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Filtered Cathodic Vacuum Arc Deposition of Nano-layered composite coatings for machining hard-to-cut materials

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Abstract

In coated tools, the grain boundaries and coating layers are areas of intense energy dissipation, which hardens the coating material by increasing its toughness and its resistance to the formation and development of cracks. An increase in the efficiency of the coatings was achieved by applying nano-dispersed multilayer composite structure. This paper proposes using nano-scale multilayer composite coating based on *TiN-CrN* compound to improve thermal stability, where, barrier layers based on *ZrNbN* have been introduced. The *ZrNbN* barrier does not interact with *TiN* and *CrN* at temperatures around 1000°C. The influence of process parameters of the filtered cathodic vacuum arc deposition on the composition, structure and properties of the coatings based on variation of *TiAlN-ZrNbN-CrN* was analyzed. The results presented here show that the hardness of the developed coatings was as high as 38 GPa. Subsequently, the carbide tools used in this study with the new coatings had an increased lifetime of 1.5–2.0 times compared to tools with commercial coatings. The coated tools were tested in turning and milling of steels, nickel and titanium alloys.

Keywords: Nano-scale multilayer composite coatings; filtered cathodic vacuum arc deposition; machining hard-to-cut materials; tool life

1. Introduction

In machining, the increase of efficiency and reliability of cutting tools is an important measure in improving process efficiency. There exist a number of methods aiming at increasing the efficiency of cutting tools. However, the most effective is wear-resistance coating, which in recent years has been widely used [1-5; 7, 9].

Tool material with coating has a composite structure that consists of a substrate with a coating deposited at its surface. Coatings may have multiple physical purposes; on the one hand, the coating in spite of its tiny thickness (few micrometers), improves substrate properties such as surface hardness, physical-chemical passivity towards workpiece material, antifriction and thermal insulation. On the other hand, during the cutting process, the coating transforms the contact characteristics such as adhesion interaction, friction and inter-diffusion between workpiece and tool materials [1, 3, 8, 13-16]. The reduction of these characteristics allows lowering stresses (normal and shear), frictional heat capacity and thermal stresses acting at the contact areas of tool. The cumulative action of these physical properties defines the intensity of tool wear [1-3].

With optimum selection of coating material along with its architectural structure and properties, it is possible to purposely modify the most important surface properties of tool material. Such modification help to improve the tool resistance to wear and to reduce thermo-mechanical stresses, which, lead to a reduce wear in a wider range of operating temperature scale, [1-2, 5-9].

Regardless of significant progress in the field of coatings with a large diversity of innovative types of wear-resistance coatings for cutting tools, there is still a lack of scientifically proven principles to form such coatings as a function of machining configuration. This leads to the used of the same composition and coatings architecture for different conditions of cutting various materials. At time different composition, properties and coating architecture is recommended for the same cutting conditions [3, 10-12]. This leads to the main objective of this paper where an attempt is made to develop nano-scale multilayer composite coatings for cutting tools. Here structurally designed coatings were engineered to keep as long as possible their performance properties and the effects of their physical interaction with surfaces of the cutting contact zones of the tool. These desired performance properties can be secured by a combination of high hardness, thermal resistance and low physical-chemical activity along with sufficient toughness and resistance to crack. This can be achieved by engineering architecture with multiple layers of coatings using nano particles. Such coatings are designed to keep their protective actions on the contact surfaces of tool and the processed material. This allows the tool to perform efficiently in a wide range of cutting conditions with cyclic processes and high thermal-mechanical tensions.

The above mentioned properties can to be obtained using nitrides of refractory metals. By varying their deposition parameters, it is possible to control the composition, structure and morphology along with the thickness and number of layers in the coating. With this approach the hardness of the coatings can reach 45-50 GPa [10-14]. The coatings retain an appreciably

high viscosity because they dissipate the brittle fracture energy at the inter-grain and interlayer boundaries [15]. The high hardness and resistance to plastic deformation of these type nano-layered composite coatings are determined by the increased strength of their adhesion to various substrates compared to that of coatings without a multilayered structure [16].

However, a number of multilayered composite coatings based on the *Ti-N/Cr-N*, *Ti-Al-N/Cr-N*, *Ti-N/Nb-N*, *Ti-N/V-N* compounds have a serious drawback that is the mutual solubility of the layer phases at temperatures below 900-1000°C [17]. Heating multi-layered two-phase system during the deposition and subsequent use of the coatings roughens the interlayer boundaries and triggers strong diffusion mixing of the components. It also leads to levelling the concentrations of nitride-forming metals over the coating thickness and forming a solid solution [18]. This process is accompanied with the deterioration of the hardness and other properties of the coatings, [19-20]. One of the methods used to stabilise the structure of these coatings above 1000 °C is to form an additional barrier layer based on refractory metal nitrides with materials that are not mutually soluble in neighbouring layers at higher temperatures.

The work presented here developed *Ti-Al-N/Cr-N* nano-scale coatings by introducing an additional *ZrN*-based obstruction layer that exhibits a limited solubility in *TiN* and *CrN* up to 1580 and 1430 °C, respectively [17]. The addition of this obstructive layer increased the thermal stability of the coating structure. This work used the filtered cathodic vacuum arc deposition (FCVAD) method to synthesize these wear-resistance nano-scale coatings for cutting tools. This was derived by analysing the principles of forming and mechanisms of material hardening of wear-resistance coating and its failure modes in cutting processes.

2. Theoretical prerequisite

The efficiency of the coating active effect on the tool material considerably depends on its durability and resistance to fracture/failure at the contact areas of tool. Typically, coatings consist of relatively brittle materials (compounds of refractory metals) that fail with no visible plastic deformation and are extremely sensitive to cracking due to low fracture toughness. Cracks drastically reduce the strength of the coating and facilitate failure by the removal of macro and micro chips of material, followed by intensive wear tool material, which further leads to loss of cutting efficiency.

The initiation of cracks in the material of the coating depends on the architectural composition, properties, cutting conditions and the characteristics of the material. The durability of the coatings can be significantly enhanced through the creation of nano-structured multilayer architecture, which effectively hinders the initiation of cracks at its source. Furthermore, the

problem of coating efficiency with increased durability can be solved by engineering a balanced combination of coatings essential characteristics, such as hardness and heat resistance on the one hand and viscous failure (crack strength) – on the other hand. Similarly, when increasing the hardness of a material it is possible to keep or to slightly increase the fracture toughness; hence this can be also achieved in the development of coatings with nano-grain structure.

Coatings have a dual nature as an "intermediate technology medium" between the tool and the workpiece materials. Using this concept of dual nature, functional requirements for coatings for cutting tools were derived to prove the concept of multilayer composite coatings with nano-scale structure [1, 4, 5, 7-9]. This concept of multiple nano-layered composite stipulates that the coatings should be based on two/three components structure consisting of an adhesive underlayer, intermediate layer and the outer wear-resistant layer.

Adhesive underlayer should have a maximum crystal-chemical compatibility with the substrate material and provide strong adhesion strength. The intermediate layer must counteract and smooth the differences in crystal-chemical properties of outer and adhesive layers. In addition, the intermediate layer can be used to block the heat flow from frictional heat sources to the substrate and the inter-diffusion between the tool and the workpiece material (barrier function). This layer can be used as a sensor which monitors the thermal and mechanical stress on the cutting tool directly in the cutting process in order to diagnose tool conditions, [11-12, 20-23].

The most important role in coating is played by the outer wear-resistant layer, which must have a maximum difference in crystal-chemical structure with respect to material to be machined. This outer layer must minimize adhesive interaction with the machined material and must have a maximum resistance to macro/micro cracks and failure (wear resistance) in order to withstand thermal/mechanical stresses generated during cutting.

Each of the layers of the nano coating can have a multilayered structure, which increases its resistance to brittle fractures that are initiated by the birth and branching of cracks. The following conceptual approaches can be used to develop the multilayered nano composite coatings for cutting tools namely, (a) the introduction of strengthening solid solutions, (b) the application of graded layers by type of connections, (c) the use of meta-stable compounds with homogeneous metalloid structure, (d) the application of multiphase nano-structured layers, and (e) the use of higher order of multilayer structures with nano-layers [11, 23, 25-26].

