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The structure and formation of functional hard coatings: a short review

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Abstract. Turning tools come in different shapes and sizes, geometry, base material and coating, according to their destination. They are widely used both for obtaining parts and for machinability tests. In this paper a short review about high-speed steel (HSS) turning tools and their coatings is presented. Hard coatings formed on the tool material should be functional depending on the tool final application. Requirements for hard coatings and technological problems for layer formation on the real cutting tool are discussed.

1 Techniques and production of hard coatings

In a statistical study made for the year 2013 [1] the 16.33 billion US-Dollars estimated industry of cutting tools includes 39% milling tools followed by 30% of turning tools, with an annual growth assumed to be 4-5%. The same study shows that in 53% of the cases, the cutting tool substrate is represented by cemented carbide and in 20% of the cases by high-speed steel (HSS).

Coatings on cutting tools are widely spread due to the improvement they provide during the cutting process. In the early 2000's made statistic 50% of HSS tools, 85% of carbide tools and 40% of super-hard tools used in industry were coated [2]. Due to the more complex phenomenology which accompanies the intermittent cutting process, in this study only coatings of HSS turning tools will be treated.

The use of coatings is expected to yield a better protection of the tool against abrasion and adhesion, diffusion, oxidation and to produce a heat barrier for the intensive heat flowing from the cutting area into the tool material [3], thus increasing productivity and tool's life. However, regarding the heat insulation the opinions are divided, as in the paper [4] it was proven that the coatings of continuous cutting tools are not able to insulate the substrate.

Mainly, depending on the method and the coating structure, the same coatings can be applied to both HSS and carbide tools, each substrate having its advantages and disadvantages according to the cutting application. The properties of the tools surface should be improved according their novelty, application and to achieve higher productivity for the manufacturing process. Depending on the turning tools destination various hard coatings can be formed on its surface. The shape of the turning tool is usually not complicated, thus techniques like physical or chemical vapor deposition for layer formation are applied. Hard

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coatings are not well defined, but it might be assumed that their hardness is between 2300-5500 (HV, 0.05). The final mechanical properties of the coatings significantly depend on their structure, phase composition and homogeneity. Besides the mechanical properties, the coatings formed on the material should exhibit oxidation and thermal resistance.

Chemical vapor deposition (CVD) or physical vapor deposition (PVD), arc ion plating, ion implantation, plasma-enhanced chemical vapor deposition (PECVD), magnetron sputtering are widely used for hard coatings formation [5]. By using PVD technique the user is allowed to play with a combination of different materials (Ti, Al, Cr, Ni, N, O, Si and C) and is able to obtain layers of 1-5μm whereas CVD normally uses a narrower range of materials (Ti(C,N), TiN and Al_2O_3) for a 4-20 μm thick coating but it lays the emphasis on control parameters such as stress state, phase composition and orientation of crystals [6].

Limitation of CVD and PVD techniques is high temperature of layer deposition (usually around 950°C), poor adhesion of the layer to the substrate and sometimes poor adhesion between interlayers in the coating. The tools market is dynamically increasing and new shapes of the turning tool are desirable. For tools with irregular shape the formed layer cannot be homogenized thought the layer or thickness. Surface roughness might be also different in some places of the material.

The coatings cannot be also brittle, due to the decrease of their working life time [7]. Thus, PVD and CVD techniques are very often combined. Nano - sized and more plastic layer may be formed on the substrate by PVD technique. Coated materials should be suitable for minimum quantity lubrication (MQL) cutting, high-speed turning and should be chemically inert, phase and thermal stable. The surface of the treated materials should be smooth, homogenous, compact and wear and abrasive resistant.

Even though carbide tools are more used, HSS tools are still the choice of professionals in many cutting applications due to their low cost, high performance in machining, especially for mild steels and due to the possibility of easy re-sharpening / re-shaping operations. Any re-sharpening or re-shaping operation must be followed by re-coating so as to achieve the best results.

