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Surface Hardening of Hard Tungsten-Carbide Alloys: A Review

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Abstract—Russian and non-Russian research on the surface hardening of hard tungsten-carbide alloys to improve the wear resistance is reviewed. There is great scope for improving the wear resistance and durability of hard-alloy components by surface strengthening on the basis of various coatings, including coatings with 100-nm structural components. On hard tungsten-carbide alloys, the most common coatings consist of titanium carbide TiC and nitride TiN, characterized by high lattice binding energy and high melting point. If such coatings are applied to hard-alloy tools, the frictional coefficient is reduced by a factor of 1.5–2.0 when cutting steel. The use of a TiN + ZrN ion-plasma coating reduces the frictional coefficient by a factor of 5.9. At present, multilayer coatings are widely employed. The most widespread are TiN + TiC and Al_2O_3 + TiC coatings. Their wear is proportional to the coating thickness. These multilayer coatings still leave room for improvement in the wear resistance of hard alloys. In Russia, the potential of hard alloys with a strength gradient from a ductile and high-strength core to a wear-resistant surface is being explored. At the Research Institute of Refractory Metals and Hard Alloys, a method has been developed for producing alloys with variable cobalt content over the thickness of the cutting insert. That permits change in alloy composition from VK20 to VK2 over the sample thickness. Correspondingly, the wear resistance of the insert's working section is equivalent to that of VK2 alloy, while the base is able to withstand considerable flexural stress. Recently, cutting tools with a diamond coating on hard alloys have been adopted in practice. To increase the durability of hard-alloy VK inserts, strengthening based on concentrated energy fluxes may be employed. Examples include treatment of hard-alloy surfaces by γ quanta, ion beams, and laser beams, electroexplosive alloying, and electrospark strengthening.

Keywords: hard-alloy tools, surface hardening, concentrated energy fluxes, hard coatings, wear resistance, hard tungsten-carbide alloys, microhardness

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Many methods are currently in use to improve the performance of cutting tools. An effective approach is to develop new types of coatings on hard alloys. The cost of coated hard-alloy inserts is 15–20% greater than that of sintered inserts, while the tool life is increased by a factor of 2–9. In Russia and elsewhere, research is underway on the creation of such coatings. At present, for example, about 35% of hard-alloy tools in the United States are produced with coatings [1].

The creation of reliable protective coatings has two aspects: (1) the development of coating compositions that prove effective in practice; (2) the development of coating-applications technologies that ensure the maximum operational reliability. That entails analysis of the coating and the base as a single composite material, which must meet specific requirements.

Coatings may be applied to hard-alloy tools by metals such as the following: gas-phase, thermodiffusional, detonation, and electron-beam methods; condensation from a plasma flux in vacuum, with ion bombardment; ion-plasma deposition; and ionic nitriding.

The possibility of applying carbide, boride, and intermetallic coatings to hard-alloy surfaces in the presence of titanium, vanadium, chromium, and boron was shown in [2]. The influence of the degree of saturation on the phase composition, structure, microhardness, transverse flexural strength, and wear resistance of hard-alloy inserts has been established. On applying protective coatings to hard-alloy inserts, the tool life in cutting 20, U8A, ShKh15, and 40Kh steel is increased by a factor of 1.2–12.7. The life is greatest for hard alloys with coatings based on titanium carbides and titanium–nickel intermetallides. However, Cutanit (England) has pointed out a deficiency of tungsten-carbide alloys: the unavoidable appearance of a sublayer of η_1 phase [1].

A mechanism for the application of a two-layer B_4C + Y_2O_3 coating on WC–20% Co hard alloy was proposed in [3–5]. It was shown that large quantities

of active boron atoms released from the agent B_4C at the surface of the workpiece diffuse into its cobalt phase, with the formation of the compound $W_2Co_{21}B_6$, in addition to the formation of boron-bearing compounds at the surface of the workpiece. In the borided layer, in contrast to boriding without rare-earth metals, the yttrium expands the temperature range of boriding in vacuum sintering and also accelerates the breakdown of the carbide B_4C and the diffusion of active boron atoms into the WC–20% Co workpiece.

The behavior of VK6 alloy samples with no coating and with an applied layer of titanium nitride TiN (thickness 15–20 μm) was investigated in [6–8]. The results indicated that the titanium-nitride coating increases the wear resistance. In addition, such coatings have deficiencies such as the sharp decline in protective properties at high cutting speeds thanks to their poor crack resistance. In this context, the introduction of zirconium in the ion-plasma titanium-nitride coating was proposed in [9, 10]. A TiN + ZrN ion-plasma coating was applied by means of separate titanium and zirconium cathodes, with nitrogen as the reactive gas; 50% Ti + 50% Zr was ensured. In ionic deposition, the energy of the ionic flux was 100 eV, the voltage was −160 V, and the current in the focusing coil was 0.3–0.4 A. Two titanium-alloy cathodes were placed in opposing positions in the chamber, with the zirconium-alloy cathode between them. It was found that additional alloying of the ion-plasma titanium-nitride coating with zirconium on VK10KS and VK8 alloys increases the nanohardness by 23%. In addition, the frictional coefficient is decreased by a factor of 5.9.

Coatings with controllable characteristics were proposed as a means of improving the wear resistance of hard-alloy parts and also increasing the productivity in [11]. The coatings, which are based on compounds of titanium with carbon and nitrogen, are produced by heating of the hard alloy in powder mixture and subsequent exposure to reactive gas—specifically, nitrogen or its mixture with ammonia. The powder mixture contains titanium nitride and/or carbonitride (67–75%), ammonium chloride (1–3%), and titanium (22–30%). The alloy is heated in an argon flux to 800–870°C, at a rate of 25–30°C/min. Then the argon supply is switched off, and the reactive gas is supplied at a rate of 1.0–1.5 l/min for 5–20 min. Finally, heating stops and the part is cooled in a nitrogen flux. The resulting wear-resistant coatings with controllable characteristics on hard-alloy inserts may be used in manufacturing, mining, and wire production.