Using aforementioned concepts a design of tool with increased coating efficiency was achieved in this work with the prerequisite that the coatings would have a maximum operational duration without partial fracture or complete failure. Here the coatings were deposited

embedding multi layered architecture with nano sub-layers and nano grain structure. Alongside this, a high adhesive strength of the coating onto the substrate material was secured.

2.1. Development of nano-structured coatings

The formation of nano structured coatings leads to an increase of the grain boundaries and triple junctions, the volume fraction of which can reach over 50% [10]. Plastic deformation in such materials occurs mainly due to inter granular boundary sliding, effectively competing with the normal movement of lattice dislocations. Inter granular boundary sliding is engendered by sliding the moving dislocations with Burgers vector parallel to the plane of the interface. The movement of grain boundary dislocations slows or completely blocks the triple junctions at grain boundaries with different angles of orientation. Therefore, to overcome these barriers, a transformation of grain boundary structures is required. In addition, it is important to account for the diffusion mechanism of plasticity associated with the diffusion of voids in the bulk of grains along their boundaries and triple junctions of these boundaries, which can also take part in the plastic transformation. Each of these mechanisms may be dominant. The transition from one dominant mechanism of plasticity to another due to grain refinement leads to changes in the deformation behaviour of the sample, which is manifested, in this particular case as a deviation from Hall-Petch relationship.

The increase of viscosity in nano-crystalline materials is a consequence of the presence in their structure of a large number of triple junctions. In the plastic deformation by mechanism of inter-grain boundary sliding there is a splitting of the dislocations at triple junctions, which leads to a significant increase in equilibrium length of incipient cracks, thus it reduces the likelihood of crack occurrence. Besides movement, the dislocation joints may be accompanied by a local amorphization of the triple junction and the formation of an embryo of the amorphous phase at the border, and a set of dislocations with less power [2-3, 10-11].

2.2. Analysis of methods for improving coating properties

The most effective way to control the properties of the coating material is the method of structural hardening. According to the dislocation theory of plastic deformation and failure, fracture of the yield strength σ_T and fracture toughness K_{IC} are functions of the following parameters [6-7]:

$$\sigma_T, K_{IC} = f(\sigma_n, \sigma_d, \sigma_p, \sigma_f, \sigma_z), \quad (1)$$

where: σ_p - Peierls-Nabarro stress (friction stress of the crystal lattice),

σ_d - hardening by increased in number of lattice defects (voids and dislocations),

σ_r - hardening by dissolved atoms;

σ_f - hardening by dispersed phase, existing or specially created in the coating structure;

σ_z - hardening by micro-structural barriers to moving dislocations at grain boundaries, at the boundaries of two phases and the secondary phase inter layers.

In expression (1), increasing the lattice friction stress σ_p leads to a slight increase in yield strength, with a sharp decrease in the critical fracture stress. σ_p strongly depends on the type of crystal bonds, and, increases the amplification in the proportion of covalent atomic bond. The inhibition of dislocation by Peierls relief is more effective at low temperature, which should be considered when assessing the impact of stress σ_p on the strength of the coating. A coating formed by physical vapour deposition of ionic phase is characterized by the number of dislocations, which is close to the critical ($\sim 10^{16} \cdot \text{m}^{-2}$). Therefore, the hardening σ_d associated with an increase in their number is not practicable.

2.2.1 Hardening of dispersed phases.

The hardening of dispersed phases σ_f is also a promising mechanism for increasing the strength wear-resistant coatings [11, 12]. However, this is possible only in systems containing two or more phases. The yield strength of dispersion-strengthened condensate with Face-centered cubic (FCC) structure can be represented by the following relationship:

$$\sigma_T = \sigma_{0M} + \frac{\alpha G_M b_M}{d} f, \quad (2)$$

where σ_{0m} - yield strength, G_M - shear modulus, b_M - Burgers vector and matrix; d - average size and f - volume fraction of second phase particles; $\alpha = 38 - 60$ - a coefficient depending on the nature and form of dispersed particles.

Hardening by dissolved atoms σ_r in forming wear-proof coatings is a major mechanism for changing the physical and mechanical properties as the coatings have been developed on the basis of concentrated solid solutions or chemical compounds. By changing the composition of the solid solution, it is possible to optimize the physical and mechanical characteristics due to changes in the type of chemical bond. In addition, the inclusion atoms strongly reduce the mobility of dislocations and increase the stability of the dislocation structure (i.e., slow the flow

of processes of return and re-crystallization). Consequently, it can provide a stable structure of the condensate and prevent or slow the aging process [1].

2.2.2 Hardening by additional alloying

Modification of solid solutions with additional alloying of the coating material is technologically achievable by two mechanisms that form [2]:

- a substituting solution in the sub-lattice metalloid by directional modification of the composition of the gas in the chamber to form compounds of the type MeG_xG_y ;
- a substituting solution in the metal sub-lattice. The process is carried out with various alloying elements to form compounds of the type Me_xMe_yG . Technologically, it is also possible to have a simultaneous occurrence of both mechanisms with the formation of complex compounds.

In the compounds of MeG_xG_y type, the introduction of a second metalloid changes the number of electrons per atom, thus, increasing the covalent bond, and the deviation from stoichiometry. The introduction of another metalloid G2 in the sub-lattice of metalloid G1 leads to a distortion of the crystal lattice due to a greater strength of association G1-G2. By varying the volume and rigidity of the bonds, the metalloids G2 get involved in a stronger consolidation of dislocations of inclusion atoms [11].

Hardening of the coating material by solid solution using the Me_xMe_yG mechanism provides more flexibility. All alloying elements in this case are divided into two groups: (a) elements that make connections with unlimited solubility and (b) elements that form compounds with limited solubility or do not interact with other. When alloying solid solution of titanium nitride with elements of the first group (Zr, Mo, Cr, V, Ta, Nb, Hf) that form nitrides with the Face-Centered Cubic (FCC) lattice shaped compound, a high hardness and wear-resistance can be achieved. Since the elements of the first group have unlimited solubility in titanium nitride, the coating composition can be adjusted within wide limits and thus, it is possible to control functional properties of the coatings.

Amongst the elements of the second nitriding group, Si, B, Al, Fe are specially highlighted. The limited mutual solubility of the nitrides of these elements as well as the presence of triple compounds, suggests that coatings based on titanium nitride alloyed with elements of the second group, a precipitation hardening mechanism is observed along with solid solution hardening mechanism. Elements of the second group are relatively inexpensive materials that react with metals and metalloids. The action various hardening mechanisms has different level of influence on the properties of the coatings. The most obvious effect of alloying elements on the metalloid

is the change of thermodynamic activity of G inclusion. A short-range order "substitution-implanting" engender obstacles like pair of Me₂-G. Depending on the displacement field, a pair of Me₂-G as an obstacle may be stronger than implanting a single atom. Therefore, hardening of the coating material alloyed with the second mechanism affects the magnitude of the Peierls force. This leads to an increased internal friction and yield strength of solutions Me₁Me₂G type, and this manifests itself more clearly with increasing temperature.

The degree of solid solution strengthening with complete dissolution of the alloying element using the theory of Motta Nabarro can be expressed by the equation:

$$\Delta\sigma = \sigma_a^{3/4} \cdot C, \quad (3)$$

where
$$\sigma_a \approx \frac{1}{a} \cdot \frac{da}{dC}$$

where σ_a is the linear parameter mismatch; a is the lattice period and C is the concentration of solute atoms. With the same concentration C the degree of hardening is higher in the case when the size of the dissolved atom is less than the solvent atom. However the degree of hardening is less with the inverse ratio of the sizes.

It is of interest to use for alloying elements that form chemical inter-metallic compounds with the coating material. For coatings application based on titanium nitride, these types of elements include nickel and copper, the introduction of which in coating composition leads to additional hardening of the coating. In the case of formation of chemical compounds, the hardening degree depends on the strength of the inter-metallic compound and the concentration of additives. This mechanism (the formation of inter-metallic compounds) is considered to be good enough to harden the wear-resistant coatings. This is because the inter-metallic compounds have a very high hardness, and are a good barrier to inter-diffusion processes that helps to increase the efficiency of the coatings.