2 Formation of hard coatings on HSS

2.1 Single ceramic coating

The coatings adhesion to the metal substrate can be improved by pre- and/or post-treatment techniques. Typical protocols of surface pretreatment include micro-blasting, grinding, sand-blasting, shot penning, etching or also for selected materials electropolishing. Procedures of the surface pretreatment play a key role for further single or multiple layer formation [8]. Post treatment includes usually thermal coating treatment. The most popular single, hard layers formed on high speed steel are composed of TiC, TiN, Al_2O_3, TiAlN [1,9]. Titanium-based materials are characterized by high wear resistance to abrasion whereas Al_2O_3 ceramic material exhibits good chemical and thermal stability. Pure aluminum dioxide (99.99%) is often used as a reference in thermal analysis techniques. These layers are formed during one step coating formation. Duplex layers composed of TiN and TiC phase are also desirable, due to high hardness of titanium carbide and toughness and plastic properties of the titanium nitride. The coatings composed of TiC/Ti(CN)/TiN enhance also corrosion resistance of steel substrate in chloride environments [10]. Multilayer coatings might exhibit much better mechanical properties, especially hardness. Thus, in recent years the new generation of tools coated by functional multilayer ceramic materials has been widely studied.

2.2 Multilayer ceramic coating

2.2.1. Titanium-based layers

Microstructure and mechanical properties of multilayer Ti/TiAlN/TiAlCN material was investigated by M.A. AL-Bukhaiti et al. [11]. The coated materials showed lower-friction coefficients than ceramic material (Al_2O_3) and higher hardness compared to the same uncoated materials. The coatings showed good cohesion within the multiple layers. The layers weren`t brittle, only spallation-chipping failure was registered according to the typical cracking or delamination during scratch-test measurement.

Tribological and mechanical properties of the material during the working of the tools are important. During the scratch measurements it was noticed that heat influences the plastic and chip deformation of the layer. Thermal stability of multilayer $Ti_{1-x}Al_xN$/TiN formed on two PM-HSS (S390PM, S290PM) substrates were investigated by T. Weirather et al. [12]. Temperature of the substrate during multilayer coating formation was between 373°C-575°C. Chemical composition of the substrate slightly influenced the thermal stability of the whole material. The difference in the hardness value was 1 HRC (66 HRC for S390PM and 67 HRC for S290PM) when coatings were formed at temperature up to 530°C. A higher temperature of the substrate during the coating process has caused the hardness to increase for both materials. Heating of the substrate also influenced on the total thickness of the layer and its tribological properties. All layers showed excellent adhesion to the substrates with Rockwell nanoindentation test. Thickness of the coatings formed on metal substrates can be between 10 nm to around 20 μm.

Depending on the applied techniques the chemical composition of the substrate could strongly influence the final effects of substrate treatment. One of the investigations about the influence of the steel's hardness over the surface treatment and the tribological behavior was presented in paper [13].

Comparison of the mechanical properties of single TiC_xN_{1-x} (x=0-1.0) layer with TiC/$TiC_{0.5}N_{0.5}$/TiN layers formed on high-speed steel was presented by M. Yasuoka et al. [14]. The layers were formed using hollow cathode discharge (HCD) ion plating method. Multilayer coatings showed higher wear and dynamic resistance compared with a single layered material. However, the success of the multilayer coating was connected with the first single layer - TiN, which exhibits excellent adhesion to the HSS substrate. TiC layer led to a much better wear resistance of the material. It was found that coatings composed of 50-70% carbon showed the highest hardness, thus the tools life should be longer. Similar investigations with TiN layer as an intermediate layer between substrate and upper ceramic layer was reported by K. Kawata et. al. [15].

The thickness of the lower layer was higher (2.5 μm) compared to the thickness of the upper (Ti,Al)N layer (1.0 μm). The layers were homogenize and well adhered. The upper layer was composed of 21.10 at.% of aluminum and 28.65 at.% of titanium (determined by EDX analysis). Addition of the aluminum caused that coating hardness increased, and coating exhibited low friction coefficient (0.47-0.55). The layers were also resistant to oxidation at air at 1073 K.

To enhance adhesion of two layers TiN and TiAlN, the surface of the HSS was additionally pretreated using plasma nitriding [16]. Then the ceramic layers were deposited by physical vapor deposition technique. The formed layer was smooth, compact with average surface roughness below 5 nm, and total layer thickness 3.1 μm. Plasma-nitrided surface was more favorable for hard coatings formation, which weren`t delaminated during surface mechanical testing.

2.2.2. Chromium-based layers

Another group of the multilayer ceramic coatings for preventing premature steel material degradation contains layers with chromium nitride. Coatings composed of Cr-X-N, where X is Ti, Si, Al or C have been investigated as a functional layer on various metal substrates. Basic chromium nitride (CrN) layer is considered as a material which prevents premature consumption of steel substrates due to their chemical inert properties. Besides increasing mechanical properties of the substrate (mainly hardness), chromium nitride also prevents corrosion and wear.

