*coatings*

*Editorial*

# Technologies of Coatings and Surface Hardening: Industrial Applications

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## 1. Introduction and Scope

The most advanced and recently developed coating and surface-hardening technologies make it possible to obtain almost the full range of physical–mechanical and crystal–chemical properties of the metalworking tool surface and electronic component surface for a wide range of applications to enlarge product operational life for working under the most extreme mechanical and thermal loads [1–3]. The scientific attitude to improving the surface layer parameters of the product made of traditional industrial materials or new advanced composites and nanocomposites requires budget material and time investments [4,5]. It hinders the industrial introduction of innovations and slows down the progress of the transition to the technological level associated with the concept of nanoindustry [6–8]. Different technological techniques, such as physical and chemical methods of coating deposition [9,10], surface hardening, and alloying, including chemical–thermal treatment and implantation technique [11,12], a combination of the above and other solutions, are widely proposed on the market. A wide range of energy sources such as vacuum-arc and laser beam in various working media (vacuum, gas–vapor medium, liquid solutions, etc.) can be used for product surface modification [2,13–15].

The product's operational life can be improved via introduced innovations in the coating and surface layer structure deposed to such materials as high-speed tool steel [16], $Al_2O_3$ + TiC ceramic [17,18], Si and hard alloy substrate [19–25], plastic substrate [26]. The innovative multilayer coatings demonstrate the destruction of the coating from the contact load passing through one layer and developing along the interface between the layers, significantly increasing the product's durability [19–25]. At the same time, nanocomposite coatings containing the amorphous phase with the introduced nano-crystallines of 3–5 nm hamper the development of the cracks and redirect them [23,24]. It is shown that annealing up to 1000 °C can transform an amorphous homogeneous coating structure into a nanocomposite one [18]. The interlayer introduced in the coating also improves its durability by improving coating adhesion [17,19,23]. Some of the coatings exhibit a self-healing effect under mechanical and thermal loads—with reaching a contact temperature of 800–1000 °C, some of the coating components may oxidize and form amorphous phases that can provide superlubricity in the processing zone and increase the operational life of the cutting tool [16,21,23]. Thin oxide films of a few nanometers effectively hamper moisture and protect microelectronics from mechanical and thermal loads [26]. The quality of the surface where the coating is supposed to be deposed plays a critical role in the product's durability [17] when special measures can reduce the adhesion of the workpiece material and favor the descent of material flow on the tool face [24]. The questions of reliable coating deposition diagnostics remain open and require special measures [27].

The surface layer plays the primary role in the potential for durability of the products operating under loads. Therefore, the coating and surface hardening technologies should be chosen individually to prolong the product's service life following the known contact loads.

This Special Issue is devoted to the latest advances in the coatings and surface hardening technologies for cutting tools and microelectronic components that can ensure a



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valuable increase in the product durability to ensure its reliable operation. The main emphasis lies in the results of the research and engineering works that have proven successful in laboratory or manufacturing conditions.

## 2. Contributions

Twelve research articles and communication were published in the presented Special Issue. The discussed subjects cover the most advanced achievements in the field of technologies of coatings and surface hardening for the tool industry. Among them, there are questions of

- Properties including high-temperature and triboproperties of the advanced multi-[19–25] and mono-layer [16,17], nanocomposite [23,24], nanostructured [18], and nanothin coatings [26];
- Tool surface conditions and micro-texturing on machining performance of hardened steel [17] and heat-resistant alloy [24], correspondingly;
- Self-healing adaptive coatings in milling titanium alloys [23], protective coatings for microelectronic needs [26], diagnostics of the coating deposition process [27];
- Coating technologies such as physical vapor deposition (PVD) [17,23,24,27], including a radio frequency magnetron sputtering [16], high-power impulse magnetron sputtering [18], a closed-field unbalanced magnetron sputtering [19,20], filtered cathodic vacuum arc deposition [21,22,25], as well as atomic layer deposition [26];
- Full-scale tests in conditions close to industrial ones in milling hardened steel 100CrMn6 [17] and titanium alloys [23], turning steel 1045 [22], nickel–chromium alloy [21,25], and iron–nickel alloy [24], annealing tests [19,20], open/short tests for electronic components [26];
- Development of a mathematical basis for future research [23,24].

