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Investigation of the properties of Ti/TiN/TiCN gradient hard coating deposited on Stavax ESR steel

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The application of hard wear-resistant coatings in the industry constantly increases because of the growing requirements for the quality of tools and products. The field of the injection molds is not an exception, there are important problems, e.g., reducing the wear of the forming elements, as well as achieving easier ejection of the finished article. These challenges could be resolved by applying an appropriate coating. In this work, a gradient Ti/TiN/TiCN hard coating was deposited on Stavax ESR steel by physical vapor deposition (PVD) method. Some important properties for its practical application were studied emphasizing on its wear resistance. For investigating the latter, a methodology based on the ball-on-flat test was used, as the wear volume was geometrically calculated on the basis of the measured track width. Data from the conducted studies of the wear resistance as a function of the normal load of the tribosystem are presented. Analysis of the results was performed and conclusions were made with regard to the practical application of the coating.

Keywords: PVD, hard coatings, mold making, wear resistance

INTRODUCTION

The worldwide use of plastic products constantly increases. Polymer products have successfully replaced a lot of the metal ones used in the past. The physico-mechanical properties of the used polymeric materials are constantly improved, and one of the promising tendencies in this direction is the addition of fillers and fibers [1]. The need for growing quantities of plastic products determines additional requirements on the durability of used injection molds [1, 2].

The working surfaces of the tools for the production of polymer parts by the casting under pressure method are subjected to a complex load. On the one hand, the mold is put to cyclic temperature fluctuations during its filling with melt and its subsequently cooling. At the same time, the working surfaces are subjected to both pressure and bending loads because of the filling of the mold. During this part of the process, the glass and mineral fillers in the polymer have a strong abrasive effect. On the other hand, tool opening and article ejecting result in strong friction upon the working surfaces. The adhesion of the polymer and its shrinkage after cooling further increase this friction and lead to great exertions required to eject the finished article from the injection mold.

In order to increase the life span of the tools for production of polymer parts, it is necessary to undertake activities which simultaneously increase the wear resistance of the upper layer of the working surfaces and reduce the adhesion of the polymer to them. Also, the mold has to possess passable toughness and temperature resistance. The good machinability of its material has a positive economic effect as well.

Based on the mentioned above, it is appropriate to use PVD hard coatings which, in combination with a suitable material for manufacturing the tool, lead to increased wear resistance [1, 3-8]. The coatings with main layer of TiCN are well accepted in the industry. Under certain deposition conditions, they could combine the useful properties of TiC and TiN, which would make them a good choice to achieve the above goal [3, 9-11]. PVD is an economical, flexible and environmentally friendly process which is increasingly used in the industry.

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The modern coating systems allow controlled gradient deposition which finely influence the composition and structure, and thus, the mechanical properties of the coatings. The aim of this work is to create a TiCN-based coating for mold making usage. It has to possess high wear resistance and its other properties have to be acceptable for practical application.

EXPERIMENTAL

Samples of material used for injection molds were prepared and a PVD coating was deposited on them. Then, their tribomechanical properties, which are more important from a practical point of view, were studied, with an emphasis on the wear resistance.

Preparation of the samples

The test samples were made of stainless tool steel which is widely used for the production of active elements for injection molding – Stavax ESR (AISI 420 modified) [1, 12].

The chemical composition of these samples (specified in the certificate of the steel manufacturer) is given in Table 1.

Table 1. Chemical composition of Stavax ESR samples in wt%

C	Si	Mn	Cr	V	P	S
0.40	0.91	0.45	13.4	0.28	0.021	0.0004

Each of the specimens was cuboid-shaped having dimensions 30 × 10 × 10 mm (length × breadth × height), as is shown in Fig. 1.

