Deposition and tribomechanical study of nanolaminate Ti/TiN/AlTiSiN/(AlTiSiN/TiAlSiN)n/AlTiSiN hard coating

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Abstract. The application of Physical Vapor Deposition (PVD) hard coatings is one time-tested practice in the modern industry. Two of the main tendencies that promise a progress in this area are the combination of more chemical elements in one coating and the creation of nanolaminate structures. Since many combinations are possible in the design of the coatings, it could be expected they would have many different properties which are difficult to predict. In an attempt to work simultaneously in both of these directions, one nanolaminate Ti/TiN/AlTiSiN/(AlTiSiN/TiAlSiN)n/AlTiSiN coating was developed and its mechanical properties were tested. The results obtained give a reason to believe that it could be widely practically applied.

1. Introduction

The hard coatings (with a hardness of 20 GPa or more) increase the life span of the cutting tools, reduce the breaks for tool replacement and subsequent machine adjustment, allow heavy work conditions without coolant lubricants, increase productivity, etc. [1]. On the other hand, depending on the parameters of the working process (operation modes, raw material, type of machining, etc.), a choice of proper coating should be made for each particular situation [1, 2].

With the progress of PVD technologies, new possibilities have been found to combine more chemical elements in one coating, as well as a precise deposition of thin layers with a thickness of several nm. At present, the creation of nanolaminate (superlattice) coatings is a notably promising trend for development of new coatings for cutting tools.

The coatings AITiN and AlTiSiN kind have long been exploited and are somewhat classic for application on cutting tools [1, 3-6]. It could be said that such monolayer, multilayer and nanocomposite coatings are well studied. However, because of the many possible combinations and the relatively new appearance of the nanolaminates, there is still a wide field to research them.

In this work one similar nanolaminate coating: Ti/TiN/AlTiSiN/(AlTiSiN/TiAlSiN)n/AlTiSiN is presented which possess good properties allowing its practical application for cutting tools.
2. Experimental details

Test samples of widely used steel were made and the mentioned above coating was deposited. Its tribomechanical properties were then investigated.

2.1. Preparation of the samples

The used samples of tool steel 1.2419 (X38CrMoV5-1) are disc-shaped: 20 mm in diameter and 6 mm in thickness. They were previously bulk annealed and ground.

The coating was deposited by Closed Field Unbalanced Magnetron Sputtering (CFUBMS) technology which was implemented in an industrial equipment HVP100RHD (Nanotech Group Ltd.).

Prior to the deposition, the samples were mechanically cleaned, treated with an alkaline detergent, washed in an ultrasonic bath using deionized water and placed in a drier. After the samples were parched, they were loaded into the vacuum chamber and fastened on a three-axial rotation carousel.

The process was started at initial pressure of \(4.0 \times 10^{-5}\) mbar. At the beginning, the samples were heated in Ar/H\(_2\) (6% H\(_2\)) atmosphere up to 390 °C for 60 min and this maximum temperature was maintained the last 10 min. Next, an etching using Ar\(^+\) ions (12 min) and Ti\(^+\) ions (10 min) was done at a pressure of 2.5\(\pm\)2.7 \(10^{-3}\) mbar and a pulsed bias voltage \(U_{bias} = -930\) V/100 kHz to the samples. The coating deposition was performed at a temperature of 378\(\pm\)370 °C (a slight drop to the end) and a pressure of 2.0\(\pm\)2.1 \(10^{-3}\) mbar using two Ti cathodes and one Al-12 at.% Si cathode operating in a N\(_2\) environment. The single deposition steps were performed according to a technology recipe, details of which could be learned by Nanotech Group Ltd. In particular, for the creation of the nanolaminate structure, a pulsed bias voltage \(U_{bias} = -54\) V/100 kHz was applied, whereby the maximum ion current to the samples \(I_{bias} = 1.6\) A was measured respectively (three working cathodes). The total duration of the entire process was 4 hours, after which the samples were cooled by Ar flowing into the chamber until a pressure rose to ca. 10 mbar. After the temperature dropped to 120 °C, the chamber was vented and the samples were unloaded.

2.2. Tribomechanical surveys

The coating thickness which is an important complex feature, was investigated by a calo tester (created by the Central Laboratory of Applied Physics, BAS). One grind ball of bearing steel with diameter of 30 mm was used to form the crater.

The roughness of the uncoated specimen and the deposited coating was evaluated by Surftest SJ-301 (Mitutoyo Corporation).

