

# Wear-resistance of nanostructured coatings based on diamond-like carbon and compounds of titanium with carbon

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**Abstract.** Multilayer coatings  $[(\text{TiC}_x/\text{Ti/a-C})+\text{ta-C}]_n$  with different composition of composite  $(\text{TiC}_x/\text{Ti/a-C})$  layers are studied. The dependences of abrasive wear resistance and  $H^3/E^2$  ratio ( $H$  – hardness,  $E$  – elastic modulus) of multilayer coatings on the carbon content in the composite layer are determined. The phase composition of the  $(\text{TiC}_x/\text{Ti/a-C})$  layer, the ratio of volume fractions of the phases and the volume fraction of interface component, interlayer adhesion and adhesion to the substrate of the multilayer coating have a synergistic effect on the wear resistance of the testing coatings.

## 1. Introduction

Recent decades, the quality of wear-resistant coatings has been improved significantly through multicomponent nanocomposite structure. Amorphous matrix, grain size and dopants affect their physical, mechanical and tribological properties. For example, the introduction of Al, Ti, Cr improve the strength properties of diamond-like carbon coatings [1]. Creating gradient structures without sharp boundaries and multilayer structures with a large number of interfaces to prevent the cracks propagation is the way for optimizing the mechanical properties of coatings [2–3]. Multilayer structures can be created by uniformly embedding layers with different components between amorphous diamond-like carbon layers [2]. The mechanical and tribological properties of the multilayer coatings should depend on the composition and structure of the embedded layers. The development of protective coatings, including multilayer coatings, depends largely on the ability to predict their properties using the experimentally measured characteristics. For a long time, hardness is considered the most important property for wear-resistant materials. Nevertheless, the parameters combining hardness ( $H$ ) and elastic modulus ( $E$ ), such as  $H/E$  and  $H^3/E^2$ , are no less important characteristics of coatings' wear resistance [4–5]. The critical load for the beginning of the plastic yielding is scaled with  $H^3/E^2$  ratio. For a given load, elastic contact will be preferred, if  $H^3/E^2$  of coating increases.

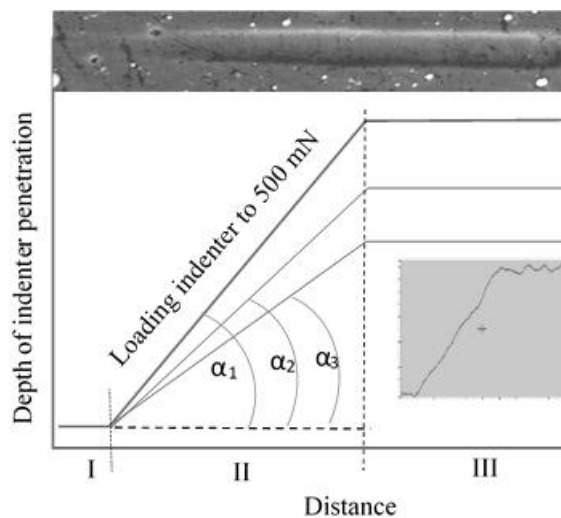
In present work there were fabricated and investigated the multilayer coatings  $[(\text{TiC}_x/\text{Ti/a-C}) + \text{ta-C}]_n$ , where the composite layers  $(\text{TiC}_x/\text{Ti/a-C})$ , consisting of titanium (Ti) or carbon (a-C) matrix with titanium carbide  $\text{TiC}_x$  grains, are embedded between amorphous diamond-like carbon (ta-C) layers.