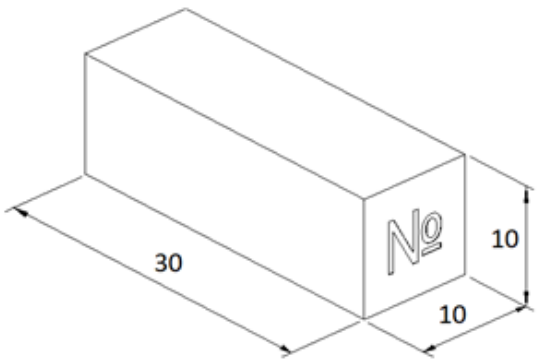

Fig. 1. Sample's appearance

Three groups of samples were prepared, which are listed in Table 2. The choice of the number of samples in each group was based on a preliminary estimation of the amount of upcoming experiments with them.

The heat treatment of the samples was performed in a chamber furnace SNOL-M ("Elprom" – Balchik). The technological process is depicted in Fig. 2.

Table 2. Groups of the studied samples

Groups	A (1-3)	B (4-8)	C (9-12)
Treatment	unhardened ground	hardened ground	hardened polished

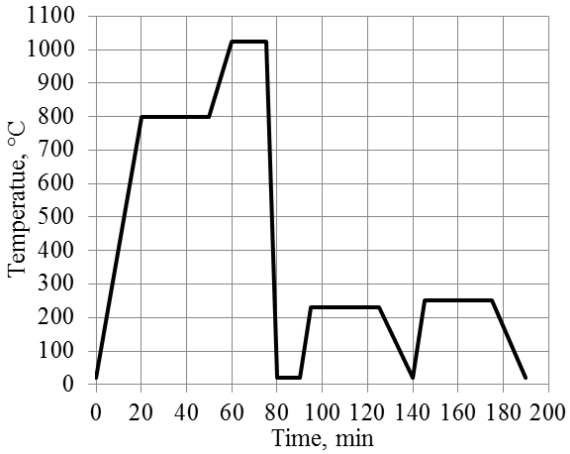

Fig. 2. Graph of the quenching and tempering process

The Ti/TiN/TiCN coating was deposited by cathodic (vacuum) arc deposition (CAD, VAD) in a coating unit π80+ (manufactured by PLATIT, Switzerland) using lateral rotating cathodes (LARC®) technology. Prior to the loading in the working chamber, the samples were mechanically cleaned, then treated in an ultrasonic bath using alkaline solvent Deconex HT 1170, rinsing in DI water and drying in a furnace at 130 °C.

The process started at initial pressure of 1.0×10^{-4} mbar in the chamber. Primarily, the heating was done in an environment of Ar (a flow rate of 6 sccm) up to 430 °C for 60 min. To improve the coating adhesion to the substrate, ion etching in a glow discharge of argon ions (Ar+) at bias voltage of -750 V and bombardment with titanium ions (Ti+) at bias voltage of -1000 V were used. The coating was applied by electric arc evaporation of Ti using a rotating cylindrical cathode in ambience of N_2 and C_2H_2. Initially, an adhesion structure was built which consists of the following layers: Ti, TiN and TiCN with a gradient composition change. Then the base layer with composition $TiC_{0.2}N_{0.8}$ was applied under the following more important parameters of the operating mode: temperature of 380 °C, working pressure of 1.2×10^{-2} mbar, cathode current of 170 A, bias voltage of -40 V. After the deposition, the vacuum chamber was isolated from the pumps and gas flows. When the temperature dropped to 350 °C, for a faster cooling N_2 was let at a flow rate of 200 sccm for 5 min. After the temperature fell to 250 °C, the chamber was opened and unloaded.

Test procedures

The bulk hardness of the samples was measured using a durometer TK-2M (ZIP).

The coating thickness was determined by a calo tester (a special construction of the Central Laboratory of Applied Physics, BAS) using a 30-mm ball of bearing steel.

