The change in the elastic modulus values for the thickness of a multilayer coating based on TiN and CrN layers

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The change in the elastic modulus values for the thickness of a multilayer coating based on TiN and CrN layers

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Abstract. The results of investigations the cross section microstructure of a multilayer coating with a thickness of about 6 μm obtained by cathode arc evaporation, are presented. The top layer of the coating is TiN with a thickness of 200 nm, and the base consists of alternating layers of CrN and CrCN with a thickness of 200 nm per layer. Microhardness (H) and elasticity modulus of (E) were measured on the coating surface, on the CrN / CrCN layer surface, and over the cross section of the coating by nanoindentation (NI). It is established that the E values gradient from the surface with E = 313 GPa to the substrate with E = 176 GPa is smooth. The critical load of adhesive strength of the coating determined in the scratch test was 120 N.

1. Introduction

The surface of the cutting tool and friction parts works in the difficult conditions of compressive and tensile mechanical stresses acting separately or together, abrasive and corrosive wear, abundant heat release. To expand the scope of structural materials, providing the ability to withstand higher loads, they are modified, forming a nanostructure or introducing nanomaterial additives and modifiers [1–3]. Coatings allow to improved adaptation of the surface to the friction loads [4–6]. Transition metal nitride coatings, often used to protect the surface, possess good mechanical properties, high hardness and elasticity modulus, good adhesion, high wear and corrosion resistance [7–9]. TiN and CrN coatings can be used as independent coatings, but also as separate layers of a multilayer composition, providing by this way the different surface properties [10–12]. Their thickness often does not exceed 5–6 μm. In the process of work strain and stresses are distributed not only over the coating, but also over the entire volume of the material close to the contact surface. Therefore, it is necessary to include not only the mechanical properties of the coating, but also the properties of a certain substrate volume [13]. In the multilayer coating the diffusion processes between the layers are possible, which makes the task of experimentally studying of the elasticity modulus and microhardness distribution over the cross section of the coated substrate extremely relevant. The method which allows to reliably determine the local elasticity modulus and microhardness of thin layers from experimental dependencies “load – penetration depth” and to calculate their values using the Oliver–Phar formula is nanoindentation [7, 14, 15].

The aim of this work is an experimental study of changes in the elastic modulus and microhardness over the cross section of the TiN – CrN / CrCN multilayer coating with a thickness of 6 μm, the upper

layer is TiN, and the lower base layer consists of alternating CrN and CrCN layers with the thickness of 200 nm by the nanoindentation method.

2. Experimental details

TiN – CrN/CrCN coatings were deposited onto hardened steel substrates HS6-5-2 (analogue of P6M5) using cathodic arc evaporation method by the TINA-900 M equipment. Ti and Cr cathodes with a purity of 99.99% and a diameter of 100 mm were used. The substrates with a diameter of 32 mm and a thickness of 3 mm were polished to a roughness Ra = 0.02 μm, and then washed in an alkaline medium in the ultrasonic bath, rinsed in the deionized water and dried with warm air. The substrates were installed in the vacuum chamber on a rotating holder parallel to the surface of the evaporating cathode. The chamber was evacuated to a base pressure of 1 mPa. The substrates were heated to a temperature of about 300°C. The deposition process was preceded by the bombadment of the substrates with argon and chromium ions at a substrate bias voltage of -600 V at argon pressure of 0.5 Pa for 10 minutes with a current of 80 A. The thin chromium layer about 200 nm improved the adhesion of the coating to the substrate. The deposition parameters of CrN and CrCN layers were: substrate bias voltage of –70 V, an arc current of 80 A, a nitrogen pressure or a mixture of nitrogen and acetylene of 1.8 Pa, and a flow rate of acetylene of 10 cm^3/min. The thickness of the CrN/CrCN double layer was 400 nm, the number of double layers was 7. The TiN layer was applied at a substrate bias voltage of –70 V, an arc current of 70 A, and a nitrogen pressure of 1 Pa. The thickness of the TiN layer was about 200 nm. The total coating thickness was about 6 μm (figure 1(a)). Coating thickness control was carried out by the method of ball abrasion (Calotest).

The morphology of the coating was studied with the use of a scanning electron microscope (SEM) Mira (Tescan, Czech Republic). The chemical composition of the coating and substrate elements was determined using Energy Dispersive Spectroscopy (EDS). Analyser was manufactured by Oxford Instruments Analytical (UK). The chemical elements distribution along the line was used. The thickness of the coating was additionaly controlled by the SEM images of the coating with the substrate fracture. The fracture was performed after cooling of sample in the liquid nitrogen medium. The sample for fracture was partly cutted from the side of the substrate to a depth of 2 mm. The fractured coating was pressed into plastic and than grinded for the cross-section according to the standard procedure.