The wear resistance of VK8 hard alloy may be increased by modifying the working surface with a quasi-amorphous coating of silicon carbide SiC, by the method in [12]. In this approach, a composite substructure of increased density is formed to a depth of tens of layers of WC grains; H_μ = 15–18 GPa. By this means, the life of hard-alloy components in impact–abrasive wear is increased by a factor of 1.5–2.5.

The microplastic and microbrittle properties of adhesive compounds of WC–Co hard alloy with thin films of titanium, boron compounds, and silicides of cobalt and titanium were investigated in [13]. The films are applied by isothermal diffusional annealing. Among the buffer coatings investigated, the titanium–silicon coating Ti_3Si was found to have the best structural and mechanical properties. Accordingly, that coating is promising as a substrate for adhesively strong diamond films.

The performance of cutting tools is largely determined by the state of their working surfaces, according to the view expressed in [14]. In the formation of a modified Cr–Al–Ti layer at the surface of a hard alloy, the contact layer of the tool is effectively blocked in two directions from harmful diffusion. At the same time, the mineral–ceramic is grown on the working surfaces of the tool; heat is released from the cutting edge; adhesion between the coating and base is increased; and friction between the tool and workpiece is reduced. The result is to improve tool performance.

Multilayer coatings are widely used at present. The best are TiN + TiC and Al_2O_3 + TiC coatings. Their wear is directly proportional to the coating thickness and depends significantly on the composition. TiN + TiC coatings are used at low cutting speeds. The life of and Al_2O_3 + TiC coatings is twice that of TiN + TiC coatings [15]. Inserts based on sintered hard alloy should have an interior coating consisting of a layer of titanium carbide, nitride, or carbonitride adjacent to the base and outer layers of aluminum oxide, according to the recommendations in [15]. The layer adjacent to the interior layer contains epitaxial ζ aluminum oxide or θ aluminum oxide. By contrast, the surface layer contains at least 90% α aluminum oxide with a grain size less than 1 μm; the remainder is ζ or θ aluminum oxide.

A metal–ceramic (cermet) hard-alloy insert was patented in [16]. This insert is especially useful for the machining of cast iron. The insert has core of cermet hard alloy, in the form of tungsten carbide WC, cubic carbonitrides, and cobalt binder alloyed with tungsten. The surface coating consists of an internal $TiC_xN_yO_z$ layer with equiaxial grains, a $TiC_xN_yO_z$ layer with columnar grains, and an Al_2O_3 layer.

Wear-resistant titanium-nitride and titanium-carbide layers are used in hybrid coatings. Metallwerk-Plansee (Austria) employs coatings consisting of several layers of titanium carbonitrides of different composition. The thickness of the multilayer coatings is 7–10 μm; the thickness of the carbide and nitride coatings is 3–6 μm. Cutanit (England) produces hard-alloy inserts with a very thin titanium-carbide layer at the surface, followed by a layer of the carbonitride and then by

titanium nitride. When using hybrid coatings, the $\eta_1(Co_3W_3C)$ phase is not present in the sublayer [1].

Tekhnologiya State Enterprise (Komsomolsk-on-Amur) has proposed a production method for VK6 hard-alloy tools in which a titanium layer is applied by condensation with ionic bombardment [17]. This tool is designed for improved performance in challenging conditions. To that end, a gradient of properties is established in the surface layers of the tool. In particular, the variation in elastic modulus and microhardness in the surface layers increases the crack resistance and strength of the surface layers. In combination with the high wear resistance and thermal stability of the part, that ensures significant increase in tool life (by a factor of two or more).

The use of multilayer coatings with elevated resistance to wear, chipping, and fusion was proposed in [18]. The coatings consist of internal, intermediate, and surface layers. The internal layer contains some combination of carbides, nitrides, borides, and oxides of elements in groups IVa, Va, and VIa and their solid solutions. The intermediate layer contains some combination of aluminum and zirconium oxides and their solid solutions. The external layer contains a columnar structure consisting of titanium carbonitrides.

Hard-alloy parts with multilayer coatings were proposed in [19]. The surface layer (thickness 2–100 μm) contains 2–25% binder; more than 25% of the nitride or carbonitride of one or more group-VIa metals; and more than 10% of the carbides or carbonitrides of vanadium, niobium, tantalum, and/or chromium. The remainder is titanium carbide TiC. Below that, the second layer (thickness 2–40 μm) has a higher nitrogen content and consists mainly of the nitride or carbonitrides of group-VIa metals. It also contains >10% of the carbides, carbonitrides, or oxycarbonitrides of tungsten, molybdenum, vanadium, niobium, tantalum, and/or chromium; and/or >5% vanadium, tantalum, and niobium dissolved in the hard alloy; >2% of chromium, tungsten, and molybdenum; and >15% binder. Under the second layer, there is a transition layer (thickness 2–100 μm), whose composition changes gradually to match that of the core.

These hybrid multilayer coatings leave further scope for improvement in the wear resistance of hard alloys.

Some studies focus on the use of aluminum-oxide coatings. For example, Sandvik Coromant (Sweden) has begun to produce inserts with a two-layer aluminum-oxide coating on a titanium-carbide layer [1].

At the Institute of Superhard Materials, Ukrainian Academy of Sciences, a method of producing alloys in which the cobalt content varies over the thickness of the insert has been developed for the manufacture of mining tools; the method is based on the steeping of sintered hard alloys [1]. By this means, it is possible to produce samples in which the alloy composition varies from VK20 to VK2 alloy over a thickness of 8 cm. As a result, the working section of the cutting inserts has wear resistance equivalent to that of VK2 alloy, while the base is able to withstand considerable flexural stress.

Experimental bits (diameter >15 mm) have been developed at Kiev Polytechnic Institute, with a core of VK15 high-cobalt alloy and peripheral sections of low-cobalt VK6 or VK8 alloy. This design permits 50–70% increase in the productivity in drilling. In that case, the stronger core withstands impacts, while the harder cutting edge has high wear resistance [1].