2.2.3 Hardening by nano-structured impediment.

A promising method of engineering high-strength wear-resistant coating material is the hardening of micro-structural impediments σ_z (grain boundary between two phases) in the second phase of the layer. In [1 and 11], it is shown that, by reducing coating thickness, there is a potential of significant increase in strength. This allows creating architectures of nano coatings consisting of thin polycrystalline sub-layers the strength of which is not achievable for macro-sized materials. The main reason for high strength sub-layers with nano thickness is grinding the

crystals down to nanometre level, which leads to strengthening of the condensate. The increase of the strength in this case can be expressed by the Hall-Petch relationship

$$\sigma = \sigma_0 + Kd^{-0.5}, \quad (4)$$

where σ_0 and K are material constants and d is grain diameter.

Hardening by nano-structured impediments can be realized in creating nano-layers materials. This hardening mechanism is typical for the physical processes of coating (PVD), which offer a wide range of possibilities in designing nano-layers materials due to the combination of complex physical processes of evaporation, sputtering and condensation while forming the coatings and moving the substrate relative to the stream of ionic steam generated by evaporation systems. By varying the thickness, composition, and properties of alternating nano-layers it is possible to adjust widely the mechanical properties of engineered materials.

Nano-thickness of coatings sub-layers can be formed by a planetary motion of the cutting tools in the vacuum-arc setting (equipped with several evaporation systems) during the transportation of the instrument through the steam generated by the ion stream evaporators. The thickness of each of the sub-layers depends on the installation layout. Here, the configuration changes in terms of number and the location of evaporators relative to each other, the distance of the cathode relative to the cutting tool. This allows precision control of the thickness of all components and transition layers, therefore purposely engineered properties of the coating can be achieved.

3. Experimental procedure

3.1. Coating deposition

A new technology based on the filtered cathodic vacuum arc deposition (FCVAD), [3, 4, 7] was used to deposit the coatings on selected tools. The FCVAD technology allows creating a solid coating adhesion to the substrate, high density and hardness that provides a substantial increase of cutting efficiency. FCVAD technology was implemented using the VIT-2 coating station, with the following configuration as illustrated in Fig.1:

- Three cathodic evaporation systems with individual power supplies;
- Filtration steam device - ion stream from micro-droplets formed by the evaporation of the cathode metals (*Ti*, *Zr*, *Cr*, *Al*, etc.);
- Extinguishing system of micro-arcs;
- Dynamic gas mixing device,

The coating process i.e. the application of the nano structured, multi layered composite coating was undertaken in three main steps, including: A preliminary preparation of cemented carbide inserts. This is followed by ion finish cleaning and thermo-activation of the inserts directly in the process chamber of installation. The final step is the actual application of the nano structured, multi layered composite coating. The Pre-treatment of carbide inserts insertion in the process chamber consisted of: a preliminary ultrasonic cleaning (at 18~20 kHz operating frequency) in a hot alkaline solution; a subsequent washing with acetone and alcohol, drying and rubbing. The cleaned sample inserts were placed in special containers that are installed in the VIT-2 process chamber on a special table (14), which had a rotary and planetary motion during the coating deposition process.

Vacuum is created in the process chamber at a pressure of $1.3 \cdot 10^{-3}$ Pa then argon neutral gas is pumped into chamber to subject the samples to further purification by argon ions in the steady pressure of $1.2 \cdot 10^{-3}$ Pa. this is followed by finishing ion cleaning and thermo-activation of the cutting inserts by metal gas ions at a potential voltage of 0.8 – 1.1 kV on the samples.

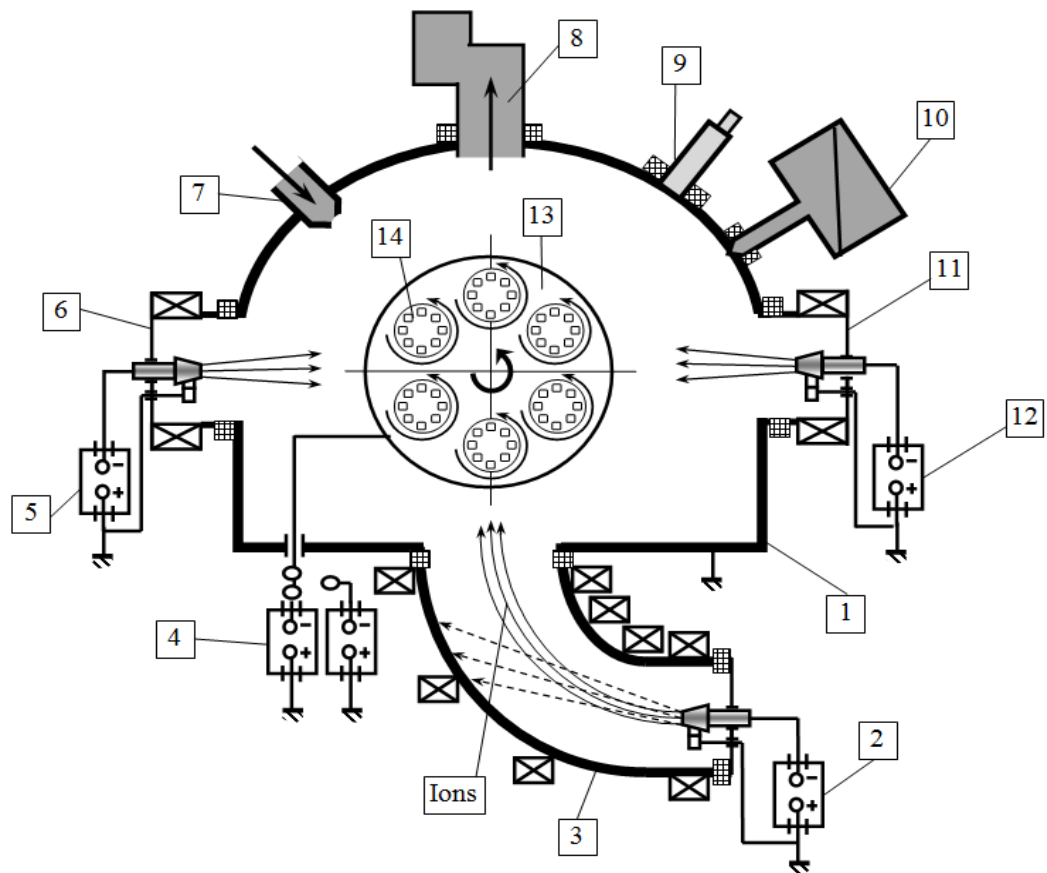


Fig.1: Configuration of VIT-2 arc-coating system and the arc type evaporator for filtering the vapour-ionic flux: 1 – gas inlet system; 2 – vacuum system; 3 - temperature monitoring system; 4 - heating and cooling system; 5,12 - standard arc evaporators; 6,11 - power supplies to

evaporators; 7 - the chamber of installation; 8 - power supplies to filtering module; 9 - filtering module; 10 - system of pulsing bias voltage supply to the specimens being coated; 13 – turntable; 14 – specimens (cutting tool)

A special device was used to extinguishing micro-arcs in the process of ion cleaning and thermo-activation to prevent electrical discharge erosion of cutting edges of the carbide inserts. The finishing process was about 8-12 minutes. However, for the cutting inserts with a high possibility of damage from thermal shock (e.g., hard alloy with a cobalt content of less than 6 %) thermo-activation performed in pulsed mode. After a thorough cleaning and thermal activation, the coatings were deposited with predefined composition, architecture and properties at a working voltage potential of 0.2 – 0.3 kV and a discharge current of 2.1 A over 50-60 minutes.

The VIT-2 equipped with three cathodic system of evaporators: *Ti-Al* (95 % at. Ti, 5 % at. Al), *Zr-Nb* (70 % Zr at, 30 % at. Nb) and Cr. In addition the *Ti-Al* cathode was installed on a filtering evaporating system. The evaporation of cathodes was produced in a medium of nitrogen which is a reactive gas. In this process the speed of rotation (n) of the sample was varied along with the arc current *ZrNb* cathode (I_{ZrNb}) and the amount of bias voltage (U_b) on the samples. However, the current of the arc of the evaporating cathodes Ti-Al and Cr was kept constant. The coatings were deposited during a planetary motion of the samples relative to the evaporators. This arrangement allows generating coatings a layered structure with the desired thickness of the coating layer.