The microhardness (H) and the elasticity modulus (E) were measured by Hysitron 750 Ubi nanoindenter (USA) via the indentation of a diamond Berkovich indenter with a curvature radius of 200 nm into the coating during continuous recording of the applied load– indentation depth curves for every layer with the preliminary scanning of the surface. The tip radius was calibrated via indentation into a calibration melted-quartz sample. H and E measurements were performed both on the coating surface with the removed microparticle phase, and on the cross section of the coating with the substrate. For the surface measurements 36 indentation curves were performed at a load of 10 μN. In the cross section 73 indentations were performed at a load of 1 μN, 8 curves per each row with an interval between rows of about 500 nm. Additionally, E and H were measured on the surface of a friction track obtained with a load of 20 N using an Al_2O_3 counterbody with a diameter of 10 mm at a speed of 0.2 m /s and a path length of 2000 m. The partial destruction of the upper TiN layer in the friction track allowed us to determine E and H on the bottom layer based on Cr. The top layer of the coating has a dark yellow color characteristic for TiN. The friction track is highlighted on the surface in gray (figure 1(b)).

Determination of adhesion strength was performed by scratching using REVETEST Scratch CSM Instruments with diamond Rockwell C indenter (R=200 μm), track distance of 10 mm, maximal normal load of 200 N, velocity of 5 mm/min. The critical load is the normal load at which the coating was totally delaminated.

3. Results and discussion

According SEM investigations the coating shows homogeneous and the coating thickness is about 5.8 μm (figure 1(c)). The coating does not stratify into two separate layers of TiN and CrN/CrCN. It is possible to note only the closed porosity inside the coating associated with the formation of

microparticles in the process of coating formation. The pores are arranged in the rows and thus divide the coating into separate sublayers (figure 1(c)). The E and H values of the TiN-CrN/CrCN coating obtained on the coating surface (TiN layer) were E = 314 ± 13 GPa and H = 31 ± 2 GPa, the values of E and H for the CrN/CrCN layer, which opened after friction tests, amounted to 276 ± 12 GPa and H = 24.6 ± 2.0 GPa.

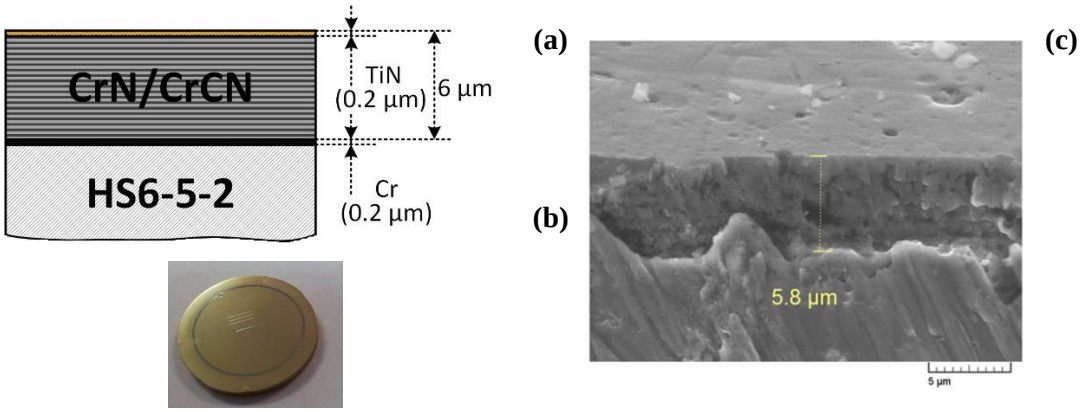

Figure 1. TiN–CrN/CrCN multilayer coating: **(a)** – scheme of layers; **(b)** – a sample with coating and wear and scrach tracks; **(c)** – a cross-section fracture of coating, SEM, x7600.

Under the TiN layer a zone of interdiffusion of Cr and Ti with a thickness of about 1.2 µm is located (figure 2). The depth of interdiffusion of Cr and Fe on the substrate boundary is about 1.2 µm. This layer is visible on the Calotest track as a wide light grey ring. The dashed lines in figure 3 connecting the image of the cross section with the data of the distribution of elements over the cross section of the coating help to see that the diffusion zones of Cr (black dashed lines) are in no way connected with the layers in the microstructure (blue dashed lines).