K. Valleti et al. [17] presented difference in microstructure and mechanical properties of single CrN and multilayer CrN coatings formed on HSS using cathodic arc physical vapor deposition. Hardness of the coatings was similar, i.e. around 22-14 GPa, but the differences were observed in the coating microstructure and adhesion to the substrate. Monolayer CrN was more compact and regular compared with multilayer CrN_x. Adhesion of the coatings wasn`t improved by formation of additional CrN_x layers. It was also reported that increasing thickness of the layer resulted in the increase of the internal stresses and could led to reduced adhesion strength of the coating to the HSS substrate. Similar results were presented by C.-M. Shi et al. [18]. The HSS was coated by various thickness ratios of CrN and Cr_2O_3 layer using an arc ion plating method. The main goal of the CrN interlayer was improvement adhesion of the outer ceramic layer to the metal substrate. It was found that CrN layer indeed improved additional ceramic layer adhesion, but also influenced on their final average surface roughness. The multilayer coatings composed of the thickness ratio 2:1 of CrN and Cr_2O_3 showed the best wear resistance. The average surface roughness of these coatings was 0.13 μm, when for the coatings composed of the layers in thickness ratio 1:4 was much higher 0.26 μm. Thus the significant difference in friction coefficient was observed. It was proved that the CrN underlayer reduced plastic deformation of the multilayer ceramic coatings.

Thermal stability of the chromium-based coating was improved by yttrium. S. Liu et al. [19] characterized the CrAlYN layers formed on the HSS by a hybrid high-power impulse magnetron sputtering – magnetron sputtering disposition method. CrN/ AlN layers were enriched by Y up to 9 at.%. Yttrium was preferentially adsorbed into the AlN layer. The layers composed of Y were more compact and better integrated after heating at 1000°C compared with layers without Y. The thermal stability of the layers was enhanced by formation of yttrium nitride (YN) which was considered as a diffusion barrier layer.

Addition of carbon in chromium nitride composite decreases layer adhesion to the substrate but increases their hardness. However the amount of carbon in the layer is limited. It was reported that more than 19 at.% of carbon content decreases wear rate at higher temperature. It was found that Cr-X-N coating with carbon content between 5 and 15 at.% reduced the friction coefficient more than 0.15 [20]. Thus, the investigation of the multilayer CrCN/CrN coatings composed of carbon (10 at.%) was investigated by A. Gilewicz et al. [21]. It was found that multilayer coatings obtained by cathodic arc evaporation technique showed much better mechanical properties and better adherence to the substrate compared to the single layer. The critical load depends on the structure of the coating, its thickness, microstructure and adhesion between each interlayer. Another multilayer coatings formed on HSS composed of Cr/CrN/CrTiN was proposed by M.S. Kabir et al. [22]. The layers were obtained using close field unbalanced magnetron sputtering (CF-UBMS). Microstructure of the coatings strongly depends on the content of titanium columnar microstructure decreased when coatings were composed of a higher content of titanium. The decrease of the columnar grain size influenced the top layer hardness. The top layer of the ceramic composite was very smooth and the average surface roughness was 21.0 nm ± nm (determined by atomic force microscopy). The influence of TiN layers on micromechanical properties of the TiN/CrN bilayer coating formed on high-speed steel by physical vapor deposition was presented by J.J. Roa et al. [23].

Chromium-based coatings may also be composed of additional elements like aluminum and/or silica. Procedures for multilayer formation and nanocomposite AlCrN and AlCrSiN obtained on the high-speed steel by arc ion plating were proposed by W. Wu et al. [24]. Addition of Si into layers caused the formation of nanocomposite solid-solution (Cr,Al)N crystallites phases and amorphous Si_3N_4. This kind of ceramic layers resulted in higher hardness 48 GPa, lower surface roughness and lower friction coefficients compared to layers without silica compounds. Physical vapor deposition technique is excellent to obtain duplex layers on nitrided substrate (CrAlN layer) during one step process [25]. The hardness, high temperature stability and extreme wear resistance significantly increased after the steel's surface treatment. The layers were composed also by intermediate Cr layer, CrN layer with the thickness of 0.3 μm. It was reported that TiAlN/CrN layer composed of chromium up to 30% reduced low oxidation rate at temperatures up to 900°C [26].