3.2. Evaluation of coating properties

The investigation of the characteristics of the structure and phase composition of the developed coating performed using X-ray diffractometer Ultima 4 (Rigaku, Japan). Images were taken in diffraction mode, step scan $\text{CoK}\alpha$ -rays, which increased the intensity. With the help of OUTSET software [12] these images were divided into lines 111 and 222, allowing to define the lattice of each phase and the analysis of the substructure parameters. Quantitative phase analysis was performed using PHAN software [16-17].

The chemical composition and binding energy of the elements in the phases of the nanomultilayered composite coating were determined using the X-ray photoelectron spectrometer (PHI 5500 ESCA XPS; Perkin-Elmer, USA). The excitation photoemission was produced at Al $\text{K}\alpha$ radiation with $h\nu \sim 1486,6$ eV and a power of 300 W. The stratified distribution of elements in the coating was studied by spraying the surface with argon ions with an energy of 2 keV, which roughly corresponds to an etching rate of 2 nm/min. The etching time was 30 minutes.

The element composition and morphology of the coatings was also investigated by scanning electron microscope JSM-6700F (JEOL, Japan) with an attachment for energy-dispersive spectrometry JED-2300F (JEOL, Japan).

The hardness (H), elastic modulus (E) and the work of plastic deformation (W_p) of the coatings was determined by measuring the indentation at low loads. This procedure followed the method of Oliver and Pharr, which was carried out on Micro-Hardness Tester (CSM Instruments, Switzerland) at a fixed load of 300 mN. In order to limit the influence of the substrate, the penetration depth of the indenter was controlled so that it does not exceed 10 – 20% of the coating thickness.

The evaluation of adhesive/cohesive strength was undertaken in the “NMKP-substrate” system. The REVETEST device (CSM Instruments, Switzerland) was used to undertake scratch tests of the sample with a certain (critical) load and the resulting peeling the coatings along the scratch was investigated. A Rockwell diamond indenter with a radius of curvature of 200 μm was used at continuously increasing load. The coating thickness was measured using a Kalotester device (Helmut Fisher, Germany) on a spherical thin section, formed by a steel ball, which was covered with super-dispersed diamond paste.

An investigation into the thermal stability for coated tools was conducted at annealing state, in a vacuum oven with a graphite heater at 10⁻³ Pa and 800-1000°C for 1 hour. The distribution of elements in the coatings was studied in the original samples and in those after annealing. The relative concentration of elements was obtained and the diffusion coefficients of main metallic elements in respective adjacent nitride layers were determined. Along this, the hardness of the coated cutting inserts was measured.

3.3. Studies of cutting properties of coated inserts

In this investigation, two types of hard-to-cut materials were used, i.e., single-phase deformable Ti-alloy VT-20 (6% Al; 1% Mo; 1% V; σ_b - (bending strength) 950-1150 MPa) and nickel alloy *NiCr20TiAl* (19-22% Cr, Ti 2.4-2.8; 1% Al, $\sigma_b = 930-1080$ MPa). The selected alloys have extremely low cutting performance due to their physical-mechanical properties.

Titanium alloy VT-20 is characterized by low plasticity at a high ratio of yield point/breaking point of $\sigma_{0.2}/\sigma_b > 0.80-0.85$. Its high chemical activity contributes to intensive interaction not only with the material being machined, but also with the environment, resulting in intensive interaction with oxygen and nitrogen, intense oxidation, scaling, brittle behaviour and increased hardness. Besides, VT-20 alloy is characterized by very low thermal conductivity that results in

concentration of thermal stresses directly in tool contact areas. This is accompanied by increased cracking process during the deformation because of intensive wear.

Nickel alloy CN77TUR is characterized by high strength, which is maintained at high cutting temperatures. At plastic deformation, the breaking point of material increases more than two times along with its hardness and wear resistance. Moreover, this alloy is characterized by low thermal conductivity, which leads to sharp increase of tool thermal stress during the cutting, intensifies adhesion and diffusion processes, and drastically increases the intensity of hardening of contact areas with subsequent failure of tool cutting edge.

Given the specifics of the cutting process and wear nature of carbide tools in machining of hard-to-cut titanium and nickel alloys, the feasibility for the development of nano-structured multilayer composite coatings was based on the following concepts. The developed coatings should be characterized by a structure and a set of physical-mechanical and crystal properties, which will ultimately modify tool contact areas and withstand harsh conditions of thermo-mechanical loading during machining of hard-to-cut materials. To meet this objective, the following was used: - a multilayer architecture with layers thickness at nanometer range in order to increase coating wear resistance due to intensive crack formation; - grain structure with size at nanometer level providing a balance between coating hardness and plasticity, which increases the resistance to brittle fracture of tool contact areas; - hetero-phase coating structures that reduces physical-chemical activity and adhesiveness at the boundaries of "machined material and carbide substrate" and increases tool resistance to adhesive-fatigue wear; - introduction of barrier layers between mutually soluble coating layers for improvement of their thermal stability.

The experimental studies involved batches of carbide inserts type WC6 ISO S20-S30 (94 % WC, 6 % Co). These batches were divided into three groups, namely: a set of uncoated inserts that was used as control reference, the second group was coated with *Ti-TiCrAlN* composite using standard arc-PVD technology ; and the third set was coated with the newly developed nano-multilayered composite based on *TiAlN-ZrNbN-CrN* using the FCAVO technology.

The machining parameters were set as follows:

Longitudinal turning: titanium alloy VT-20 - $v = 80 - 120$ m/min; $f = 0.1 - 0.3$ mm/rev; $a_p = 0.5 - 1.0$ mm; nickel alloy CN77TUR - $v = 20 - 50$ m/min; $f = 0.1 - 0.3$ mm/rev; $a_p = 0.5$.

Face milling: titanium alloy VT-20: $v = 80-110$ m/min; $a_p = 1.0-1.5$ mm; $f_z = 0.05-0.15$ mm/tooth; nickel alloy CN77TUR: $v = 20 - 50$ m/min; $a_p = 0.5$ mm; $f_z = 0.1 - 0.3$ mm/rev;

Following is the geometry of the cutting inserts:

Turning: rake angle $\gamma_0 = 8^\circ$; clearance angle $\alpha_0 = 6^\circ$; tool cutting angle $k = 45^\circ$; corner radius $r=0.8$ mm;

Milling: $\gamma_0 = -4^\circ$; $\alpha_0 = 6^\circ$; $k = 75^\circ$; $r = 0.8$ mm.

The machining tests were undertaken in dry in longitudinal turning on a universal lathe 16K20 that allowed maintaining constant cutting speed. For the symmetrical face milling a vertical milling machine tool was used.

To assess the efficiency of the cutting inserts, in this investigation the tool life (T) was measured by setting the maximum flank wear, VB_{max} around 0.4-0.5 mm in turning and $VB_{max} = 0.3-0.4$ mm in milling.

4. The results

4.1. The structure and properties of Nano Multilayered Composite Coating

The quality of coatings deposited on the working surfaces of carbide tools is extremely important. Vacuum-arc processes are usually characterized by the formation of macro and micro droplets during deposition of coatings, and this is a serious defect in coatings, since their presence within the boundaries of "coating-substrate" interface sharply reduces the strength of adhesion and increases the probability of delamination of the coating from the substrate. The most dangerous defect is the formation of micro droplets of cathode material on the coating surface. In this case, it drastically increases the probability of adhesion between tool material and machined material, which leads to intensive adhesion-fatigue tool wear. This phenomenon is typical for the cutting of hard-to-cut titanium and nickel alloys [1, 4, 11]. In this context, it should be noted that the use of FCVAD technology for formation of coatings with filtered vapor-ion flow significantly reduce dangerous defects in coatings in the form of macro- and micro droplets and increase coating wear resistance to failure arising from adhesion-fatigue processes at tool contact areas.

The morphology of the coating surface is similar to the one produced by arc-PVD, however with this new method, there is a negligible content of droplets (less than 10 %). This is illustrated in Fig. 2. The formation of the droplets is undesired as it has a detrimental effect on coating performance, especially when the droplets are located at the interface between the coating layers and the substrate. In the case when droplets are at the surface of the coating, droplets become centres of nucleation sites of adhesion between the rake face of the tool and the chip during the cutting process. This drastically intensifies the adhesion fatigue wear of tool. This finding confirmed results of studies [8] that indicated the prevailing influence of the arc current on the droplet phase. In particular, when the arc current of the zirconium- niobium cathode I_{ZrNb} was increased from 135 to 170 A, the amount of droplet phase at the surface of the coatings also increased from 1-2 % up to about 5-6 %.

