feasibility of reliable determination of inherent value of H_f of coating material is demonstrated experimentally. The express and simple method for determination of σ_0 values in coatings is presented.

Basing on available data on H_f and E, and obtained here data on σ_0, the interrelations between H_f, E and σ_0 in hard DLCs (H_f ranging from 40 to 100 GPa) were found. These interrelations allow estimating H_f, E, σ_0 within 10–15% inaccuracy basing on known values of one of these quantities.

1. Introduction

The devices based on STM and ATF techniques are widely used now for determination of basic mechanical properties in super hard materials, including DLCs [1–2]. The microhardness and elasticity modulus values, H_f and E respectively, are commonly found from indenter penetration depth in loading-unloading cycle. The internal stresses σ_0 are calculated from change in bending radius value of a thin strip after coating deposition [3]. However, two factors do not allow employing these methods widely as in scientific research for certification of films properties as in industrial practice for control of reproducibly of strengthening DLCs quality. First, the weight and surface area of articles that can be investigated by the above methods do not exceed tens of grams and several square centimetres, respectively. Second, thickness of DLCs that are used in practice for strengthening of cutting tools and friction details has to be about several micrometers. The surface relief (roughness) of coatings having such thickness causes strong scattering in the formal results of microhardness measurements with the use of micro-indenter. In this case the main postulate – the surface of test samples is ideally flat – used in the measurement data treatment, is violated. Also, the feasibility of correct determination of effective microhardness in multi-layered films by means of micro-indenter seems rather problematical. These factors and also the necessity in methods for DLCs quality certification in various conditions of coating deposition stimulate the search for simple and, at same time, reliable methods for determination of H_f, E and σ_0. This work is devoted to solving of this problem.

2. DLCs Preparation

DLCs were obtained by impulse-arc sputtering method of carbon target at a pulse frequency ranging from 1 to 30 Hz. The use of different frequencies allows conducting DLC depositions at different substrate temperatures (T_S): for f = (1–5) Hz – T_S ~ (70–120) °C; for f = 20 Hz – T_S ~ 300 °C. The substrate temperature at all deposition stages was calibrated in special experiments by means of chromel-alumel thermocouple.

Substrates with different initial microhardness values H_S ranging from 0,8 GPa (Al) to 18 GPa (WC(Co) alloys) were used in experiments. The coating thickness was about several micrometers. The adhesion quality was checked by a visual microscope inspection of the standard Rockwell imprints.

3. Microhardness Measurement

The inherent microhardness H_f of the coating material was determined from linear extrapolation of the plot log ($H_m - H_S$) vs d to zero d values, where H_m and H_S are measured substrate microhardness values with and without coating, respectively, and d is imprint penetration depth under different indenter load P. Such extrapolation seems reasonable when formula 1 from [4] is used, where $d = D/7$. D is the Berckovich pyramid imprint size.

The microhardness measurements were conducted by means of the PMT-3 (P = 0,2–2 N) and "Akashi" (P = 0,05–1 N) microhardnessmeters [5]. The typical log ($H_m - H_S$) vs D plots for DLCs deposited on substrates with different initial microhardness H_S are shown in Fig. 1.

The numerical values of H_f obtained in such manner are presented in Table 1. As is seen from the table, the H_f values of the DLCs deposited in identical deposition conditions on substrates having different H_S,

coincide within 10%. At the same time H_f values are reducing with impulse frequency increase that is to say with increase of films condensation temperature.