Analogous research at the Research Institute of Refractory Metals and Hard Alloys (Moscow) was based on the theoretical concepts regarding the production producing a strength gradient in hard alloy from a ductile high-strength core to a wear resistance surface [20]. It is possible to produce a hard alloy with variable binder content, such that, on pressing the blank, the composition changes from the surface to the core of the insert: VK3–VK6–VK10–VK15. However, dosing of the charge by means of several feeders in an automatic press is problematic when the plate thickness is 4.75 mm. In practice, it is not possible to produce a plate with an optimal combination of wear resistance, hardness, and ductility by this means. Hard-alloy inserts with gradient structure may be produced by electrospark alloying, as shown in [21, 22]. In this case, the two components are wear-resistant VK6-OM alloy and a strong but poorly wear-resistant VK10KS alloy base. In electrospark alloying, an electrode of VK6-OM alloy is eroded in a spark discharge and the erosion products are transferred to VK10KS alloy. That increases the surface hardness to 22000 MPa and reduces the frictional coefficient μ to 0.23, from a value of 0.41 for uncoated VK10KS alloy.

Cutting tools with a diamond coating are gaining favor in Russia and elsewhere [23. 24]. For example, a cutting tool based on a diamond component sintered under superhigh pressure at high temperatures has been proposed in the United States [24]. A hard-alloy WC + Co substrate is bound to the diamond component by solid soldering at 700–800°C. For this purpose, solder based on silver (30–70% Ag + Cu, Zn, Ni) is employed. The thickness ratio of the substrate and the sintered diamond layer varies in the range 0.8–3.0. The thickness of the diamond layer is 0.05–0.50 mm (preferably 0.12–0.36 mm), while the thickness of the hard-alloy substrate is 0.1–0.9 mm. The grain size in the diamond component must be 1–10 μm.

Recently, growing attention has focused on the machining of abrasive hard materials (for the drilling of circuit boards and the turning of titanium, magnesium, and aluminum alloys without cooling). For that purpose, the tool must have excellent wear resistance, strength, and thermal stability. Nanostructured hard WC + Co alloys may be used here [25–34]. The few examples of turning, drilling, and milling by nanostructured alloys currently available demonstrate the

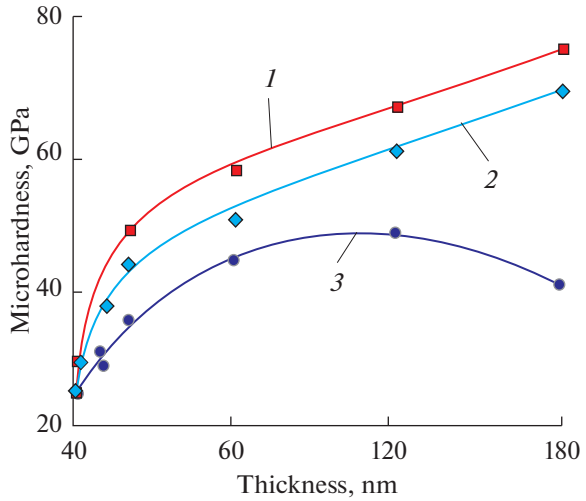

Fig. 1. Influence of the layer thickness in multilayer TiN/NbN (*1*), TiN/ZrN (*2*), and TiN/CrN (*3*) coatings on the microhardness.

prospects for the use in more challenging conditions. In the drilling of circuit boards, the life of tools made from ultrafine hard alloys exceeds that of standard alloys by a factor of 2–3, as noted in [25].

In the creation of nanostructured tungsten-carbide hard alloys and coatings, the size of the basic structural components is between 1–2 and 100 nm [26–34]. Nanostructured alloys and coatings are characterized by high values of the hardness, strength, and other physicochemical properties. Therefore, the production of tungsten-carbide powder with minimum particle size is the precondition for the creation of superfine-grain alloys.

In addition to nanostructured tungsten-carbide hard alloys, their use with nanocomposite coatings is of interest [35].

The importance of traditional superhard materials based on diamond and sodium boride is well understood. They are widely used in tool production and in mining. The influence of TiN/NbN, TiN/ZrN, and TiN/CrN coatings on the microhardness, with a total

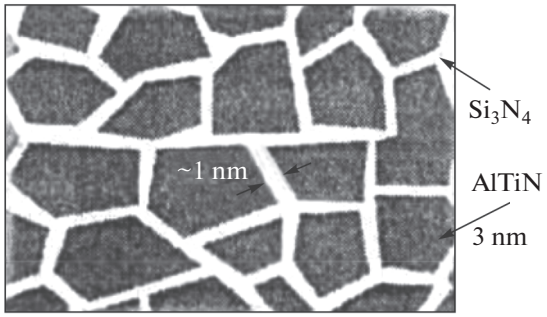

Fig. 2. Structure of (Al, Ti)N–Si_3N_4 nanocomposite film.

film thickness of 2 μm, was shown in [26] (Fig. 1). In all cases, the microhardness increased considerably with increase in the number of such layers and correspondingly with increase in the number of interfaces, which obstruct the motion of dislocations and cracks.

Table 1 presents some properties of traditional (*1–3*) and nanostructured (*4–8*) coatings (thickness 2–3 μm). Nanostructured coatings may be regarded as a superhard and thermostable nanocomposite where nitride nanoparticles such as TiN and (Ti, Al)N are located in an amorphous silicon-nitride matrix (Fig. 2).

In thin heterophase coatings, nanostructured components significantly improve the strength of the coating as a whole. In particular, superhardness in nanocomposites is associated with high internal stress, as assumed in [36, 37]. In such coatings, internal compressive stress exceeding 10 GPa may be observed [36, 38–41]. However, superhardness of the coatings is retained on relaxation to ordinary values of the compressive stress: $\sigma = 0.5–1.0$ GPa.