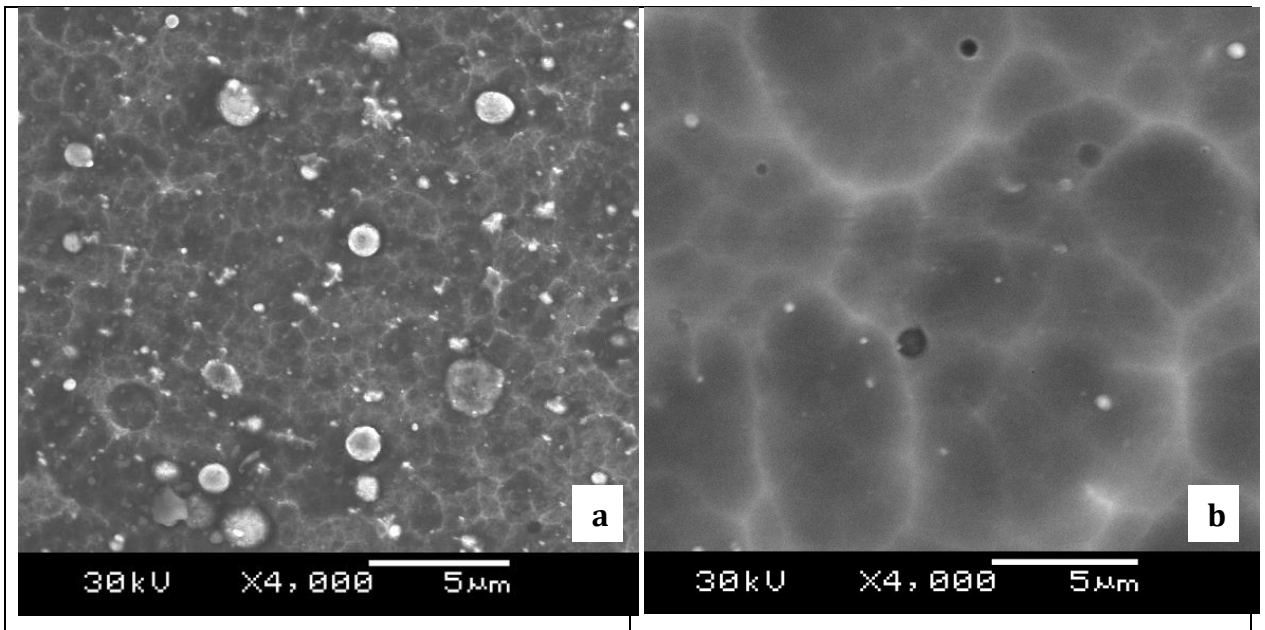


Fig.2. Surface morphology of *Ti-TiCrAlN*: (a) - standard arc-PVD; (b) - *TiAlN-ZrNbN-CrN* (FCVAD):

It was established that the variation of the FCVAD process parameters practically had little or no effect on the surface roughness (R_a) of the coating, which was about $R_a = 0.15 \mu\text{m}$. The coating thickness is a function of time. For a process time of 55 to 60 minutes with three simultaneously operating evaporators the coating thickness achieved was about 3.5-4.0 μm . It was observed that an increase in the rotational speed of the table (13 in Fig. 1) lead to the reduction of a coating thickness for the same time of deposition. A gradual disappearance of the layered structure was observed and at table speed of 3 rev/min the multi-layering aspect of the coating completely disappeared leaving a monolith structure.

Using a thin micro-section of the coatings, the structure of the cross section was analysed with the help of a scanning (SEM HD) and transmission electron microscopy (TEM). This allowed establishing the multi-layered structure of the coating where the sub-layers had a nano-scale thickness in the range of 10-15 nm as illustrated in Fig. 3

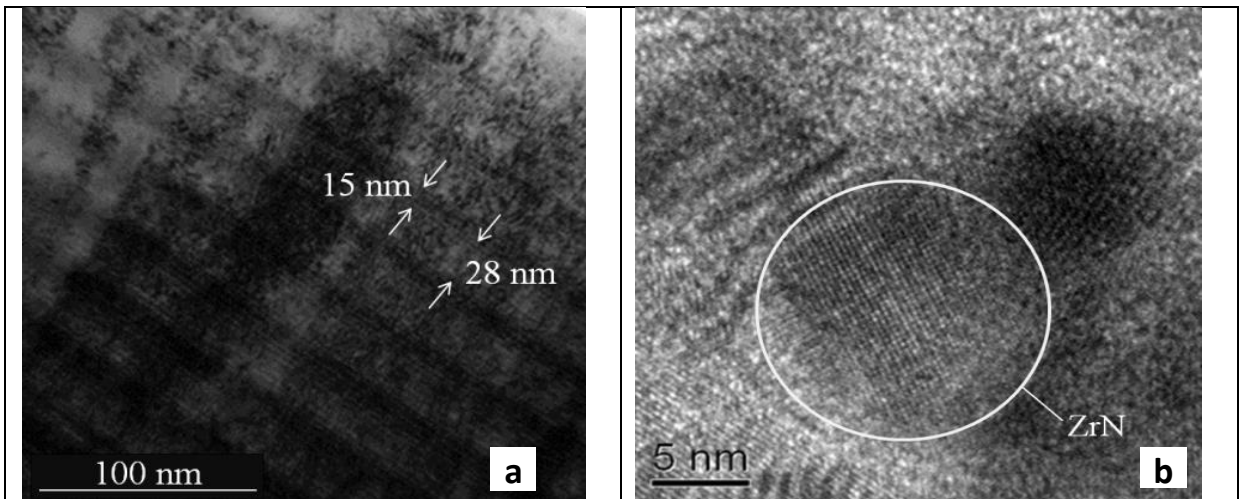


Fig. 3: Cross sectional structure of a *TiAlN-ZrNbN-CrN* coating :

a): Scanning electron picture of thin section for bias voltage $U_b = -120$ V and table rotation $n = 1$ rev/min

b): Transmission Electron microscopic (ETM) for bias voltage $U_b = -80$ V and table rotation $n = 1$ rev/min

The average size of the crystals within the layers estimated by dark-field image of the coatings structure (Fig. 3a) was about 5-10 nm. This was consistent with the data obtained by the approximation of the largest physical line broadening of X-ray diffraction ($D = 6 \pm 2$ nm). However, crystals of size below values characteristic to multi-component nano-structured coatings indicated the lack of multi-layer structure.

Table 1: Chemical composition of the developed *TiAlN-ZrNbN-CrN*

Process Parameters for FCVAD		Content of elements in coatings, % at.					
I_{ZrNb} , A	U_b , V	Ti	Al	Cr	Zr	Nb	N
135	-80	17	2	26	7	1	47
135	-100	17	2	26	7	1	47
135	-120	17	2	27	8	1	45
170	-120	16	2	25	12	2	43
135	-160	17	1	28	9	2	43

Table 1 illustrates the element composition of the deposited nano scaled multi-layered composite coatings. It shows that, depending on process parameters, the coatings contain 23-26 at. % Cr, 16-18 at. % Ti, 7-13 at. % Zr, 42-47 at. % N, 1-2 at. % Al and 2-3 at. % Nb.

Thermal stability studies of developed coating base on *TiAlN-ZrNbN-CrN* compound

showed that the introduction of the *ZrNbN* barrier layer between the *TiAlN* and *CrN* layers led to an increase of its thermal stability [15]. This is because *TiAlN* and *CrN* compounds dissolve in one another; therefore, the *ZrNbN* layer creates a barrier to their mutual solvency. The diffusion coefficients of the coatings key metal elements in respective nitride layer were estimated at temperatures of 800-1000°C. This showed a lack of noticeable diffusion erosion of the boundary sub-layers in the presence of the *ZrNbN* barrier layer between *TiN* and *Cr₂N* (*CrN*), which are mutually solvent.