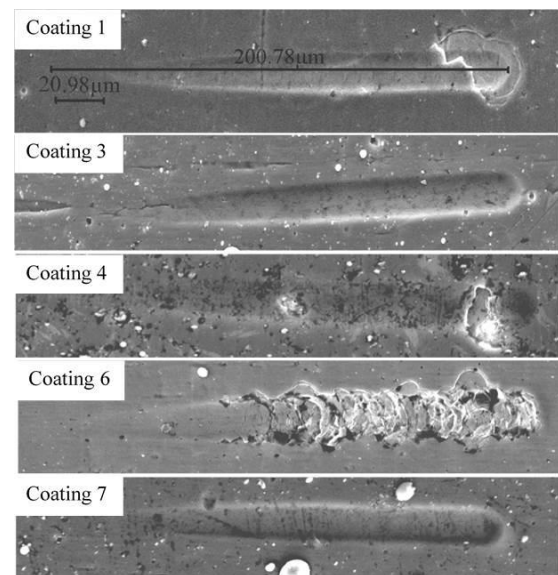
## 2. Materials and methods

Multilayer coatings were deposited on polished tool steel and stainless steel substrates by the PVD technique using UVNIPA-1-001 machine. The substrates were cleaned with distilled water and ethanol in an ultrasonic bath and by ion etching in vacuum chamber. Ta-C layers were deposited by arc pulse sputtering of graphite target, while the composite layers ( $\text{TiC}_x/\text{Ti/a-C}$ ) were deposited by simultaneous sputtering of titanium and graphite targets [6]. The titanium target was sputtered using an arc technique at a direct current of the arc source, whereas a graphite target was sputtered using a pulsed arc technique at various arc pulse frequencies ( $f = 1, 3, 5, 10, 15, 20$  and  $25$  Hz). The thickness of multilayer coatings and the composition of composite layers were determined using scanning electron microscope QUANTA 200 with EDAX analyser. The hardness and elastic modulus of the multilayer coatings were evaluated using a nanoindentation method (NanoTest 600, Micro Materials Ltd, UK) with a Berkovich diamond indenter. The loading was carried out with the automatic control mode of indenter depth penetration at loads from 1 to 256 mN. There were made five nanoindentations at each load.

The scratch tests were evaluated according to the following scheme. A diamond ball of  $50\text{ }\mu\text{m}$  in diameter slid over the coating surface at a rate of  $1\text{ }\mu\text{m/s}$ . The ball passed a distance of  $20\text{ }\mu\text{m}$  without load (stage I, figure 1), then a distance of  $100\text{ }\mu\text{m}$  with a constant loading rate of  $5\text{ mN/s}$  up to load  $P = 500\text{ mN}$  (stage II, figure 1), and a distance of  $80\text{ }\mu\text{m}$  at  $P = 500\text{ mN}$  (stage III, figure 1). Figure 2 shows the SEM images of scratches for various multilayer coatings. Abrasive wear resistance of multilayer coatings were tested in a jet of corundum particles of  $120\text{--}150\text{ }\mu\text{m}$  in size at a speed of  $20\text{ m/s}$  and an attack angle of  $90^\circ$ . The relative wear resistance was determined from the following relation:  $(I/I_0)^{-1} = (\Delta m/m_c + 1)$ .  $I, I_0$  are the wear rate of the multilayer coating and the substrate material, respectively,  $\Delta m$  – the difference between the wear of the test substrate and the wear of substrate with completely worn multilayer coatings at the same dose of abrasive particles,  $m_c$  – weight of worn multilayer coating.



**Figure 1.** Scheme of the scratch test:  $\alpha$  – angle of slope of the straight line in the loading region (stage 2) for different coatings.



**Figure 2.** Images of scratches, created during scratch test (scanning electron microscopy).

## 3. Results and discussion

The deposition conditions and characteristics of the multilayer coatings are presented in table 1. Figure 3 demonstrates the  $f = H^3/E^2(C_C)$  and  $f = (I/I_0)^{-1}(C_C)$  dependences. The increase of carbon content in the composite layer to  $\sim 25\text{ wt. \%}$  leads to an increase of the  $H^3/E^2$  ratio. Further increase of  $C_C$  is accompanied by a decrease and then by an increase of the  $H^3/E^2$  ratio. In the ranges of carbon content  $6 < C_C < 15\text{ wt. \%}$  and at  $C_C > 30\text{ wt. \%}$  a direct relationship between relative wear resistance of

multilayer coating  $(I/I_0)^{-1}$  and the  $H^3/E^2$  ratio is observed: the wear resistance increases with increasing  $H^3/E^2$  ratio. Multilayer coatings 1 and 6 have the lower relative wear resistance in compare with the coatings 1 and 7 (table 1, figure 3). After the scratch test, multilayer coatings 1 and 6 partially are peeled off at the edges of the scratch. Numerous cracks are marked on the scratch of coating 6. The scratches of coating 3 and 7 have not visible peeling. Only small crosscut cracks formed inside the scratch of coating 7.