In TiN–Cu coatings, the microstructure of a thin coating layer (thickness <150 nm) adjacent to the substrate is nonuniform. A characteristic of this coating is a nanocrystalline state with grains of almost equilibrium form (Fig. 3). The grain size $d < 20–25$ nm.

In Ti–Si–B–N coatings, a two-level structure is observed. The titanium-nitride grains measure 0.1–

Table 1. Traditional and nanostructured coatings (thickness 2–3 μm) and their properties

Coating	Composition	H_V, GPA	Thermal stability, °C	R_a, μm	μ
1	TiN	25	~550	0.08–0.12	0.55
2	(Ti, Al)N	33	>900	0.10–0.13	0.50
3	(Ti, Al)N–SiN	33	~850	0.13–0.13	0.60
4	(Al, Ti)N–SiN	43	>1000	0.10–0.15	–
5	(Ti, Al)N–SiN	39	~900	0.10–0.15	–
6	(Ti, Al)N–SiN	40	~900	0.05–0.10	–
7	(Ti, Al)N–SiN	45	~1200	–	0.45
8	(Al, Cr)N–SiN	42	~1100	–	0.35

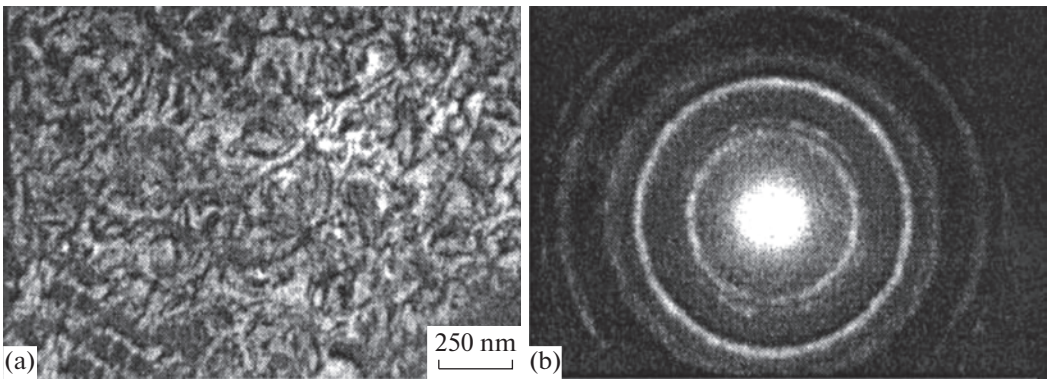

Fig. 3. Light-field image (a) and diffraction pattern (b) of the structure of a TiN–Cu nanocomposite coating at a distance of 2–3 μm from the junction with the substrate.

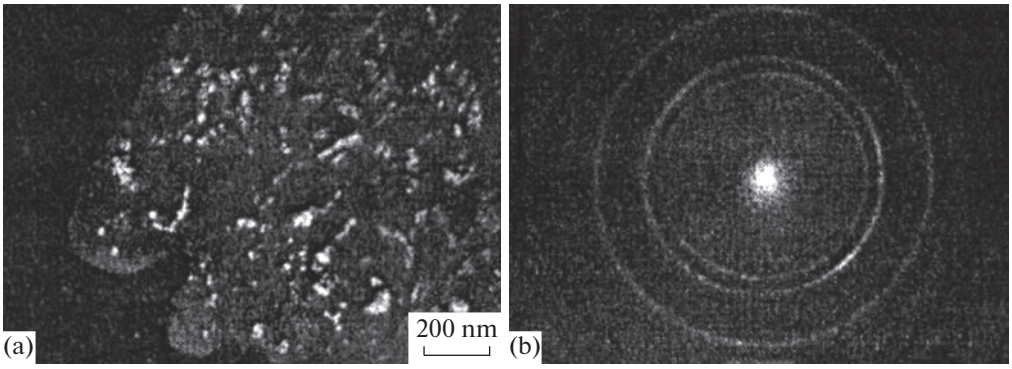

Fig. 4. Dark-field image (a) and diffraction pattern (b) of the structure of a TiN–Si–B–N coating deposited at 450°C.

0.2 μm and are fragmented in some regions to 15–20 nm (Fig. 4).

In Fig. 5, we show examples of loading–unloading curves with nanoindentation.

The development of nanotechnology depends on the creation of superhard nanocomposite coatings and analysis of the formation of their structural and phase states and their distinctive mechanical properties. In addition, it is of great interest to assign specific physical properties (thermal and electrical conductivity, frictional coefficient, corrosion resistance, etc.) to new materials, by adjusting their phase composition. Modification of their structure (the formation of nanocrystalline states of grain size no greater than 3 nm) gives rise to distinctive mechanical properties,

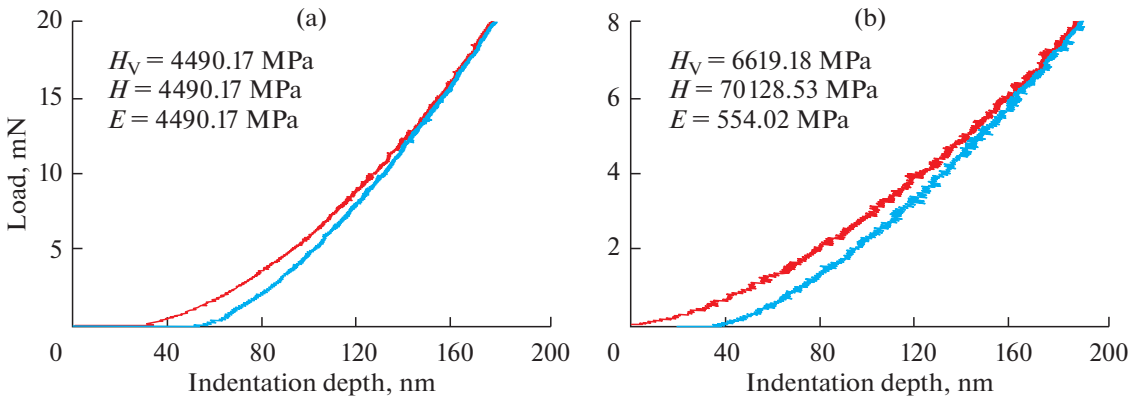

Fig. 5. Loading–unloading curves of a TiN–Si–B–N coating with nanoindentation, when the maximum load on the indenter is 20 (a) and 8 (b) mN.

including high fracture strength and adhesive strength. Accordingly, widespread use of superhard nanocomposite coatings may be expected.