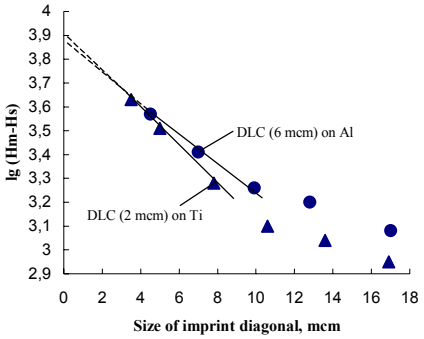

Fig. 1. The typical log ($H_m - H_S$) vs D dependencies for DLCs deposited on different substrates

Table 1. Microhardness of DLCs deposited on different substrates

№	Type of substrate	H_s, GPa	f, Hz	DLCs thicken., μm	H_f, GPa	
					1	2
1	Al	0.8	5	6	75	
2	Ti	4	3	2.1	80	
3	Stainless steel	2.9	3	2	85	
4	Carbon steel	2	5	7	95	
5	Carbon steel	2	20	1	55	60
6	HSS	9.5	1	1.5	100	90
7	HSS	9.5	20	1	60	60
8	WC(Co) alloys	18	5	1.5	110	

1 – PMT-3 measurement
2 – "Akashi" measurement

Thus, our method of determination of inherent coating microhardness value is sufficiently sensitive and accurate to indicate changes in H_f with deposition condition.

The H_f values can be found also from micro-indenter penetration depth x, using dependencies $P = f(x)$, where load P does not exceed 10 mH {3–5]. Such measurements for our DLCs samples were performed in ISM (Kiev, Ukraine) and in Lanzhou Institute of Physics (China). The location of measurement points was chosen fortuitously. Large scattering in H_f values was found. The measurements indicating microhardness low values ($H_f \leq 40$ GPa) were also characterised by abnormal (with break) $P = f(x)$ dependencies, and normal dependencies were observed in case of high microhardness values ($H_f \geq 40$ GPa). It was concluded [6] that the main cause of this scattering is marked surface relief typical for DLCs obtained from carbon beams. This relief at extremely low loads leads to the violation of the main condition of microhardness measurements – hard indenter at the ideal plane, that is accompanied by abnormal dependencies $P = f(x)$ and, commonly, underestimated H_f values. Besides, the relief roughness impedes the correct measurement of the imprint size thus leading also to the underestimated H_f values. Actually, the relief smoothing by additional mechanical polishing or ion etching removes the error origin and leads to increase in measured values of H_f. In particular, the microhardness of coatings deposited at low frequencies (low substrate temperature) turned out above 100GPa that is close to the microhardness of solid diamond [7].

For analysis of interrelation between E and H_f the available in literature data [3, 8–9], data of our own measurements and data of independent measurements of our samples in laboratories of other companies were collected in one plot (Fig. 2). As is seen from the figure clear linear correlation between E and H_f values is observed, which can be described with the following expression:

$$E_C = -(3.5 \pm 52) + (8.5 \pm 0.9)H_f. \qquad (1)$$

Thus, microhardness measurements allow estimating elasticity module E_C basing on expression (1) with accuracy about 10%.

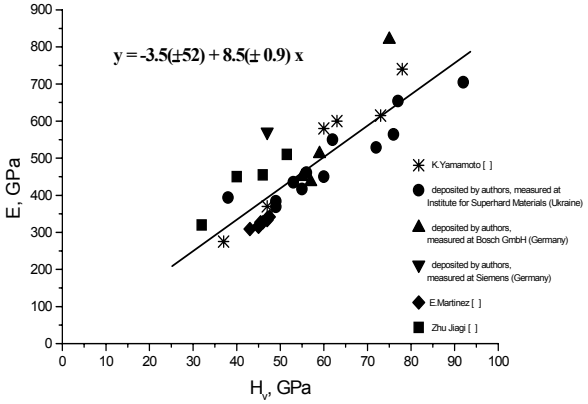

Fig. 2. Interrelation between elasticity module E and DLCs microhardness H_f (✳ – [8], ❶ – [3], ⑤ – [9]).