**Table 1.** Deposition conditions and characteristics of multilayer coatings.

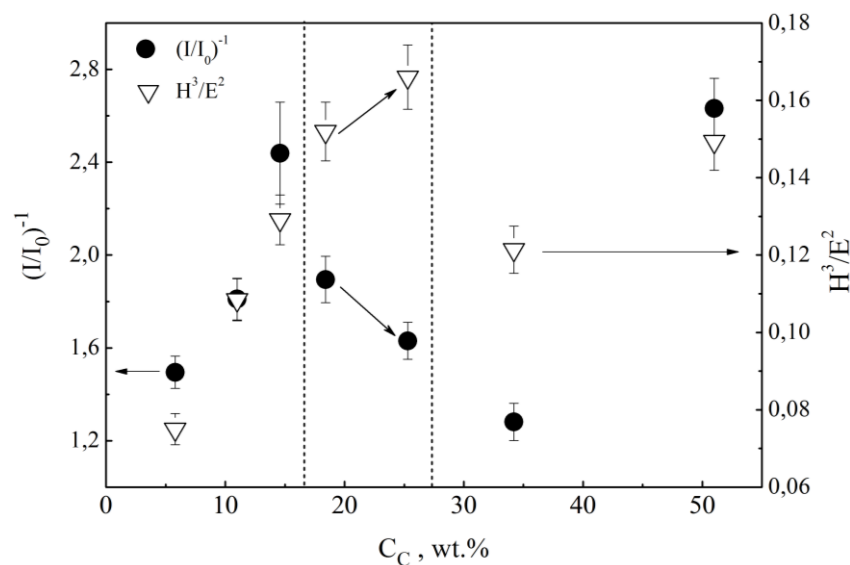
Coating	$f$ , Hz <sup>a</sup>	$C_C$ , wt. % <sup>b</sup>	$d$ , nm <sup>c</sup>	$H$ , GPa	$E$ , GPa	$H^3/E^2$
1	1	5.8	1500	17.9	266	0.08
2	3	11.2	1500	18.6	243	0.11
3	5	14.6	1700	20.8	264	0.13
4	10	18.4	2500	21.1	249	0.15
5	15	25.3	2000	22.1	255	0.17
6	20	34.2	1500	18.1	221	0.12
7	25	51.0	2000	22.0	267	0.15

<sup>a</sup> Frequency of graphite target sputtering during deposition of (TiC<sub>x</sub>/Ti/a-C) layer.

<sup>b</sup> Carbon content in (TiC<sub>x</sub>/Ti/a-C) layer.

<sup>c</sup> Thickness of multilayer coating.

In the range of  $C_C$  from 18 to 25 wt. %, the discrepancy between  $(I/I_0)^{-1}$  and  $H^3/E^2$  is observed. In this range, the embedded composite layers have the maximum volume fraction of TiC<sub>x</sub> grains and the minimum volume fraction of amorphous matrix [6–7]. Moreover, in this range the phase composition of composite layer changed. The composite layer consists of titanium and titanium carbide grains (TiC<sub>x</sub>/Ti) at  $C_C < 20$  wt. %, and an amorphous carbon matrix with grains of titanium carbide (TiC<sub>x</sub>/a-C) at  $C_C > 20$  wt. %. The structural features of composite layer can affect both the wear of the embedded layer and the interlayer adhesion. After the scratch test, coating 4 ( $C_C = 18$  wt. %) has a no uniformity surface with a partial delamination of separate layers (figure 2). The theoretically calculated volume fraction of the interface component in the (TiC<sub>x</sub>/Ti/a-C) composite coatings has a minimum at  $C_C = 20$  wt. % and two maxima near the carbon content at which the multilayer coatings demonstrate the greatest relative wear resistance.



**Figure 3.** Dependences of the relative wear resistance of the multilayer coatings (black circles) and the  $H^3/E^2$  ratio (open triangles) on the carbon content ( $C_C$ ) in composite layer of multilayer coating.

#### 4. Conclusion

The phase composition of (TiC<sub>x</sub>/Ti/a-C) layer, the volume fraction of titanium carbide grains, the volume fraction of interface component, the interlayer adhesion and the adhesion of the multilayer coatings to the substrate have a synergistic effect on wear resistance of nanostructured coatings formed by layer-by-layer deposition of the ta-C and (TiC<sub>x</sub>/Ti/a-C) layers. The results have shown that two coatings demonstrated the most wear-resistance. The one is formed by layers of ta-C and (TiC<sub>x</sub>/Ti) with a carbon content of ~15 wt. %. The other is formed by layers of ta-C and (TiC<sub>x</sub>/a-C) with a carbon content of ~50 wt. %.

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