Strengthening by means of high-energy perturbations provides great scope for increase in the life of hard-alloy components. Such methods are widely used at present in tool manufacture, with severalfold increase in the working life [42–64].

Laser treatment is an effective method of increasing the life of hard-alloy tools. In that case, both the carbide and cobalt phases of the alloys are modified. The fine structure of the carbide phase plays the main role in increasing the wear resistance, according to research on the structural changes in low-cobalt VK6 and VK8 hard alloys in the laser-treatment zone [43, 46]. In addition to low-cobalt hard alloys, the fine crystalline structure of the carbide phase in VK20 alloy has been investigated after treatment in the following conditions: energy density $J = 0.8–2.0$ J/mm^2; pulse length $\tau = 8–11$ ms; radiation wavelength $\lambda = 1.06$ μm [43, 44]. One-time ($N = 1$) and repeated ($N = 10$) irradiation was considered.

In the given energy-density range, according to X-ray structural analysis, the phases W_2C and WC_{cub} are consistently observed in the treatment zone at $J = 2.0$ J/mm^2 ($N = 1$) and $J > 1.6$ J/mm^2 ($N = 10$) in VK6 alloy. In VK20 alloy, by contrast, change in phase composition is only observed at $J > 1.6$ J/mm^2 when $N = 10$. Laser treatment leads to hardening of the α-WC grains. In that case, the content of crystalline defects in the carbide phase of the low-cobalt hard alloys is greatest when $J > 1.5$ J/mm^2, $N = 1$ or 10 [43–45]. Hardening of the carbide grains in repeated laser treatment is also indicated by the block size and microdistortion in the lattice of the WC phase [46]. When VK20 alloy undergoes laser treatment, the fine structure of the WC phase is qualitatively the same as in VK6 alloy. The 10–20% decrease in dislocation density observed in some cases indicates that deformed α WC grains are present in the laser-treatment zone. The distortion of the carbide lattice is considerable and exceeds the initial value by 20–50%. That is especially apparent in repeated laser treatment.

In VK20 alloy, the number of contacts between the WC grains and the area of the grains are much less than in VK6 alloy, while the contact forces in deformation at the crystallite boundaries considerably exceed those in alloys with a smaller cobalt content. Therefore, plastic deformation occurs more rapidly in the carbides of high-cobalt alloys. It is first apparent in repeated laser treatment ($N = 10$) with lower energy density [44]. Pulsed laser treatment of the surface of VK8 hard alloy increases the wear resistance [47].

The influence of microwave radiation on the performance of hard-alloy inserts based on tungsten carbide was studied in [48, 49]. Hard-alloy tools based on tungsten carbide WC were subjected to 2.45-GHz microwave radiation. The influence of the microwave radiation on the structure, the state of the cobalt binder, and the strength of the tool with WC inserts was studied by X-ray diffraction, X-ray photoelectron spectroscopy, and hardness measurements. It was found that the performance of the hard-alloy inserts is improved by activation of the grains, selective heating of the WC grains, and the formation of the mixed phase W_2C–Co.

In investigating the influence of modification by ion-plasma application of titanium-nitride TiN and titanium-carbide TiC coatings and subsequent treatment with a powerful ion beam, it was established that the wear resistance of a WC–TiC–Co hard alloy is significantly increased by such modification [50].

At Omsk State University, the structural and phase changes in the surface layers of hard alloy under the action of powerful ion beams has been investigated [51]. Attention focused on the evolution of the structural and phase state in the surface layers initiated by annealing after ion-beam treatment. Kinetic formulas were presented for the wear of the modified hard alloys in cutting. The wear resistance of modified tool materials in the cutting of structural steel at a wide range of cutting speeds was investigated in [51]. A TiN coating was applied to VK8 hard-alloy cutting inserts by condensation with ion bombardment. It was found that, after complex modification, the wear rate at the tool's rear surface is less than after ion-plasma and ion-beam treatment. Complex modification increases the wear resistance of hard alloys in the high-speed cutting of steel by a function of 1.5–2.0. The increase of wear resistance by complex modification is greatest after ion-beam treatment with a current density of 150 A/cm^2.

The effect of a powerful ion beam on the structure and properties of the surface layers of hard alloys was studied in [52–54]. It was found that pulsed treatment changes the phase composition of the material and the fine crystalline structure of the surface layer; considerably improves its physicomechanical properties; produces a coating with high and controllable hardness, strength, and plasticity on the hard alloy; and improves the wear resistance of tools based on such alloys. For example, change in the properties of VK8 hard alloy under the influence of a 40-keV beam of Ar^+ ions with a flux density of 1.5×10^{18} cm^{-2}, at target temperatures of 120–700°C, was observed in [53]. It was found that such treatment increases the microhardness by 30–40%. The greatest hardening is observed in the range 400–600°C. The depth of the hardened layer (with change in the microstructure) at the irradiated surface is 30–35 μm. That indicates the presence of a long-range effect. The basic parameter determining the relief formed and the phase composition of the surface layers is the energy density of the ion beam.