The influence mechanism of temperature on the tribological properties of hexagonal boron nitride coatings deposed on the high-speed tool steel by radio frequency magnetron sputtering method (PVD) was investigated in [16]. Thermotribological behavior was evaluated in friction pair against $ZrO_2$ ball in the range of temperatures from 500 to 800 °C and compared with the steel sample. It is experimentally shown that the coefficient of friction of h-BN coating and steel sample decreases to 600 °C and grandly decreases to 800 °C when the coefficient of friction of h-BN coating decreases from 0.135 to 0.02, and it decreased from 0.3 to 0.14 for the uncoated sample. Thus, h-BN coating exhibits high-temperature superlubricity at 800 °C. The wear mechanism of h-BN coatings is tribooxidation; $\alpha$-$Fe_2O_3$, $Fe_3O_4$, and $\gamma$-$Fe_2O_3$ were detected on the disc's worn surface, and $\alpha$-$Fe_2O_3$, $\gamma$-FeOOH, $\gamma$-$Fe_2O_3$ and $TiO_2$ were detected on the ball worn surface at 800 °C, which is the main factor for the antifriction behavior at high temperature. The superlubricity mechanism is attributed to the $\gamma$-$Fe_2O_3$/h-BN formation due to tribochemistry.

An increase in the tool's average resistance by 1.4 times compared to the base-coated tool was shown in milling hardened steels of the 100CrMn type by $Al_2O_3$ + TiC ceramic inserts with the (TiZr)N, (TiAl)N, TiN coatings deposed by PVD method [17]. However, the detected tool resistance values significantly varied (by 30%). Additional surface lapping and polishing increase the wear resistance by two times, and the coefficient of resistance variation decreases by more than two times (14%). The additionally lapped and polished $Al_2O_3$ + TiC ceramic inserts with (TiZr)N coating demonstrate an increase in the average resistance by 1.7 times compared to the ceramic inserts without additional pre-processing. The increase in average resistance is 1.2-foldcompared to ceramic inserts after diamond grinding and (TiZr)N coating. Additional pre-processing of the inserts decreases surface roughness parameter Ra from 0.33 to 0.034 µm, reduces the coefficient of friction during high-temperature heating at 800 °C from 0.6 to 0.2 at the beginning of friction, demonstrates more stable behavior in the friction path, and results in a decrease in the range of change in the average resistance by ~1.9 times. The variation in the dispersion of resistance decreases up to 15%, which is two times less than for (TiZr)N-coated ceramic inserts.

The Mo-Zr-Si-B coatings of the dense and homogeneous structure were deposed by high-power impulse magnetron sputtering on industrial $Al_2O_3$ + TiC ceramic inserts at frequencies of 10, 50, and 200 Hz [18]. The minimal growth rate of 7.5 nm/min was observed at 10 Hz for the highest maximum peak current. The growth rate increased to 17.5 and 67.5 nm/min when the frequency was increased to 50 and 200 Hz. The maximum hardness of the Mo-Zr-Si-B coatings was 23 GPa and obtained at 200 Hz, when the coefficient of friction was 0.81. The coating deposed at 50 Hz was characterized by higher wear resistance, cyclic–dynamic impact loading, and high-temperature oxidation resistance at 1300 and 1500 °C. The coating deposed at 50 Hz remained amorphous during heating in the transmission electron microscope column at 20–1000 °C. The segregation and growth of $MoSi_2$ phase grains were observed in the temperature range of 600–1000 °C during vacuum annealing. The hardness and Young's modulus of the coatings that were deposed at frequencies of 10 and 200 Hz decreased after vacuum annealing. The hardness and Young's modulus increased from 15 and 250 GPa to 37 and 380 GPa, respectively, when heating from normal temperature to 1000 °C due to the crystallization and transformation to a nanocomposite structure.