4. Measurement of Internal Stresses

Earlier [10] we had considered a problem of a thin strip with length L much larger then its width elastically bent under the effect of thin deposited coating having internal stresses σ_0. The following formula was obtained for internal stresses calculation accounting for coating elasticity modulus E_C:

$$\sigma_0 = \frac{h_S E_C}{R}\left[\frac{E_S E_C^{-1} h_S\, h_C^{-1}}{3(1-v_s^2)} + 1\right], \qquad (2)$$

where h_c, E_c, h_s, E_s are the thickness and elastic module of the DLC and metallic strip, respectively, v_s is Poisson' s ratio of strip material and R is bending radius. R was calculated within approximation of parabolic bend with circle. We had used known relation for segment length of crossed cords:

$$X(2R - X) = (L/2)^2, \qquad (3)$$

where L is the distance between ends of bending strip and L is the maximum distance from surface of bent strip to line connecting her ends.

If to estimate accuracy of σ_0 determination taking into account inaccuracies in R, h_C and E_C [10], the following expression for inaccuracy in σ_0 can be obtained $\Delta\sigma_0 = (\Delta h_C/\Delta R)\,\Delta E_C$. Typical error in σ_0 in our conditions is about ±0.5 GPa at the level of 8–10 GPa if inaccuracy in E_C is about ± 300 GPa at the level of 800 GPa. The error in σ_0 can be significantly reduced if to replace in (2) the measured E_C value with one calculated basing on (1). Namely, in such way the σ_0 values were calculated. Therefore, in our experiments always near the strip sample in the sample holder was located the test sample (mechanically pressed to the holder) for H_f measurement. Strip samples were made from ferromagnetic material (permalloy) and were pressed to the holder surface with magnets located in the holder. Such holder construction allows avoiding of strips overheat during DLC deposition (Fig. 3).

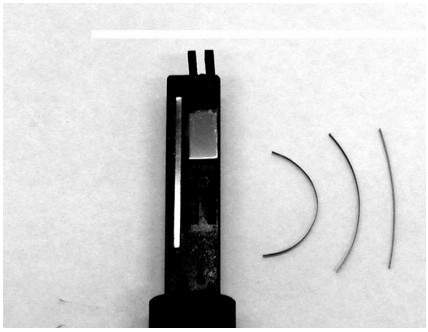

Fig. 3. Sample holder and strips for determination of σ_0 values

The identity of deposition conditions for magnetically and mechanically pressed samples was tested in the special experiment. The σ_0 values determined in permalloy (h_S = 100 μm, E_C = 120 GPa) and mechanically pressed tantalum strips (h_S = 80 μm, E_C = 185 GPa) almost coincide (6 GPa) giving evidence that the coating deposition conditions in both cases were almost the same.

The described methods for reliable estimation of the DLC mechanical properties were applied for the investigation of DLCs deposited with addition of nitrogen and argon into vacuum chamber and exposed to anneal at elevated temperatures. The nitrogen content in films deposited in nitrogen was about 15 at.%. All these procedures lead to coating properties modification due to reduction of sp^3 diamond bond fraction. As an example, the results of DLC properties modification under air stepwise annealing over 300–550 °C are shown in Fig. 4. To avoid additional inaccuracies, the probable variation in substrate E_S was estimated after each annealing step by means of mechanical loading of underposited test strip. This measurements had demonstrated that E_S values stayed invariable under annealing over used temperature interval.

As is seen in Fig. 4 the values of σ_0 and H_f stay invariable up to 450°C. Above 450°C abrupt, almost simultaneous, reduction in values of both σ_0 and H_f is observed. The coating doping with nitrogen also induces reduction in σ_0 and H_f values.

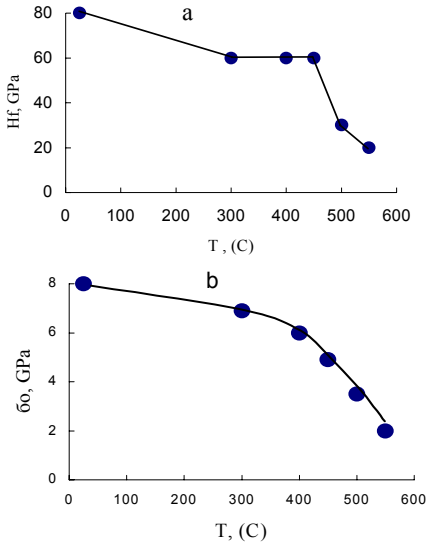

Fig. 4. Variation in H_f (a) and σ_0 (b) in the DLCs under stepwise air annealing (temperature step was 50°C and exposition time at each step was 0.5 h: DLCs deposited in vacuum

The interrelation between σ_0 and H_f for hard DLCs ($H_f \geq 40$ GPa) deposited in vacuum, argon and nitrogen is shown in Fig. 5.