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Table 2: Physical-mechanical properties of the developed Nano scaled Multi-layered Composite Coatings

Process Parameters for FCVAD		Physical-mechanical properties of coatings based on <i>TiAlN-ZrNbN-CrN</i> compound				
U_b , V	Table rotation n , rev/min	H , GPa	λ , GPa	H/λ	H^3/λ^2 , GPa	W_p , %
-80	1	28,1	440	0,06	0,11	58
-100	1	29,5	460	0,06	0,12	57
-120	1	32,3	490	0,07	0,14	55
-160	1	25,9	430	0,06	0,09	61
-120	2	36,6	580	0,06	0,15	56
-120	3	34,5	570	0,06	0,13	53

Table 2 depicts the investigation into the physical and mechanical properties of the developed coatings that showed that the coatings have a balanced combination of hardness (H), elastic modulus (E) and viscosity (W_p). The correlation between the change of physical- mechanical properties of the coatings and their structure depends on the bias voltage and the rotation speed of the substrate. In addition, the variation of the hardness and elastic modulus is similar to the micro-deformation at the crystal level. It can be concluded here, that, there is now a possibility to functionally modify the structure of the coating layers, as a direct relationship with the deposition processing parameters. Consequently, this provides a room for improving the properties of cutting tools with corresponding increased cutting efficiency.

4.2. Coating performance in actual cutting

The performance of cutting inserts coated with the newly developed Filtered Cathodic Vacuum Arc Deposition (FCVAD) technology is shown in Figs 4-7. Here cutting inserts made of carbide VC6 were used in turning and milling of titanium alloy and heat resistant alloy, and milling of steel 45 and titanium alloy VT-20. In the experiment there were sets of uncoated inserts and sets of inserts coated with $Ti-TiCrAlN$ and newly developed $TiAlN-ZrNbN-CrN$. The tool life is presented as a function of cutting speed for a depth of cut ($a_p = 1.5\text{mm}$) and feed rate ($f = 1\text{ mm/rev}$ in turning and $f_z = 0.1\text{ mm/tooth}$ in milling).

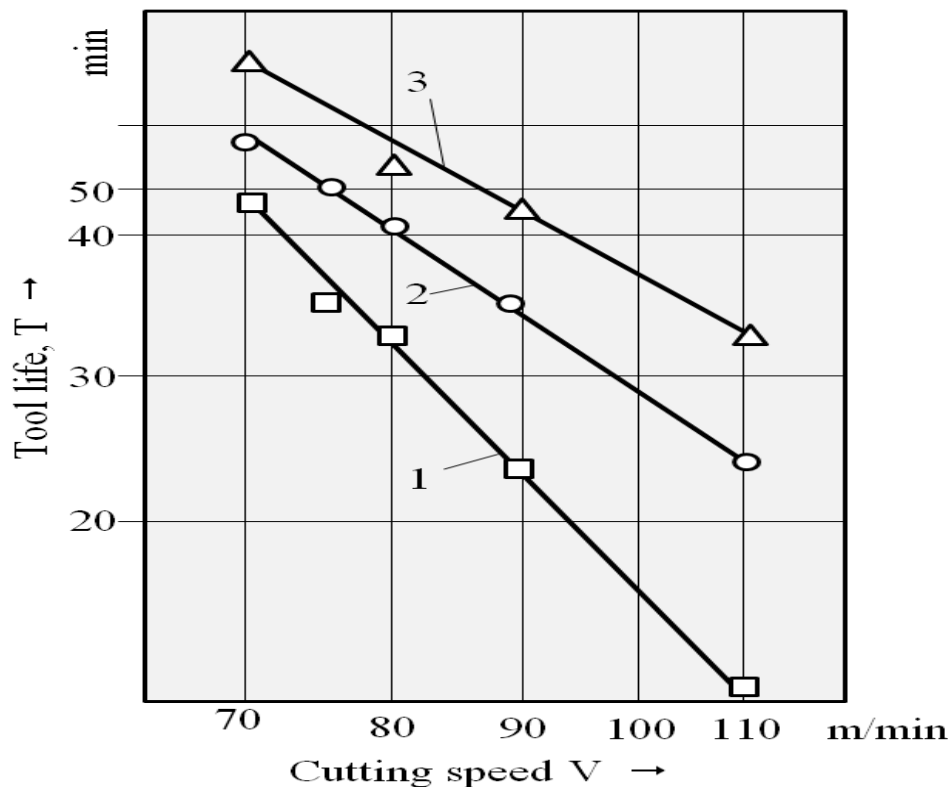


Fig. 4: WC6 tool life as a function of cutting speed in turning titanium alloy for $a_p = 1.0\text{ mm}$; $f = 0.2\text{ mm/rev}$:

1- uncoated; 2 - $Ti-TiCrAlN$ coating (arc-PVD); 3 - $TiAlN-ZrNbN-CrN$ (FCVAD).

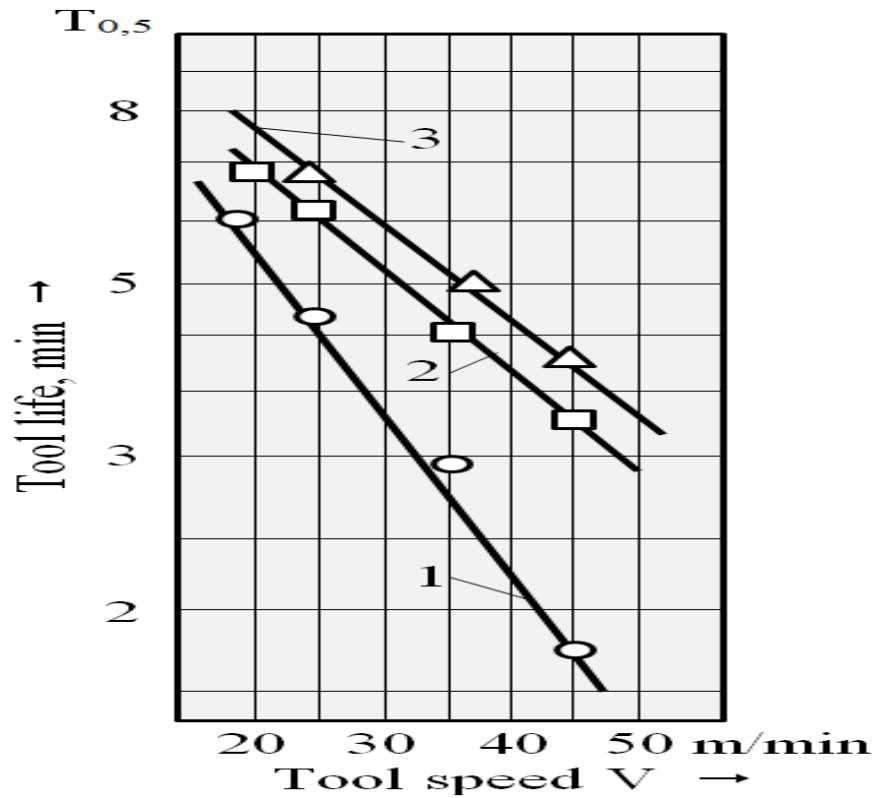


Fig. 5: VK6 tool life as a function of cutting speed in turning nickel alloy CN77TUR for $a_p = 0.5$ mm; $f = 0.15$ mm/rev;.

1 – uncoated; 2 - $Ti-TiCrAlN$ coating (arc-PVD); 3 - $TiAlN-ZrNbN-CrN$ (FCVAD).