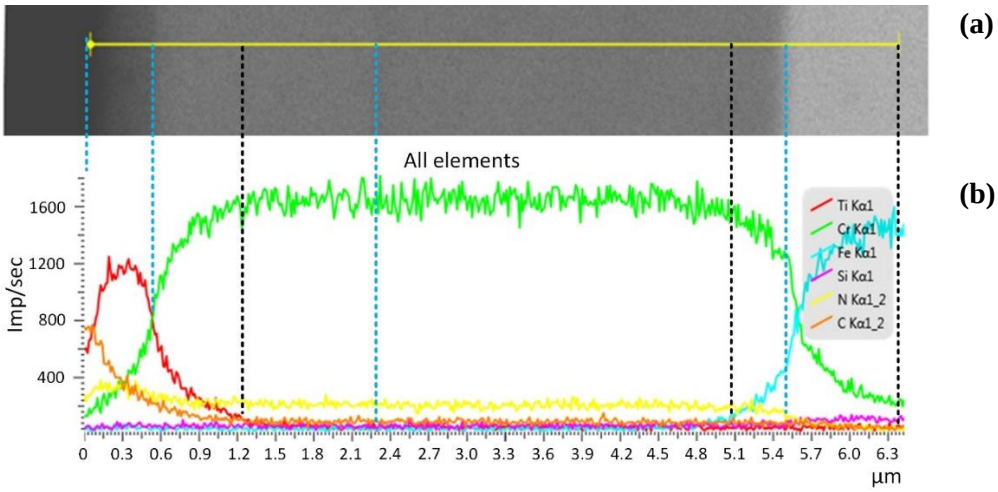

Figure 2. SEM image of the cross section of TiN–CrN/CrCN coating, magnification 40000 **(a)** and EDX line analysis across the coating **(b)**.

The CrN/CrCN layer microstructure does not consist of alternating CrN and CrCN sublayers with a thickness of 200 nm, what we can clearly see on the Calotest track, but is divided into the upper layer with a thickness of 1.6 µm and under layer of 3.3 µm. Nitrogen diffuses into the chromium underlayer on the depth about 200 nm. A probe scan image of TiN – CrN / CrCN coating cross section obtained by nanoindenter with the points of indentation is presented in figure 3(a). Indentation points arranged in the rows. The indentation curves from the areas with the different mechanical properties are separated in several typical groups. The values of E and H of upper diffusion zone between Cr and Ti

are E = 292 ± 9 GPa and H = 27.6 ± 1.4 GPa lower than that on the TiN surface, but higher than that of CrN/CrCN. For the CrN/CrCN layer, it is E = 278 ± 13 GPa and H = 25.6 ± 0.7 GPa, which is practically similar with the values determined from the surface. However, these values correspond only to a thickness of no more than 0.5 μm, and further deeper into the substrate, the properties decrease. It is impossible to attribute such a decrease to the account of Cr diffusion into the substrate, since the amount of Cr practically persists to a depth of 3 μm.

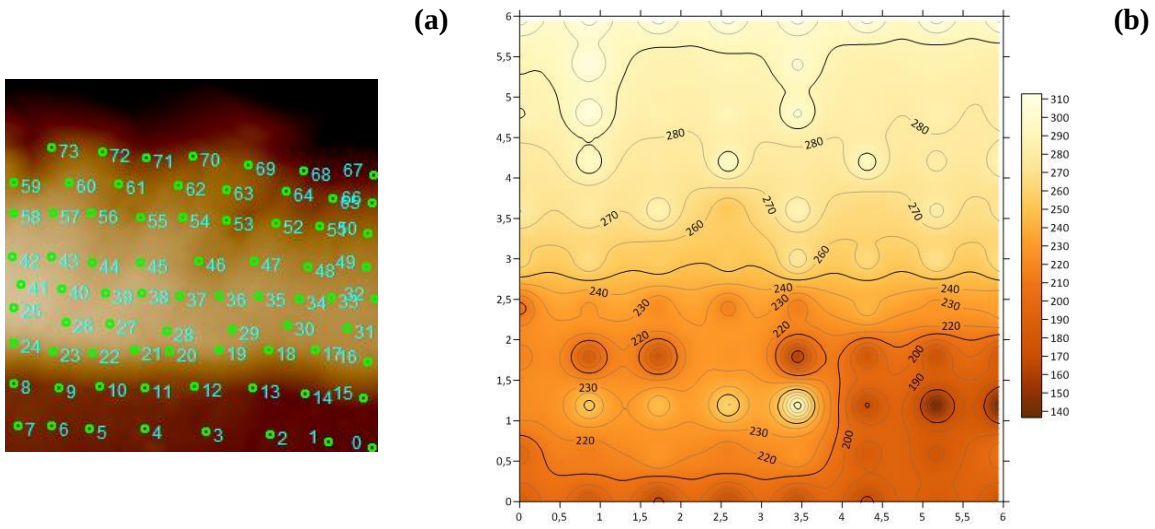

Figure 3. Nanoindentation results: **(a)** – a probe scan image of TiN – CrN / CrCN coating of 6x6 μm with the points of indentation; **(b)** – the map of elasticity modulus in TiN-CrN /CrCN coating.