The CrAlN coatings with three interlayers (CrN, CrZrN, and CrN/CrZrSiN) were deposed by a closed-field unbalanced magnetron sputtering system (PVD) on Si and hard alloy (WC-6 wt.% Co) substrates [19]. The coefficient of friction of the CrAlN coating with the CrN/CrZrSiN interlayer was ~0.3, which is less than for the CrN and CrZrN interlayer, where the coefficient of friction was 0.35 and 0.45, respectively. The adhesion strength of the CrAlN coating with the CrN and CrN/CrZrSiN interlayer was 69.3 N and 69.2 N, which is ~3–4 times higher than for those with CrZrN interlayer and without interlayer. The hardness of the CrAlN coating with the CrN/CrZrSiN interlayer was approximately 28 GPa up to 1000 °C after annealing test in the air for 30 min, which is 1.6 times higher than for the samples with CrN, CrZrN interlayer and the sample without interlayer. Up to 500 °C, all considered coatings' surface roughness and coefficient of friction were similar. The oxidation by the residual oxygen explains the variation in the coating surface roughness. Thus, introducing an interlayer could improve the mechanical properties and thermal stability of the CrAlN coatings. These properties increase the operational life of the hard alloy tool in milling in the conditions of the thermal loads.

The CrZrN/CrZrSiN multilayer coatings with different bilayer periods were deposed by a closed-field unbalanced magnetron sputtering (PVD) on Si and hard alloy (WC-6 wt.% Co) substrates to improve their mechanical properties and thermal stability [20]. The thickness of the bilayer periods varied from 1.35 to 0.45 µm. The hardness and elastic modulus of the CrZrN/CrZrSiN multilayer coatings gradually increased with the decrease in the bilayer period from 1.35 to 0.54 µm when coating with 0.45 µm bilayer period thickness showed a trend to decrease in the hardness and elastic modulus. The coefficient of friction showed the same trend: the lowest coefficient of friction of 0.24 was achieved for the CrZrN/CrZrSiN multilayer coating with a bilayer period of 0.54 µm. The adhesion strength increased with the decrease in the bilayer period. The highest values of 75 and 79 N were observed for a bilayer period of 0.54 and 0.45 µm. The chipping or delamination was not detected for coatings with a bilayer thickness of 0.67–0.45 µm. The hardness of the developed coatings was approximately above 27 GPa up to 800 °C, demonstrating excellent thermal stability. The CrZrN/CrZrSiN multilayer coatings with a bilayer period showed improved hardness, friction coefficient, adhesion, and thermal stability compared to monolithic one that corresponds to the requirements of the high-performance cutting-tool application.