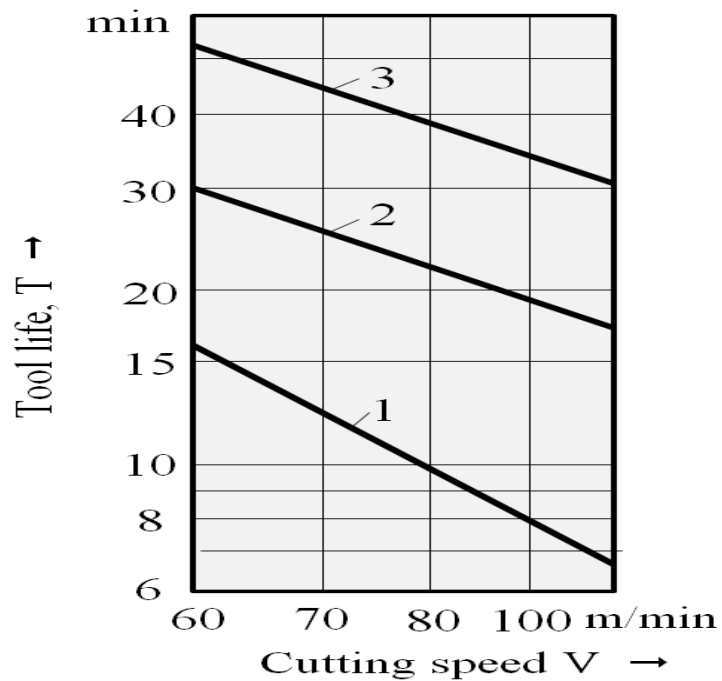


Fig. 6: WC6 tool life as a function of cutting speed in face milling of titanium alloy VT20 for $a_p=0,1$ mm; $f_z=0,1$ mm/tooth;

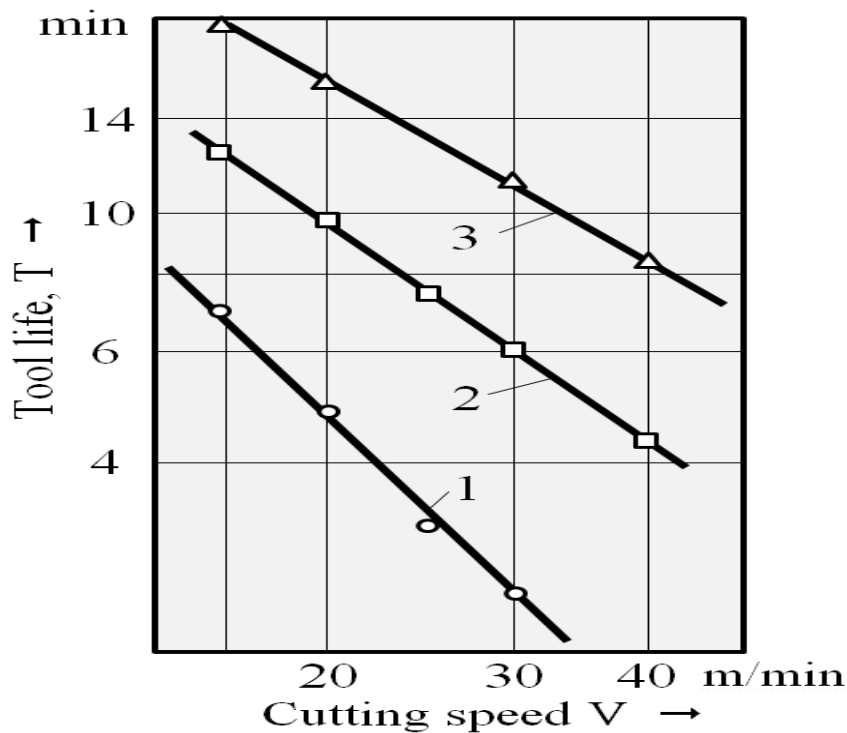


Fig. 7: VK6 tool life as a function of cutting speed in face milling of Ni- alloy for $a_p = 1.5$ mm; $f_z = 0.1$ mm/tooth; 1 – uncoated; 2 - *Ti-ZrCrAlN* coating (standard technology arc-PVD); 3 - *TiAlN-ZrNbN-CrN* (elaborated technology FCVAD).

Therefore, tool life is denoted by $T_{0.5}$ (min) on the graphs meaning time when the wear flat reached 0.5 mm. A comparison of the wear rate of the inserts WC6 with the developed coating having a nano laminated, multilayer and composite structure showed the superiority of the newly developed nano-scale multilayer composite coatings using this elaborated technology of Filtered Cathodic Vacuum Arc Deposition.

As shown in Fig. 4-7, these new coatings have a higher hardness and heat resistance, which determines their increased resistance to wear under the influence of high thermo-mechanical stresses in harsh conditions (turning and milling of hard-to-cut titanium and nickel alloy). Along with this, these new nano coatings effectively resist against crack formation, even under the action of cyclic thermo-mechanical stresses, which are specific in interrupted cutting (milling). These key properties are particularly secured by the nano-grain structure and the nano thickness of sub-layers in these composite coatings. These properties allow for a longer cutting time maintaining key physical properties that the coatings induce in the interface between the cutting tool material and the materials being machined. The physical properties induced by these new nano composites coating include:

- A reduced tendency of the tool to adhere with the material being machined;

- The hindrance of the inter-diffusion process between the tool material and the material being machined that prevents the softening of carbide by diffusion of the machined material elements in the tungsten carbide and simultaneous hardening of the machined material by diffusion of elements of a carbide.

These elaborated coatings effectively block the frictional heat flow into the tool while reducing the power of heat sources at the contact areas of the rake and flank surfaces. Therefore, they lead to an increase in the operational time of the coated carbide tools without failure and to a significantly improved performance. The analysis of the operational time or tool life (T) as a function of cutting speed in a turning (see Fig.4, 5) and in face milling (see Fig.6, 7) shows a high increase in cutting efficiency in machining hard-to-cut alloys VT-20 and CN77TUR. It is observed that the inserts coated with the engineered nano-layered composite coating have a superior performance in comparison with the uncoated carbide inserts and inserts coated with standard *Ti-TiCrAlN* recommended for cutting hard-to-cut alloys.

The certification tests have shown that the use of carbide tools with *WC6-(TiAlN-ZrNbN-CrN)* coating increased tool life with the increase of cutting speed, for both longitudinal turning and face milling of titanium and heat resistant nickel alloys. In particular, during turning of VT-20 titanium alloy at cutting speeds from 70 m/min up to 110 m/min, the tool life of *WC6-(TiAlN-ZrNbN-CrN)* exceeds the tool life of the uncoated tool by 1.4-2.8 times, and it exceeds the tool life of *WC6-Ti-TiCrAlN* (see Figure 4) by 1.47-1.22 times. During longitudinal turning of heat resistant CN77TUR nickel alloy, when cutting speed increases from 20 m/min up to 45 m/min, the tool life of the tool of *WC6-Ti-TiCrAlN* increases by 1.3-2.35 times with reference to uncoated tool and by 1.16-1.25 times compared with the standard coating *WC6-Ti-TiCrAlN* (see Figure 4).

Given the fact that the cutting speed has the strongest influence on the thermal state of the cutting tool system, the studies carried out have revealed that carbide tool of *WC6-TiAlN-ZrNbN-CrN* effectively resists wear even with a significant increase in thermal stress of the cutting tool with the increasing cutting speed. This fact demonstrates the advantages of *TiAlN-ZrNbN-CrN* coating, which is characterized by higher thermal resistance due to the introduction of barrier layer of *NbZrN* between mutually soluble layers of *TiAlN* and *CrN* as compared with thermal resistance of standard coating of *Ti-TiCrAlN*. This also demonstrates the opportunities for wider use of carbide tool with *TiAlN-ZrNbN-CrN* coating for high performance machining of hard-to-cut materials. This effect has also been observed in face milling of CN77TUR nickel alloy (see Figure 7); however, in this case, the advantages of the tool with the developed coating are less

evident because of the extremely severe thermal conditions on the tool of WC6-TiAlN-ZrNbN-CrN.

It observed from Fig.4 to Fig. 7 that the developed coating based on the *TiAlN-ZrNbN-CrN* compound drastically improved the performance of the cutting tool, and the efficiency of the coating maintained at high cutting speeds in machine hard-to-cut materials. The findings suggest that the superiority of *TiAlN-ZrNbN-CrN* coatings is determined by their high hardness and heat resistance along with a balanced viscosity and resistance to crack formation.