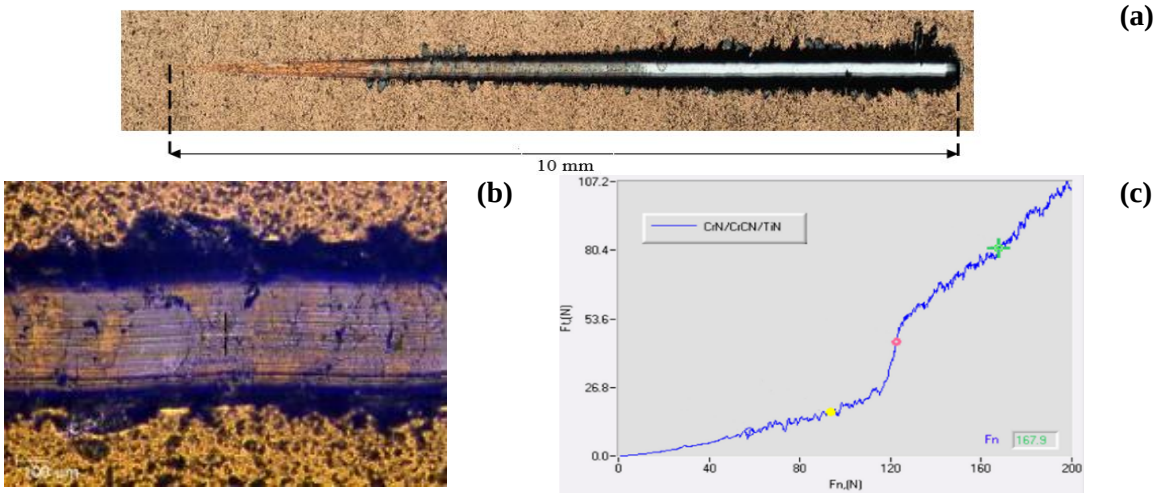

Figure 4. The results of the scratch test of TiN-CrN/CrCN coating: **(a)** – a micrograph of 10 mm track distance with maximal load of 200 N; **(b)** – a part of the scratch track at the load 120 N; **(c)** – friction force for a progressive load scratch test.

The decrease in properties can be explained by a decrease in the concentration of N and C from the depth of 3.3 μm and below. In addition, the values may decrease due to the presence of pores in the coating. The map of elasticity modulus in TiN-CrN /CrCN coating is presented in figure 3(b). Thus, a smooth gradient of the elastic modulus from 314 GPa to 174 GPa and a stepwise decrease in microhardness is formed in the coating from the surface to the substrate. A smooth gradient of properties from the surface to the substrate allows to avoid the concentration of mechanical stresses and the formation of cracks during operation of the coating. The presence of the TiN layer on the surface of the main CrN/CrCN coating hardenes it by diffusion of Ti. The results show the importance

not only the values determined on the surface, but also the characteristics of coatings studied over the cross section. The smooth gradient of E and H values from the surface of the coating to the substrate explains the high characteristics of adhesive strength, which amounted to 120 N (figure 4).

4. Conclusions

The value of elasticity modulus and microhardness of the arc deposited TiN–CrN/CrCN multilayer coating were obtained using nanoindentation method in three areas: on the surface of coating, on the surface of CrN/CrCN layer, and over the cross section of the coating.

The distribution of chemical elements over the coating section was established using SEM with EDX analysis. The interdiffusion of Ti and Cr in the upper layer of the coating, Cr and Fe on the substrate boundary was revealed on the depth of 0.4–0.6 μm. Due to this interdiffusion the values of E and H vary from the surface to the substrate very smoothly. The deposition of TiN layer with the thickness of 200 nm contributes to the hardening of the upper coating layer. Thus, a smooth gradient of the elastic modulus from 314 GPa to 174 GPa and a stepwise decrease in microhardness is formed in the coating from the surface to the substrate. Smooth gradient E and H explains the good adhesion and high value of the critical load, 120 N. The results show the importance not only the values determined on the surface, but also the characteristics of coatings studied over the cross section.

Acknowledgments

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