The nanohardness and modulus of elasticity were investigated by a compact platform CPX (MHT/NHT) (CSM Instruments). A Berkovich-type diamond indenter was applied. The data processing was performed using the Oliver-Pharr method (by the software embedded in the equipment). Four load values were used: 10, 20, 50 and 100 mN, with 3 measurements performed with each of them, thereafter the corresponding results were averaged.

A micro scratch tester (MST) module which is a part of the last-mentioned equipment, was used to study the adhesion. A Rockwell diamond indenter with 200 µm top rounding was applied at a sliding distance of 3 mm. A friction coefficient value was also obtained during this test.

The roughness of the samples was measured using a mobile surface measuring instrument Handysurf E-30A (ZEISS).

Methodology for experimental study of the wear resistance

The wear resistance of the samples was assessed employing a stand created at the Faculty of Physics and Technology, PU "Paisii Hilendarski". Its construction is described in detail in [13].

The experimental studies were performed by a ball-on-flat friction method with horizontal orientation of the tested surface. The counter-part was an alumina ceramic (Al_2O_3) ball with a diameter of 3.0 mm fixed in a holder. The sample acted a reciprocating motion with length of 11 mm. The stand worked at a temperature of 20 °C, without lubricant. Loads of 1, 2, 3, 4 and 5 N were applied to the counter-part. The width of the tracks was surveyed using a non-contact PC-based measurement system TESA VISIO-300 (Brown & Sharpe TESA) at 100× magnification (resolution of 0.001 mm). Its average value was calculated by the equation:

$$b_{av} = \frac{1}{n}\sum_{i=1}^{n} b_i \qquad (1)$$

where b_{av} – average width of the track (mm), n – number of selected sections along the track (-), b_i – measured width in each of these sections (mm). On each of the tracks, five evenly longitudinally distributed sections were selected (n=5).

With a calculated average width of the track, the volume of the latter was evaluated. It is assumed that it consists of segment of a sphere (both ends of the trace if concatenated) and segment of a cylinder (main element of the trace – between the ends). The used methodology is described in [13].

The wear intensity was assessed by the equation [4, 13]:

$$I_w = \frac{V}{F.L} \qquad (2)$$

where I_w – wear rate (mm^3/Nm), V - wear volume, i.e., volume of the amount of the removed material (of the track) (mm^3), F – normal load (N), L - sliding distance which is the distance traveled by the sample relative to the fixed counter-part (m).

RESULTS AND DISCUSSION

Initially, some of the mechanical parameters related to wear resistance were studied.

The hardness of the unhardened samples was 191 HB, while of the hardened ones - 53 HRC.

The measured thickness of the copper-red colored coating was *ca.* 2.00 µm. The calotte section looked clear, with no signs of destruction, suggesting low internal stress in the coating.

The determination of nanohardness was performed using indenter loads of 10, 20, 50 and 100 mN. The obtained curves are presented in Fig. 3.

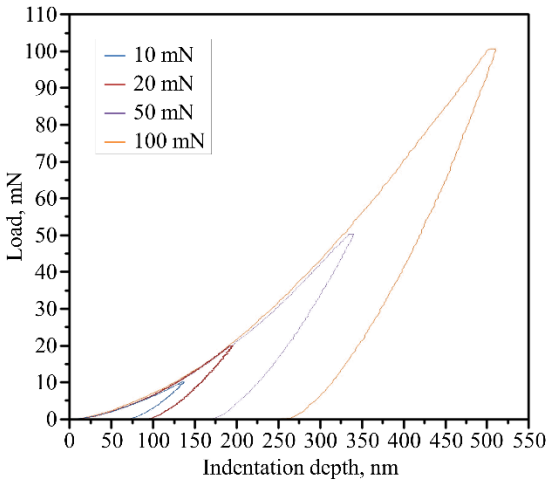

Fig. 3. Load-displacement curves at different loads

It can be seen that the curves have a very good coincidence at different loads (which are also applied at different positions on the sample). This proves that the coating possesses a good uniformity. Moreover, these curves are quite smooth which proves that no cracks appear during the indentation [14].