It was shown in [21] that the substrate Zr-ZrN-(Zr,Mo,Al)N coating deposed by PVD to hard alloy consisted of two cubic nitride phases, (Zr,Mo,Al)N (ZrN-based solid solution) and (Mo,Zr,Al)N (MoN-based solid solution). Cr-CrN-(Cr,Mo,Al)N and Ti-TiN-(Ti,Mo,Al)N coatings were characterized by a single cubic nitride phase, (Ti,Mo,Al)N (TiN-based solid solution) or (Cr,Mo,Al)N (CrN-based solid solution). The tool with the Zr-ZrN-(Zr,Mo,Al)N coating had the highest wear intensity in turning Ni-Cr alloy at the cutting speed of 45 m/min, when the wear intensity was similar for three coatings at the cutting speed of 60 m/min. The tool with the Zr-ZrN-(Zr,Mo,Al)N coating demonstrated the lowest wear intensity at cutting speed of 75 and 90 m/min, when the average flank wear for the Zr-ZrN-(Zr,Mo,Al)N coated tool was ~30% lower compared to Cr-CrN-(Cr,Mo,Al)N and Ti-TiN-(Ti,Mo,Al)N coatings. A reliably identified transition layer of $ZrO_2$ at the interface between the Zr-ZrN-(Zr,Mo,Al)N coating and the machined workpiece was observed at the cutting speed of 90 m/min. A transition layer of the same thickness was also detected for the Cr-CrN-(Cr,Mo,Al)N coating. Such a transition layer was absent for the Ti-TiN-(Ti,Mo,Al)N coating. That may indicate the process of tribooxidation under the influence of probable increased mechanical and thermal loads (turning Ni-based alloys) and create conditions for increased lubricity [28]. There is supposed to be a dependence between the protective transition oxide layer that exhibits thermochemical inertness and phase stability up to ~1200 °C for $ZrO_2$ (zirconium dioxide is polymorphic—when heated up to ~1200 °C, it changes from monoclinic phase m-$ZrO_2$ to tetragonal one t-$ZrO_2$ by a martensitic mechanism with volumetric changes up to ~5%–9%; upon further heating to 2300 °C, it diffusional passes into the cubic phase c-$ZrO_2$) and more than ~1000 °C for chromium trioxide $CrO_3$ (different oxidation states of chromium are achieved by calcination, $CrO_3 \rightarrow Cr_2O_3 \rightarrow CrO$) and the depth of nickel diffusion [29–31]. The Zr-ZrN-(Zr,Mo,Al)N coating demonstrated Ni-diffusion up to the depth of 360 nm where the transition layer was detected. The Cr-CrN-(Cr,Mo,Al)N coating demonstrated that the diffusion of nickel into the coating was less than 260 nm.

It was shown that Cr,Mo-(Cr,Mo,)N-(Cr,Mo,Al)N coating with the introduction of 20 at.% Mo deposed on hard alloy tool by PVD increases its wear resistance compared to (Cr,Al)N coating [22]. The developed Cr,Mo-(Cr,Mo,)N-(Cr,Mo,Al)N coating had detected a nanolayer structure with a modulation period λ = 50 nm. The (Cr,Al)N coating exhibits more active wear crater growth on the rake face in turning steel 1045 than the (Cr,Mo,Al)N system nanolayer coating. The detected pattern of nanolayer coating wear reveals the following fracture mechanisms:

- Penetration of particles of the workpiece between nanolayers, resulting in interlayer delamination;
- Plastic deformation of nanolayers of the coating under the influence of the moving flow of the machined steel;
- Fracture of fragments of the coating's nanolayers with their further removal by the cut material.

The Fe-diffusion into the coating up to the depth up to 200 nm was observed when the Cr- and Mo-diffusion did not exceed the depths of 250 nm. Possible impact on wear resistance of the considered coatings and the operational life of the tool can have formed oxides of iron $Fe_xO_y$ detected at the "coating—machined steel" interface that exhibit hardness superior to the workpiece material.

The thermodynamic model of wear of the hard alloy cutting tool coated by PVD for face milling two types of titanium alloy (Ti64 and Ti811) is proposed in [23]. It allows determining the ways to reduce the wear intensity and presents the dissipative function of the tool material shape change and the conditions for improving the wear resistance of the cutting tool using the phenomenon of adaptation (self-organization) under friction. Experimental studies on the wear resistance of cutting tools coated with innovative multilayer nanostructured coatings show an increase in the average operational life of the tool by 1.5–2 times. The following coatings with a thickness of less than 10 μm were under study:

- (CrAlSi)N + diamond-like carbon (DLC);
- $TiB_2$ (nanocomposite coating);
- nACRo (nanocomposite coating based on chrome and aluminum carbonitrides with microhardness of 42 GPa, coefficient of friction is 0.45);
- $nACo_3$ (nanocomposite coating based on aluminum nitride and titanium with microhardness of 45 GPa, coefficient of friction is 0.35);
- nACRo + $TiB_2$;
- $nACo_3$ + $TiB_2$;
- nACRo + $TiB_2$ + epilama;

- nACo3 + epilama;
- uncoated + epilama.