The influence of electron-beam treatment on the structure and phase composition of hard alloys was investigated in [55, 56]: decrease in microstress and in

the size and volume of primary WC grains was observed. It was assumed that radiation-induced ordering and disordering of the tungsten carbides and redistribution of the tungsten-carbide particles in the cobalt (segregation) occur in the hard alloy. Those processes had previously been disregarded. In investigating the structural changes and some mechanical characteristics of the hard alloy in electron-beam treatment with different energy and density of the flux, the researchers noted change in the lattice parameters of the carbides WC and (Ti, W)C and the cobalt binder, the state of the phase boundaries, and the mechanical characteristics, as well as relaxation of the interphase microstress due to the difference in thermal-expansion coefficients of the cobalt and the carbide skeleton and the microstress in the skeleton itself consisting of the carbides WC and (Ti, W)C.

Researchers at Tomsk Polytechnic University have proposed a new hardening technology for a hard-alloy and diamond-coated rock-breaking tools, with subsequent irradiation by small doses of γ quanta [57]. In this method, the tool was subjected to cryogenic treatment: immersion in liquid nitrogen for 15–20 min. Then it was treated with γ quanta from a Kobalt-60 source in an Issledovatel' system, at a dose rate of 20 R/s. The total dose was around 10^6 R. The results indicate that such treatment of the rock-breaking tool increases its working life. Irradiation by γ quanta increases the hardness of hard alloys and hence the working life of the corresponding tools thanks to increased wear resistance, as established in [58, 59].

Researchers at the Institute of Strength Physics and Materials Science (Siberian Branch, Russian Academy of Sciences, Tomsk) proposed a method of increasing the wear resistance of hard-alloy tools by electron-beam technology [60]. In this method, substitutional solid solutions are created in the surface layers. After nitriding of the surface for 5–7 min at a pressure of $(2–7) \times 10^{-2}$ Pa (energy range 5–10 keV), the alloys are exposed to a radiation dose of 5×10^{16}–10^{18} ion/cm^2. The alloy is bombarded first with zirconium ions, then with molybdenum ions, and finally with zirconium ions again. The use of Zr^+ and Mo^+ ions permits the creation of substitutional solid solutions. Another benefit of these ions is their considerable ability to form carbides and nitrides. Therefore, besides the formation of solid solutions, the corresponding compounds may be formed. The zirconium ions introduced in the matrix are centers for solid-solution formation, associated with disordering of the structure in the surface layer. Subsequent implantation of Mo^+ ions stabilizes the disordered state and permits the introduction of zirconium atoms at the lattice points.

The final bombardment with zirconium ions knocks the molybdenum atoms to deeper layers. That ensures mixing and exchange of the zirconium and molybdenum atoms introduced. Their concentrations are equalized. In this method, no transition layer is formed in the cutting tool. By such treatment, the life of a hard-alloy tool may be increased by a factor of five.

Pulsed plasma accelerators are used to intensify the production of hardened surface layers and to increase their purity and adhesion to the substrate. In pulsed plasma coating application, denser plasma fluxes are used than in ion-plasma spraying. The rate of particle deposition may be increased by several orders of magnitude and hence the productivity may be increased.

Electroexplosive alloying is a type of pulsed plasma treatment. The plasma accelerator used in this method is based on energy storage by a battery of pulsed capacitors and the release of a 10-kJ burst of energy within 100 μs through a wire, which undergoes explosive disintegration. In this method, the surface of a hard tungsten-carbide alloy is heated and saturated by the explosion products, with subsequent transfer of heat to the surroundings and into the depth of the material. The source of both the heating and the alloying elements is a pulsed multiphase plasma jet formed from the material in the exploding wire, which is attached to coaxial electrodes of the plasma accelerator. The explosion is confined by a conical discharge chamber, which sends the explosion products through a cylindrical nozzle into a vacuum chamber (residual pressure 100 Pa). In the formation of the jet, the condensed explosion products move away from the plasma component, and the jet consists of a fast high-energy plasma front that gradually transitions to a slow heterogeneous tail.

In the electroexplosive alloying of VK10KS hard alloy, the explosive components employed were carbon (graphite fibers), aluminum, and titanium (foil) [61, 62]. The hardening of the surface of VK hard alloys may be improved by the combined explosion of powder wires containing refractory compounds (carbides, silicides, borides, etc.), which are transferred to the alloy surface by the plasma jet [63, 64]. It was found that surface hardening of VK10KS hard alloy to 28000 MPa is associated with reduction in size of the structural components in the surface layers and the formation of new hard phases consisting of elements from both the alloy and the exploded wires.

CONCLUSIONS

The various technologies now available for applying coatings to hard alloys and modifying their surface may be used to extend the life of alloy components in many fields.

REFERENCES

1. Panov, V.S., Chuvilin, A.M., and Fal'kovskii, V.A., *Tekhnologiya i svoistva spechennykh tverdykh splavov i izdelii iz nikh* (Technology and Properties of Sintered Hard Alloys and their Products), Moscow: Mosk. Inst. Stali Splavov, 2004.