The nanohardness and the modulus of elasticity were studied by means of Compact Platform CPX (MHT/NHT) (CSM Instruments). In this study, a Berkovich diamond tip was used. To determine the hardness values, the Oliver-Pharr method (which is software embedded in the equipment) was applied. There 3 measurements were done with each of the loads: 15, 25, 50 mN and the obtained results were averaged. The bulk hardness was evaluated using durometer TK-2М (ЗИП).

The adhesion was estimated using a Micro Scratch Tester (MST) module which is included in the mentioned above equipment of CSM Instruments. A Rockwell diamond indenter possessing a 200 µm peak rounding and a sliding distance of 3 mm were applied. The coefficient of friction and penetration depth were also taken into account during this test.

The wear resistance of the coating was assessed by two methods: ball-on-flat and ball-on-disc. In the first case, a stand СИИП-1 (developed by Faculty of Physics and Technology, PU “Paisii Hilendarski”) was applied. The plied counter-part was one Al\(_2\)O\(_3\) ball with diameter of 3 mm. The sample performed 11,000 mm long linear reciprocating motions. A total of 5 tracks were made and their average width (over 5 measurements for each) was accepted to calculate the wear volume. The second method was applied by means of a stand developed by Milko Angelov Consulting Co. Ltd. The loaded counter-part was one Al\(_2\)O\(_3\) ball with diameter of 3/16\(\circ\). The sample was rotated, the average diameter of the formed circular track is 12.2 mm. Just 1 track was grooved (the purpose was to use the same sample for the two methods for greater reliability, but there cannot be grooved many non-intersecting tracks, especially in the shape of a circle), but its width was averaged over 5 measurements of different
places. In the both cases, the tracks were inspected and their width was measured by means of microscopic equipment: non-contact PC-based measurement system TESA VISIO 300 (Brown&Sharpe TESA) at 100x magnification (resolution: 0,001 mm).

3. Results and discussion
A structure scheme of the deposited coating and view of the calotte section are shown in Fig. 1. The general appearance of the crater leads to the conclusion that there is relatively low internal stress in the coating because of absence of destruction traces. The color of the coating is brown, its thickness is 2,25 μm and the particular layers in it are clearly distinguished.

![Figure 1. Structure scheme and calotte section: a) external Al-enriched AlTiSiN layer; b) nanolaminate structure (AlTiSiN/TiAlSiN)n; c) cohesive gradient AlTiSiN layer; d) adhesive Ti/TiN layers.](image)

The outermost area is shown in Fig. 1a: external Al-enriched AlTiSiN layer (thickness of 0,82 μm) – it starts gradient with a smoothly increase of Al, but after reaching its optimum quantity (Al: 29,5 at.%, Ti: 16,5 at.%, Si: 4,0 at.%, N and impurities: the rest), the layer already grows up at constant parameters. Its function is to increase the oxidation and corrosion resistance by the formation of a passivation Al2O3 layer (it also has more Si which further favors this feature [4]). The nanolaminate structure (AlTiSiN/TiAlSiN)n could be seen in Fig. 1b (thickness of 0,49 μm) – it implements several functions: unloading of the stress in the coating, a barrier against oxidation and corrosion, increasing of some mechanical characteristics, etc. It possesses a bilayer period Λ of 24,5 nm (AlTiSiN – 10,0 nm and TiAlSiN – 14,5 nm) – a total of 20 repeating sublayers (in Fig. 1b they cannot be distinguished because of their small thickness, the values presented are evaluated by calculations based on the experience with other processes using this deposition equipment). The cohesive gradient AlTiSiN layer (thickness of 0,52 μm) is presented in Fig. 1c – it serves as a smooth transition to mentioned nanolaminate structure. The gradient adhesive Ti/TiN layers (thickness of 0,42 μm) are depicted in Fig. 1d – their purpose is to provide a better adhesion of the coating to the substrate and a smooth transition to the functional layers, they are typical of such coatings.

The measured roughness of the deposited coating is Ra 0,23 μm. The results of the roughness measurements of the uncoated sample (Ra 0,48 μm) and subsequently the same having a deposited coating are shown in Fig. 2. It should be noted that the vertical scales of the diagrams used for the bare substrate (Fig. 2a) and the coated sample (Fig. 2b) are different. One can see that the roughness was decreased after the deposition. It could be assumed that this is due to the intense Ar+ and Ti+ etching [7] which destroys the peaks on the surface. On the other hand, the CFUBMS method does not create droplets from the target’s material which fall on the substrate and increase the roughness respectively. In a nutshell, the applied coating practically reproduces the relief of the surface which is already smoothed during the etching.
A plot of nanoindentation load/unload curve using a load of 25 mN (averaged over three measurements) is shown in Fig. 3. Here the penetration in the sample is 266.7 nm which represents 11.9% of its coating thickness. The curve is apparently smooth giving a prof any cracks did not occur during the indentation [8].