The grain size of nanocomposite coatings was in the range of 3–5 nm. A decrease in temperature–force loading in the cutting zone was 15%–25% and can be explained by the formation of secondary structures on the friction surfaces of aluminum and titanium oxides that were detected by X-ray spectral analysis. As it is known, oxides provide heat-reflecting (shielding) and lubricating properties and exhibit thermochemical inertness and stability up to 800 °C (properties of γ-$Al_2O_3$ obtained at 450–600 °C persist up to 800 °C when the formation of a new crystalline phase σ-$Al_2O_3$ begins; it forms thermodynamically stable amorphous α-$Al_2O_3$ at 850–1000 °C [32,33]; thermal stability of amorphous anatase is up to 500–800 °C and even higher for crystalline rutile). It should be noted that the thermal stability of oxides is determined by Tamman and Hüttig temperatures. There is a noticeable mobility of the atoms of the crystal lattice at 0.5 Tm and surface mobility of the atoms at 0.3 Tm, where Tm is the melting point. Accordingly, the higher melting temperature provides higher thermal stability. A decrease in the coefficient of friction (adhesive component) by 13%–17% was observed in a temperature range of 550–950 °C. Contact processes reveal a phenomenon of adaptation (self-organization) of friction surfaces at milling by a coated cutting tool, promoting the formation of oxide films of amorphous structure that exhibit protective and lubricating properties.

The problem of increasing the efficiency of iron–nickel heat-resistant alloy turning with a hard alloy tool is aimed to be solved by tool surface microtexturing and multilayer nanocomposite PVD-coating in [24]. Microtexturing of the rake face of carbide insert in the form of strips were provided by nanosecond laser ablation and in the form of mesh structure by an indenter. The obtained microtexture by laser beam revealed fragile phases' formation from molten material that were resolidified on the surface of the texture when easy-to-melt components of the material are sublimated in the environment. At the same time, ejections of material from the molten pool were observed, characterized by the explosive behavior of the liquid from the impact of laser pulses. The indenter allowed obtaining meshes by plastic deformation with improved surface properties with a force of 20 N. The square-shaped prints were with a width of 30 µm and a maximum depth of 7 µm. The multilayer nATCRo3 on (TiCrAlSi)N basis that includes (CrTi)N and (AlTi)N layers alternation and (AlTiCr)N/SiN nanocomposite layer formed by (AlTiCr)N crystals of 5 nm evenly distributed in amorphous $Si_3N_4$. It is shown that a carbide insert with a microtexture filled with a $MoS_2$-based lubricant decreases the workpiece material adhesion. The tests of cutting tool operational life under various turning modes with cutting depth from 0.3 to 0.5 mm and feed from 0.1 to 0.15 mm/rev shows temperatures increased up to 240–330 °C in the processing zone. The temperature measurements provided a basis for the mathematical modeling of the cutting thermal power parameters. The function of predictive evaluation is proposed and justified using the criterion of relative efficiency. Predictive estimates of the turning efficiency established that the calculated values converged highly with the experiments. The microtextured tool's operational life was increased by 1.3–1.5 times.

The properties of Ti-TiN-(Ti,Y,Al)N multilayer composite PVD-coating with the high content (approximately 40 at.%) of yttrium in its wear-resistant layer were studied comparing Ti-TiN-(Ti,Cr,Al)N coated and uncoated hard alloy tools in turning nickel–chromium alloy [25]. The hardness was HV 2758 ± 78, and the elastic modulus was 356 ± 24 GPa. The coating was characterized by cubic phases c-(Ti,Y,Al)N and c-(Y,Ti,Al)N. The wear resistance on the rake face was improved by 250%–270% for the tools with both coatings under consideration. The wear rates were similar when the operational life of the carbide tool with (Ti,Cr,Al)N coating was increased by 10%–15%. The active oxidation of the Ti-TiN-(Ti,Y,Al)N coating in contact with the workpiece material with $Y_2O_3$ formation was detected. Thus, the dominant wear mechanism was oxidation. Despite the known chemical activity of Y towards an oxygen-containing environment when heating and hydrolysis (actively forms $Y(OH)_3$ that decreases to YO(OH) in the presence of water under pressure at 90–350 °C), the rake face of the tool with the Ti-TiN-(Ti,Y,Al)N coating demonstrated undamaged fragments in the transition layer and the wear-resistant layer after 16 min of turning. The oxide layers formed on the surface of the coating improve the tribological conditions in the cutting zone and reduce the tool wear rate.