2. Khizhnyak, V.G., Dolgikh, V.Yu., and Korol', V.I., Structure and some properties of diffusion coatings of titanium, vanadium, chromium and boron on hard alloys, *Vestn. Kiev. Politekh. Inst.*, 2002, no. 1, pp. 74–79.
3. Liu, S., Hao, J., Zuo, L., and Song, J., Dynamic XRD phase analysis of rare earth-boronization for WC–Co cemented carbides, *J. Chin. Rare Earth Soc.*, 2002, vol. 20, no. 1, pp. 26–29.
4. Liu, S., Hao, J., Chu, L., and Song, J., Mechanism of hard-facing alloy's WC-Co boronizing with rare-earth metals, *Rare Metal. Mater. Eng.*, 2003, vol. 32, no. 4, pp. 305–308.
5. Liu, S., Hao, J., Chu, L., and Song, J., Phase analysis of cemented carbide WC-Co boronised with yttrium, *J. Chin. Rare Earths Soc.*, 2002, vol. 40, no. 4, pp. 287–290.
6. Vereshchaka, A.S. and Vereshchaka, A.A., Increasing effectiveness of the tool by controlling composition, structure and properties of coatings, *Uprochnyayushchie Tekhnol. Pokrytiya*, 2005, no. 9, pp. 9–18.
7. Tabakov, V.P., *Formirovanie iznosostoikikh ionno-plazmennykh pokrytii rezhushchego instrumenta* (Formation of Wear-Resistant Ion-Plasma Coatings for Cutting Tools), Moscow: Mashinostroenie, 2008.
8. Vereshchaka, A.S., Some methodological principles of creating functional coatings for cutting tools, in *Sovremennye tekhnologii v mashinostroenii* (Modern technologies in mechanical engineering), Kharkov: Khar'kovsk. Politekh.o Inst., 2007, pp. 210–231.
9. Oskolkova, T.N., Wear resistant coating on hard alloy, *Appl. Mech. Mater.*, 2015, vol. 788, pp. 281–285.
10. Oskolkova, T.N., Tungsten carbide hard alloy with wear-resistant coating, *Izv. Samar. Nauch. Tsentra, Ross. Akad. Nauk*, 2013, vol. 15, no. 4 (2), pp. 473–475.
11. Panteleev, I.B., Vladimirova, M.D., Shavrova, O.I., and Ordan'yan, S.S., Hard alloys on the base of tungsten carbide and complicated titanium (tungsten) carbonitride, *Tsvetn. Met.*, 2004, no. 8, pp. 100–105.
12. Chekhovoi, A.N., Prokopova, T.I., and Bychkov, V.M., Quasiamorphous metal-ceramic tool of the new generation, *Konstr. Kompoz. Mater.*, 1999, no. 3, pp. 13–19.
13. Andryushin, S.G., Kasatkin, A.V., and Kuchumova, V.M., Mechanical features of adhesive compounds of buffer thin-film coatings with carbide supporting plate, *Materialovedenie*, 2003, no. 6, pp. 43–51.
14. Kruglov, A.I., Senchilo, I.A., and Fomichev, A.M., Development of structure and composition of modified layer of working surfaces of metal-ceramic carbide cutting tools, *Instrum. Tekhnol.*, 2004, nos. 17–18, pp. 100–103.
15. Chatfield, C., Lindstrom, J., Sestrand, M., and Colleen, M., RF Patent 2010888, 1994.
16. Larsson, A. and Zackrisson, J., RF Patent 1531187, 2005.
17. Fadeev, V.S., Chigrin, Yu.N., Mokritskii, B.Ya., and Konakov, A.V., RF Patent 2211879, *Byull. Izobret.*, 2003, no. 25.
18. Okada, Y., Moriguchi, H., and Ikegaya, A., US Patent 6756111, *Byull. Izobret.*, 2003, no. 25.
19. Lengauer, W., Ucakar, V., Dreyer, K., Kassel, D., and Daub, H., DE Patent 10342364, 2005.
20. Anikin, V.N., Zolotareva, N.N., Kazantsev, N.I., Tambovtseva, A.A., Pel'ts, A.D., Ermolaev, A.V., Fadeev, V.S., and Blinkov, I.V., RF Patent 2302925, *Byull. Izobret.*, 2007, no. 20.
21. Oskolkova, T.N., RF Patent 2401720, *Byull. Izobret.*, 2010, no. 29.
22. Oskolkova, T.N., A new technology for producing carbide alloys with gradient structure, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2015, vol. 91, pp. 012019.
23. Langford, J.V., Jr., and Delviche, R., RF Patent 2167262, *Byull. Izobret.*, 2001, no. 14.
24. Katsuhito, Y., Junichi, S., and Tetsuo, N., US Patent 6358624, 2000.
25. Fal'kovskii, V.A., Klyachko, L.I., and Smirnov, V.A., *Nanokristallicheskie i ul'tradispersnye poroshki vol'frama, karbida vol'frama i volframokobal'tovye tverdye splavy na ikh osnove* (Nanocrystalline and Ultradisperse Powders of Tungsten, Tungsten Carbide, and Tungsten-Cobalt Hard Alloys), Moscow: Vseross. Nauchno-Issled. Proektn. Inst. Tugoplavkikh Met. Tverd. Splavov, 2004.
26. Andrievskii, R.A., Superhard nanostructured materials based on refractory compounds, *Zh. Funkts. Mater.*, 2007, vol. 1, no. 4, pp. 129–133.
27. Panov, V.S., Nanotechnology in the production of hard alloys: a review, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 2007, no. 2, pp. 63–68.
28. Bock, A. and Zeiler, B., Production and characterization of ultrafine WC powders, *Int. J. Refract. Met. Hard Mater.*, 2002, vol. 20, pp. 23–30.
29. Blinkov, I.V. and Manukhin, A.V., *Nanodispersnye i granulirovannye materialy, poluchennye v impul'snoi plazme* (Nanodispersed and Granulated Materials Obtained in Pulsed Plasma), Moscow: Mosk. Inst. Stali Splavov, 2004.
30. Amosov, A.P., Borovinskaya, I.P., Merzhanov, A.G., and Sychev, A.E., Self-propagating high-temperature synthesis as the advanced technology for nanopowders production, *Konstr. Kompoz. Mater.*, 2006, no. 4, pp. 17–19.
31. Klyachko, L.I., Fine and ultrafine hard metals at Plansee, *Met. Powder Rep.*, 2001, vol. 56, no. 11, pp. 24.
32. Liu, Y.Y., Yu, J., Huang, H., Xu, B.H., Liu, X.L., Gao, Y., and Dong, X.L., Synthesis and tribological of electroless Ni–P–WC nanocomposite coatings, *Surf. Coat. Technol.*, 2007, vol. 201, nos. 16–17, pp. 7246–7251.
33. Samokhin, A.V., Alekseev, N.V., and Tsvetkov, Yu.V., Plasma-assisted processes for manufacturing nanosized powder materials, *High Energy Chem.*, 2006, vol. 40, no. 2, pp. 93–97.
34. Ban, Z.-G. and Shaw, L.L., Synthesis and processing of nanostructured WC–Co materials, *J. Mater. Sci.*, 2002, vol. 37, no. 16, pp. 3397–3403.
35. Korotaev, A.D., Moshkov, V.Yu., Ovchinnikov, S.V., Pinzhin, Yu.P., Savostikov, V.M., and Tyumentsev, A.N., Nanostructured and nanocomposite superhard coatings, *Fiz. Mezomekh.*, 2005, vol. 8, no. 3, pp. 103–116.
36. Veprek, S., Veprek-Hejman, M.G.J., Kavrankova, P., and Prohazka, J., Different approaches to superhard coatings and nanocomposite, *Thin Solid Films*, 2005, vol. 476, pp. 1–29.
37. Musil, J., Hruby, H., and Zeeman, P., Hard and superhard nanocomposite Al–Co–N films prepared by magnetron sputtering, *Surf. Coat. Technol.*, 1999, vol. 155, pp. 32–37.