At a load of 20 mN, an indentation depth of average 193 nm was reached, while a nanohardness of average 35 GPa was measured. At higher loads, the indentation depth exceeded 10% of the coating thickness and the value obtained was already somewhat one integral hardness of the substrate-coating system. At lower loads, smaller nanohardness values were obtained, probably due to indentation size effects (ISEs). Therefore, it could be assumed that the nanohardness of the coating is 35 GPa which is an excellent value for similar coatings [3, 9-11]. It is in accordance with the measured Young's modulus of average 434.0 GPa. Loading and unloading curves enclosed a wide area which suggests that the coating is relatively tough [3].

No adhesion or cohesion disturbances were observed during the scratch test until the maximum stylus load of 30 N was reached. The measured coefficient of friction has a constant value of *ca*. 0.15. In Fig. 4 the end of the trace is displayed, where penetration depth of *ca*. 7.1 μm is marked.

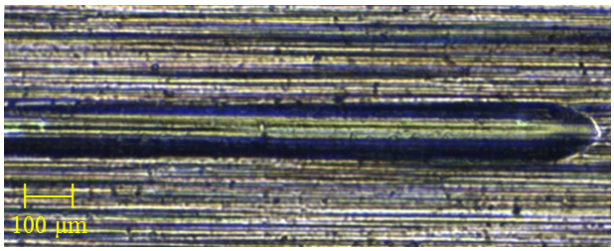

Fig. 4. End of the trace

The sample roughness is pointed out in Table 3. Obviously, it has a higher value after deposition of the coating which is clearly noticeable in the polished samples. Such an increase in the roughness is typical when the initial roughness Ra < 0.4÷0.5 μm [15].

It is known that metal ions tend to accumulate on the surface peaks in the beginning of the coating formation, which phenomenon enhances the roughness. Meanwhile, the intense Ar+ and Ti+ etching disrupts the surface's peaks, which results in roughness reduction. However, these two opposing mechanisms are not highly significant on very smooth surfaces (such as those used), as the peaks are smaller and lower.

Table 3. Data about the test samples

Group of the sample	Roughness of bare sample, Ra (μm)	Roughness with coating, Ra (μm)
A1	0.29	0.30
A2	0.24	0.24
A3	0.25	0.30
B4	0.18	0.22
B5	0.19	0.20
B6	0.18	0.20
B7	0.19	0.20
B8	0.17	0.18
C9	0.04	0.10
C10	0.03	0.10
C11	0.03	0.10
C12	0.04	0.10

The main influence upon the roughness increase have the droplets which are thermally evaporated from the cathode during the VAD process [5]. Despite the modern equipment used, the droplets have a permanent presence in the coating.

The main goal of this work is to investigate the wear resistance which is particularly important in the operation of injection molds.

The experimental studies about the influence of the normal load on the wear intensity of the presented Ti/TiN/TiCN coating were performed at the following constant parameters of the tribosystem: average sliding speed of 10 mm/s; sliding distance of 50 m.

The summarized data about the values of the volume of wear tracks as a function of the normal load $V = f(F)$ are given in Table 4.

Table 4. Wear volume at different loads of the counter-part

Load (N)	Sample group A ($\times 10^6$, mm^3)	Sample group B ($\times 10^6$, mm^3)	Sample group C ($\times 10^6$, mm^3)
1	814.044	596.299	214.064
2	1095.596	805.161	215.896
3	1334.027	1042.121	269.406
4	1397.017	1377.916	286.809
5	1583.903	1468.136	377.097

Based on these data, the diagram in Fig. 5 was built. As expected, the increase in normal load leads to higher values of wear volume for all groups of samples. Unhardened ground samples display the most intensive wear.

The reported data on the values of wear rate as a function of the normal load $I_w = f(F)$ are presented in Table 5.