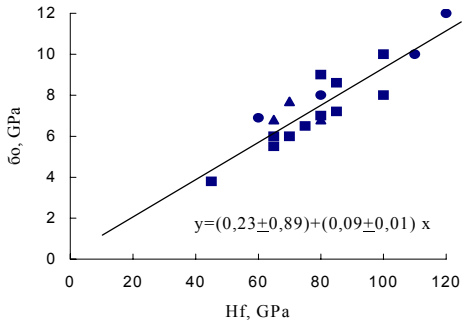

Fig. 5. Interrelation between σ_0 and H_f for DLCs deposited in various conditions (● – in vacuum, ■ – in nitrogen, ▲ – in argon)

As is seen in Fig. 5 that one more linear correlation, now between H_f and σ_0 is also observed in DLCs:

$$\sigma_0 = (0.23 \pm 0.89) + (0.09 \pm 0.01)H_f \qquad (5)$$

This interrelation together with (1) is very useful for practical application to control the technological process by reproducibility of coating properties on test samples and so far for express estimation of two properties from three ones (H_f, σ_0 and E_f) knowing one of them – for example σ_0, as the property, which can be measured in the simplest way.

5. Conclusions

1. It is demonstrated experimentally the feasibility of determination of inherent microhardness of coating

material through linear extrapolation to zero indenter load of microhardness dependence vs indenter imprint size.

2. The simple method for determination of internal stresses σ_0 in DLCs is proposed, which takes into account the coating material elastic properties.

3. The linear interrelations between elastic modulus E_f, microhardness H_f and internal stresses σ_0 for hard DLCs ($H_f \geq 40$ GPa) are found, which allow express estimating mechanical properties of coatings basing on known values of one of them.

Acknowledgements

The work was supported financially within the programs of RAS Presidium "The synthesis of materials with specified properties and production of multifunctional materials on their base" and RAS Department Physical Sciences "New materials and structures".

References

[1] A.C. Ferrari, S.E. Rodil, J. Robertson, W.I. Milne, Diamond and Related Materials **11**, 994 (2002).

[2] W. Clauss, M. Freitag, D.J. Bergeron, A.T. Johnson, Carbon **38**, 1735 (2000).

[3] E. Martinez, J.L. Andujar, M.C. Polo et al., Diamond and Related Materials **10**, 145 (2001).

[4] C.N. Dub, *in: Proceeding of 15th International Symposium, ISTFE-15*, Kharkov, Ukraina, 2003, p. 343.

[5] Yu. Tolmachev, V.L. Bukhovets, I.G. Varshavskaya, N. Ravi, *in: Proceeding of ISDF4,* Kharkov, Ukraina, 1999, p. 207.

[6] I.Sh. Trakhtenberg, A.B. Vladimirov, A.P. Rubstein et al., Diamond and Related Materials **12**, 1788 (2003).

[7] V. Blank, M. Popov et al., Diamond and Related Materials **7**, 427 (1999).

[8] K. Yamomoto et al., Diamond and Related Materials **11**, 1130 (2002).

[9] Zhu Jiaqi, Han jiecai et al., *in: Proceeding of the Seventh Applied Diamond Conference (ADC/FCT 2003),* Tsukuba, Japan, 2003, p. 512.

[10] I.Sh. Trakhtenberg, A.B. Vladimirov, A.P. Rubstein et al., *in: Proceeding of 15th International Symposium, ISTFE-15,* Kharkov, Ukraina, 2003, p. 217.