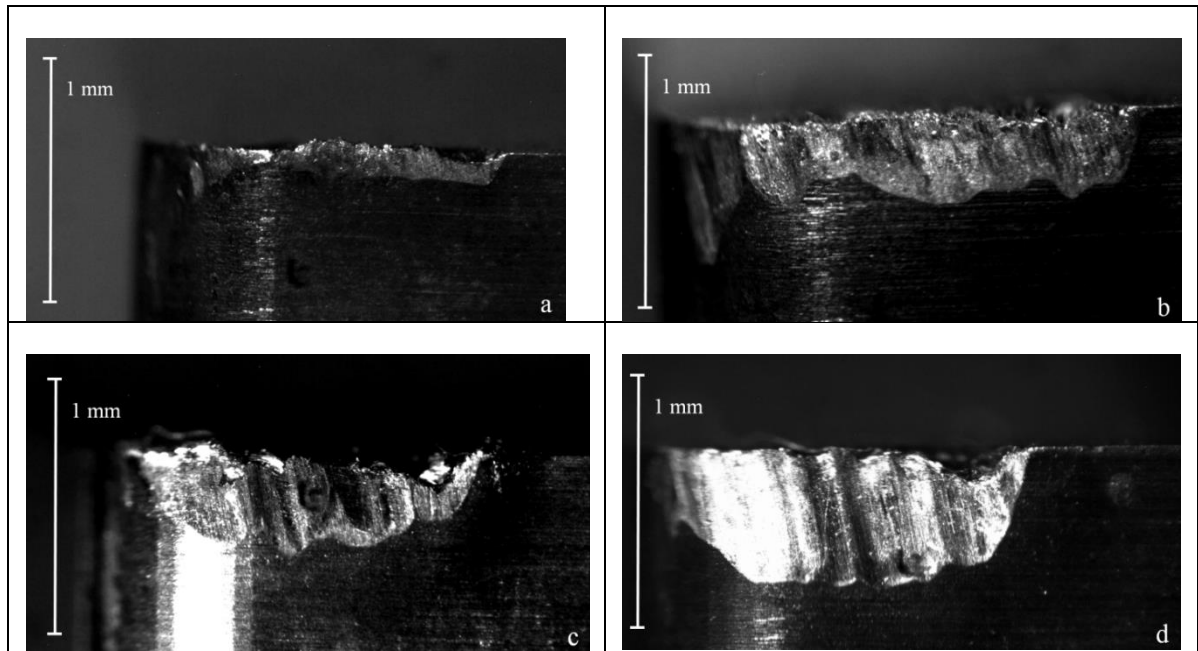


Fig. 8: Wear flat in milling nickel alloy with WC6 cutting inserts coated with:
a): *TiAlN-ZrNbN-CrN*, (FCVAD); b): *Ti-TiAlN-TiN*, (FCVAD);
c): *Ti-TiCrAlN*, (standard arc-PVD); d): *Ti-TiN*, (standard arc-PVD);
Machining time – 8 min; $v = 40$ m/min; $a_p = 1.0$ mm; $f_z = 0.15$ mm/tooth

The cutting carbide inserts were also examined after 8 min of continuous milling nickel alloy CN77TUR. Here, WC6 carbide inserts were coated with *TiAlN-ZrNbN-CrN* and *Ti-TiAlN-TiN* using FCVAD technology, and, *Ti-TiCrAlN* and *Ti-TiN* using standard arc-PVD. Results in Fig. 8a show that the *TiAlN-ZrNbN-CrN* coatings have the highest resistance to wear and brittle macro/micro fracture which are inherent to uncoated carbide tools and to those with standard commercial coatings. Here, it is observed that the tool flank wear is minimal, continuous and smooth with no apparent chipping, and in Fig. 8b with *Ti-TiAlN-TiN* coating (FCVAD), the tool wear is moderate with no sign of brittle failure. However, the tools coated with a standard PVD technology suffered more wear with elements of brittle fracture (see Fig. 8c). In Fig. 8d, it is seen that the tool without the coating has been drastically worn out under the same machining conditions and micro chipping of a cutting edge is observed.

Machining of hard-to-cut nickel super alloys CN77TUR based is widely used in the aerospace industry, however this is a challenge due to high contact stresses (normal and shear) in the cutting zone with temperatures reaching over 850-950°C and high adhesion of the material machined to the cutting tool. This leads to a rapid wear of the tool due to adhesive-fatigue and the cutting edge is highly prone to deform thermo-plastically. Under these conditions, there are high demands on the properties of the coatings in terms of hardness, the ability to maintain target performance at high cutting temperatures and resistance to crack formation when the cutting edge is under increased loads inducing plastic deformation. In addition, the coating should reduce the tendency of the tool material to the physical-chemical reaction with the machined material. The aforementioned requirements and properties are secured by the nano-scale multilayer composite coating based on TiAlN-ZrNbN-CrN, which provide higher thermal stability at temperatures up to 1000 °C. In addition, these coatings keep the metallic bonds in the multilayered structure for a relatively longer period due to the introduction of ZrNbN, which is a barrier layer between TiAlN and CrN. These coatings have demonstrated an excellent resistance to fracture due to their ability to dissipate process input energy and the energy of plastic deformation.

The newly developed coatings based on the requirements analyzed this work have shown a high fracture resistance especially under cyclic thermo-mechanical loads (interrupted cutting). These coatings present an alternative and possibly the best way of increasing the efficiency of carbide inserts designed for cutting hard-to-machine materials.

Conclusion

This paper proves a scientific concept for the formation of functional coatings on working surfaces of carbide tools designed for machining hard-to-cut materials. The developments were carried out on the basis of the conceptual role of coatings on tool working surfaces as a technological medium between tool and the machined material, which is capable to simultaneously improve the surface properties of the tool material (hardness, heat resistance, chemical passivity, and wear resistance in a wide temperature range, etc.) and highly reduce thermo-mechanical stresses acting on tool contact areas during machining with a better performance of the coatings operation without its failure. The paper presents the detailed analysis of the methods and technological means for the formation of coatings, taking into account the impact of high contact stresses and temperatures on the tool, physical and chemical processes of adhesive interaction, inter-diffusion, and oxidation.

In this context, the coatings on working surfaces of carbide tools were formed on the basis of nano structure, multilayer composite architecture, balanced hardness and toughness, high strength of

adhesion to substrate, and multi-phase composite structure, in combination with the highest thermal stability and chemical inactivity relative to the material being machined.

To implement the developed concepts, the study has applied innovative process of filtered cathodic vacuum arc deposition, where the influence of parameters on composition, structure, and properties of the coatings formed were determined. It was shown that when the speed of tool motion in the vacuum chamber relative to evaporating cathode increases, the thickness of layers of multilayer structure and crystallite sizes of material phases decrease. The increase in the negative potential on the tool increased the level of micro-deformation and compaction of coatings due to the effect of ion peening. The produced coatings are characterized by high hardness of up to 37 GPa, high resistance to plastic deformation of up to 0.14 GPa, low coefficient of friction of 0.45, and plastic deformation influence of up to 61%.

It was defined that (e.g. TiAlN-ZrNbN-CrN coating) that the introduction of additional barrier ZrNbN layer into multilayer nano-structured coating between mutually soluble layers of TiAlN and CrN led to an increase in its thermal stability. The calculated coefficients of diffusion of basic metal coating elements into the corresponding nitride layers at temperatures 800-1000 °C showed no significant diffusion blur (?) of sublayers of coatings in the presence of the barrier ZrNbN layer between mutually soluble TiAlN and CrN layers.

The results of the studies of the cutting properties of carbide tools of WC-TiAlN-ZrNbN-CrN during the longitudinal turning of titanium and nickel alloys have confirmed the high wear resistance of the developed coatings, the advantages of which increase with the increase of cutting speed not only in comparison with the uncoated carbide tools, but also for tools with standard Ti-TiCrAlN coatings. It was revealed that during the turning of VT-20 titanium alloy at cutting speeds from 70 m/min up to 110 m/min, the tool life of WC6-(TiAlN-ZrNbN-CrN) exceeds the tool life of the uncoated tool by 1.4-2.8 times, and the tool life of WC6-Ti-TiCrAlN by 1.47-1.22 times. During the longitudinal turning of heat resistant CN77TUR nickel alloy, when the cutting speed was increased from 20 m/min up to 45 m/min, the tool life of the tool of WC6-Ti-TiCrAlN increase by 1.3-2.35 times compared with the tool life of the control uncoated tool of WC6, and by 1.16-1.25 times as compared with the tool life of the tool with standard coating.

The effect described above has also been observed during the face milling of VT20 titanium and CN77TUR nickel alloys; however, during the face milling of the latter, the advantages of the developed coatings are less evident because of the extremely harsh thermal conditions.

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