The indentation depth, Young's modulus and nanohardness at three loads: 15, 25, 50 mN (averaged over three measurements) are shown in Fig. 4. Below the depth is also given its percentage of the coating thickness. It could be assumed that the actual values of nanohardness: 21.5 GPa and Young's modulus: 312.7 GPa are those at a load of 25 mN. Then the penetration is relatively small (see above) hence the substrate hardness does not influence on the values. On the other hand, it is large enough preventing from Indentation Size Effects (ISEs). As for the bulk hardness of the sample, it is 53 HRC.
The scratch test is depicted in Fig. 5. The indenter is pressed by a force $F_n$ which changes linearly from 0 to 30 N during a run $x$ of 3 mm (Fig. 5a). The first critical load $L_{C1}$ arises at ca. 15,0 N (first coating damages: Fig. 5b). Any delamination, i.e. - exposure of the sample, is not seen until the end of the test hence the second critical load $L_{C2}$ is not detected. However, there are increasingly hemispherical crevices and breakages. The used equipment does not allow higher loads than 30 N.

Looking on the diagram in Fig. 5a, one can see that the values of the friction force $F_t$ and the friction coefficient $\mu$ start to fluctuate obviously from the middle of the distance to its end. Probably, the reason is the existence of coating damages. However, $F_t$ changes relatively linearly and smoothly. The coefficient of friction $\mu$ is almost constant, slightly increasing after the middle of the distance. This behavior of these two dimensions implies relatively low internal stress in the coating, probably because of the presence of a nanolaminate structure. The low friction coefficient $\mu$ is largely due to the use of a diamond tip. It is obvious that this coefficient increases slightly until the end of scratching when the penetration depth $P_d$ is maximal and there are increasingly interactions with the indenter [9].

The two tests of wear resistance were carried out at room temperature without use of a lubricant. Tracks of their implementation could be seen in Fig. 6. The wear rate $I_w$ was calculated using the well-known equation:

$$I_w = V.F^{-1}.L^{-1}$$

where $V$ - wear volume (mm$^3$), $F$ - normal load (N), $L$ - sliding distance (m). The wear volume was calculated geometrically after initial measurement of the track width using a microscope.

The ball-on-flat test was accomplished under the following conditions: $F = 2$ N, $L = 50$ m (2273 double strokes of 11,0 mm). Average sliding speed of the sample was 20 mm/s (of course, the moment value of sliding speed is different, since at the ends of a track the sample changes its movement direction). From a geometric point of view, the track is a relatively complex figure because of its different profile - at the edges and the middle. For the exact calculation of the wear volume, the method described in [10] was applied. A wear rate $I_w$ of 57,8.10$^{-6}$ mm$^3$/Nm was calculated.

The ball-on-disc test was implemented under the following conditions: $F=5$ N, $L=200$ m. Average sliding speed of the sample was 20 mm/s as well which was also a moment value of the speed because of an uniform sample rotation. A wear rate $I_w$ of 26,0.10$^{-6}$ mm$^3$/Nm was computed.
The values given by the two methods are of one order, but are remarkably different - about twice. As a reason, one different depth penetration (consequently – a contact with layers possessing different properties) could be excluded: it is 3.70 μm for ball-on-flat and 3.79 μm for ball-on-disc respectively. The probable reason is the difference in relative movement between the sample and counter-part. During the linear motion in two directions, it is possible to arise one increased shear stress in the track which causes a local fatigue wear, hence the track is carved faster. One scratch in the middle of the track width is noticeable in Fig. 6a which supports such an assumption. According to the studies in [11] where the same two methods under similar conditions had been used, the wear rate is about 4 times greater using ball-on-flat test. Nevertheless, the results obtained here using also the both methods are close to these known for similar coatings [5, 12].

4. Conclusions
The presented studies of the considered nanolaminate Ti/TiN/AITiSiN/(AITiSiN/TiAlSiN)n/AITiSiN hard coating give a reason to assume that it is suitable for deposition on cutting tools. In the same batch, similar tools (mills) from WC-Co alloy were coated and preliminary results show that their life span is increased ca. 2.9 times compared to uncoated ones under the same operating mode. This achievement is not surprising [1, 5, 6]. However, after further experiments, even better results could probably be expected.

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