The $Al_2O_3$ protective thin film layer with a thickness of 14–15 nm deposed by atomic layer deposition technology to protect electronic components improves their service life in harsh environments [26]. The excavator integrated circuit is prone to generating high heat during operation as a packaging technology in a flip-chip land grid array package type, whereby the stress caused by high temperature can destroy the interface between plastic substrates, solder, and metal mats and reduce their service life. The protective thin film significantly reduces the component damage caused by thermal stress and shows the same lowest operation voltage at 0.66 V before and after the 1000 h unbiased highly accelerated temperature and humidity stress test. The atomic layer can effectively block moisture and oxygen from entering electronic devices to avoid their rapid deterioration, improve mechanical protection and reduce the damage caused by moving collisions, which has potential applications in organic light-emitting diodes, micro light-emitting diodes, and semiconductor packages for resisting moisture. The atomic layer deposition can be used to fabricate luminescent material layers, biomedicine sensor components, and water-resistant thin films for use in energy engineering and other applications related to coating technology.

The diagnostic methods concerning the flow of technology processing in a vacuum for solid bodies' surface modification are shown in [27]. The analysis of energy distribution curves shows that the average ion energy decreases with a decrease in the discharge current, and the ratio of the average ion energy to the discharge voltage is approximately 0.68–0.71. The magnetic induction method of diagnostics presented in the study allows controlling the parameters of glow discharge plasma, determining the moment when the unit enters the operating mode and the moment of completion of technology transitions and correcting the process according to the changes in electromagnetic pulses. The presented electromagnetic radiation signal spectrum analyzer is based on a multichannel inductive sensor. It makes it possible to survey broadband plasma electromagnetic radiation signals, obtain spectra at the sensor output, and resolve the signal spectrum of glow discharge plasma electromagnetic radiation into its constituent elements.

## 3. Conclusions and Outlook

Various technologies of coating and surface hardening of manufacturing tools, including the study of tribotechnical properties of multilayer nanostructured coatings, the study of the polishing impact on coating performance, surface texturing effect, the study of coating low friction behavior, the study of the interlayer effect on properties and thermal stability of a CrAlN coating, the study of structure and properties of Mo-Zr-Si-B coatings, the study of Zr-ZrN-(Zr,Mo,Al)N, Cr-CrN-(Cr,Mo,Al)N and Ti-TiN-(Ti,Mo,Al)N multilayer coatings, the study of adaptive and self-organized nanocomposite coatings based on chrome and aluminum carbonitrides and aluminum nitride and titanium, the study of Ti-TiN-(Ti,Y,Al)N and Ti-TiN-(Ti,Cr,Al)N multilayer composite coatings, $Al_2O_3$ nanofilm, and diagnostics of plasma vapor deposition processes, have been presented in the Special Issue. It covers current evolution of achievements in coating techniques for providing the most advanced structures offering superior properties and technologies of deposition for traditional and the most-advanced coating basis. However, there are still many steps that should be taken to transfer a few of the most outstanding results and proposals into applications in the tool industry. The Guest Editor of the Special Issue hopes that the presented studies will complete the previously published advances in the first Special Issue devoted to the same topic and contribute to the transfer of the tool industry to the next technological paradigm.

Guest Editor highly appreciates the high requirements of Coatings for the quality of published papers' presentation, their up-to-date scientifically valuable theoretical and practical content provided by the Authors, and the kind efforts of the team of Reviewers, Editors, and Assistants in contributing to the Special Issue.

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