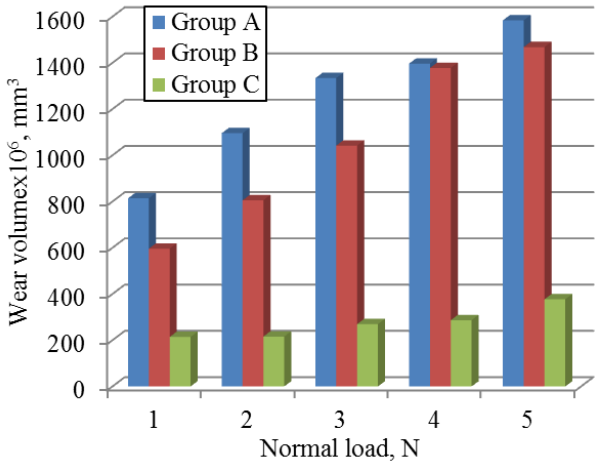

Fig. 5. Wear volume V as a function of normal load F

Table 5. Wear rate at different loads of the counter-part

Load (N)	Sample group A ($\times 10^6$, mm³/Nm)	Sample group B ($\times 10^6$, mm³/Nm)	Sample group C ($\times 10^6$, mm³/Nm)
1	16.281	11.926	4.281
2	10.956	8.052	2.159
3	8.894	6.947	1.796
4	6.985	6.889	1.434
5	6.675	5.874	1.508

In Fig. 6. a graphical representation of the above data is shown.

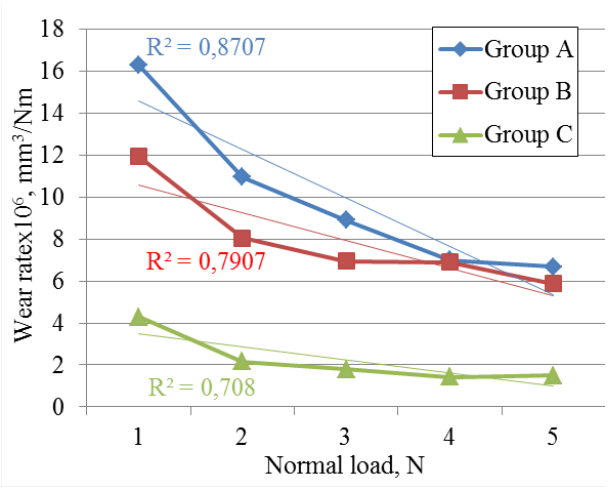

Fig. 6. Wear rate I_w as a function of normal load F

It can be seen that the value of the coefficient of determination R^2 is greater than 0.7 which gives a reason to believe that the dependence $I_w = f(F)$ is close to linear, at least in the range of applied normal loads. One can see that for hardened polished samples, the slope of the line is the smallest and the value of the wear rate is almost constant.

CONCLUSIONS

There is a slight increase in the roughness after coating deposition, which is more noticeable in the polished samples. This is probably due to the presence of droplets (non-ionized metal particles) which are specific for the process [15]. However, the coefficient of friction is not high. In addition, it could be assumed that soon after the injection mold activation, some of the droplets will fall away from the coating. If it is necessary, simple methods could be used to remove them before the tool be exploited [16].

To determine the wear, the volume is used as a criterion. The volume of the track increases with load increasing, this is quite expected. The wear rate decreases with load increasing. Such a coating, deposited on Stavax ESR steel, is suitable for elements which are subject to high loads. The attenuation of the wear rate practically takes place according to a linear law.

The roughness of the samples significantly influences the wear intensity of the coating. The coating deposited on a hardened and polished sample has the lowest wear volume compared to these on hardened ground and unhardened ground specimens (Fig. 5). It is advisable to polish the surfaces where it is possible before coating deposition.

The obtained values of wear rate are low, they are close to the lower limit of the results shown in similar studies [3, 9], which further determines the coating as suitable for application on injection molds.

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