3 Summary and conclusions

Various techniques are used to obtain hard coatings on high-speed steel surface. Chemical composition of the layers is varied, but mainly composed of elements such as Ti, Cr, Al, N, C, Si. The formed ceramic layers are usually crystals, and phase composition includes compounds like TiC, TiN, TiAlN, CrN, CrCN. These layers are usually chemical and thermal stable in the temperature range of the cutting tools. Single layer formed on the substrate exhibits usually good adhesion. It is desirable to obtain tools with much longer tool life. Thus, investigations on the multilayer hard coatings have been extensively carried out. Indeed some single interlayers such as TiN, CrN enhance adhesion between harder outer layer with the metal substrate. Multilayer coatings are characterized by higher thickness and this may influence their fragility. As it was mentioned, chemical and phase stability is one of the main requirements of the hard coatings formed on the cutting tools. The ceramic layer might be formed as a separate layer (one by one) or as a layer with diffusion phase between these layers.

The chemical composition of course influences on the final mechanical properties of the material, however the microstructure and surface roughness play the main role in the cutting tool's life. In order to better synthesize the amount of information above, Figure 1 is proposed to illustrate some key aspects of the 2 type of coatings, i.e. single layer and multilayer.

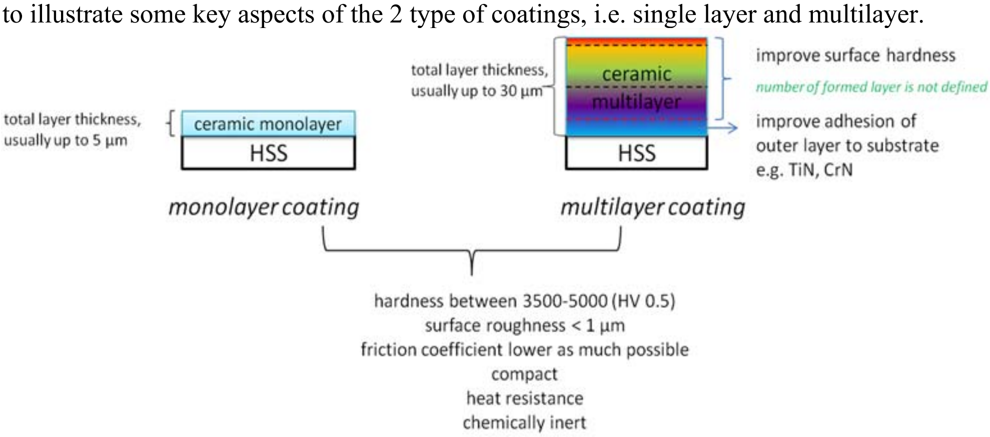

Fig. 1. Single layer and multilayer coatings.

The chemical composition of the single and multilayer coatings might be the same or very similar. However, the structure and phase composition of the layers can be strongly different. The final results of the metal surface modification depend on the number and type of applied techniques. Due to the condition during surface treatment e.g. temperature, the same chemical compounds may exist in various crystal structures due to phase transitions. In some cases the amorphous form of one phase might form and change the physical properties of the coatings. Due to the goal of the surface treatment - strong adhesion of the layers to the substrate and high hardness value - the number of the applied techniques for multilayer coatings formation might be limited. It is important to apply the appropriate instrumental techniques to control the properties of the multilayer coatings as they might be expensive and time consuming. Thus it’s recommended that the formation of multilayer coatings should be correlated with the basic investigations as well as with the applied investigations which are desirable to be conducted in the industrial environment. Many techniques are appropriate for the formation of functional hard coatings. The parameters applied during surface treatment are important, and the quality of the used substance determines the final effects of the multilayer coating formation. As pointed out by [6] through the 4 phases identified within the dynamic analysis of the cutting process, the cutting conditions are very much different in continuous cutting than in interrupted cutting. Thus the coatings which are applied on the cutting tool must be adapted to the requirements of the cutting process besides to those of the substrate material. When it comes to turning processes, even though amongst the most important properties of the coatings to be focused on should be hardness when it comes to abrasion wear and surface roughness for adhesion wear, it’s not enough to properly assess the quality and behavior of that particular coating during cutting. Each multilayer coating should be designed based on some general aspects of the cutting process and coating properties but the custom structure and properties of the coating should be devised after some real cutting tests.

The comparison of the coatings is complicated due to the various parameters applied during mechanical measurements. Thus, it is not possible to find the optimal method, parameters and the best phase composition for hard coating formation on high-speed stainless steel.

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