38. Holubár, P., Jílek, M., and Šíma, M., Nanocomposite nc-TiAlSiN and nc-TiN–BN coatings: their applications on substrates made of cemented carbide and results of cutting tests, *Surf. Coat. Technol.*, 1999, vols. 120–121, pp. 184–188.
39. Vaz, F., Rebouta, L., Goudeau, Ph., et al., Residual stress in sputtered $Ti_{1-x}Si_xN_y$ films, *Thin Solid Films*, 2002, vol. 402, pp. 195–202.
40. Jedrzejonski, P., Klemberg-Sapieha, J.E., and Martinu, L., Relationship between the mechanical properties and the microstructure of nanocomposite $TiN/SiN_{1.3}$ coatings prepared by low temperature plasma enhanced chemical vapor deposition, *Thin Solid Films*, 2003, vol. 426, pp. 150–159.
41. Mayrhofer, P.H., Kunc, F., Musil, J., and Mitterer, C., A comparative study on reactive and non-reactive unbalanced magnetron sputter deposition of TiN coatings, *Thin Solid Films*, 2002, vol. 415, pp. 151–159.
42. Pinakhin, I.A. and Kopchenkov, V.G., Increase of working capacity of metal-cutting tool made of hard alloys by pulse laser treatment, *Vestn. Sev. Kavk. Gos. Tekh. Univ.*, 2010, no. 4, pp. 90.
43. Grigor'yants, A.G. and Yares'ko, S.I., Investigation of stressed state of carbide phase of VK6 hard alloy under pulsed laser treatment, *Sverkhtverd. Mater.*, 1991, no. 1, pp. 49–56.
44. Yares'ko, S.I. and Kobeleva, T.K., Change in fine structure of carbide phase of solid alloys of WC–Co system under laser treatment, *Sverkhtverd. Mater.*, 1996, no. 1, pp. 52–57.
45. Iskhakova, G.A. and Sindeev, V.I., Study of high-speed deformation of tungsten carbide, *Sverkhtverd. Mater.*, 1983, no. 5, pp. 49–54.
46. Gureev, D.M., Laletin, A.P., Chulkin, V.N., and Yares'ko, S.I., On the state of fine structure of carbides in VK8 hard alloy in pulsed laser treatment zone, *Fiz. Khim. Obrab. Mater.*, 1987, no. 6, pp. 36–40.
47. Nesterenko, V.P., Aref'ev, K.P., Kondratyuk, A.A., Merkulov, V.I., and Surkov, A.S., Electric strength of polyoxide structures formed on the surface of composite materials under heating after preliminary laser treatment, *Fiz. Khim. Obrab. Mater.*, 2002, no. 5, pp. 9–13.
48. Ramkumar, J., Aravindan, S., Malhotra, S.K., and Krishnamurthy, R., Enhancing the metallurgical properties of WC insert (K-20) cutting tool through microwave treatment, *Mater. Lett.*, 2002, vol. 53, no. 3, pp. 200–204.
49. Ivanov, A.N., Korshunov, A.B., and Yakovtsova, M.M., Effect of high-speed heat treatment on fine structure of tungsten carbide in a VK8 shard alloy, *Trudy 6-go mezhgosudarstvennogo seminara "Strukturnye osnovy modifikatsii materialov metodami netraditsionnykh tekhnologii"* (Proc. Sixth Int. Conf. "Structural Fundamentals of Material Modification by Non-Traditional Technologies), Obninsk, 2001, p. 21.
50. Poleshchenko, K.N., Povoroznyuk, S.N., Boboi, A.O., and Ivanov, Yu.F., Changes in tribological properties of metal-ceramic hard alloys by ion-plasma and ion-beam treatment, *Fiz. Khim. Obrab. Mater.*, 2002, no. 2, pp. 5–8.
51. Boboi, A.O., Poleshchenko, K.N., Povoroznyuk, S.N., et al., Complex modification of carbide cutting tools using ion beams of high specific power, in *Materialy i tekhnologii 21-go veka* (Materials and Technologies of the 21st Century), Penza: Privolzhsk. Dom Znanii, 2001, part 1, pp. 87–89.
52. Remnev, G.E., Semukhin, B.S., Struts, V.K., et al., Investigation of structure of hard alloy based on tungsten carbides and titanium subjected to powerful-pulsed ion irradiation, *Fiz. Khim. Obrab. Mater.*, 1998, no. 5, pp. 19–22.
53. Ivanov, A.N., Khmelevskaya, V.S., Antoshina, I.A., and Korshunov, A.B., Structural changes in VK8 hard alloy under ion irradiation, *Perspekt. Mater.*, 2003, no. 1, pp. 89–92.
54. Tarbokov, V.A., Remnev, G.E., and Kuznetsov, P.V., Modification of carbide plates based on tungsten carbide by powerful-pulsed ion beam, *Fiz. Khim. Obrab. Mater.*, 2004, no. 3, pp. 11–17.
55. Petrenko, P.V., Gritskevich, A.L., Kulish, N.P., Mel'nikova, N.A., and Rozhkovskii, A.N., Influence of radiation defects on structural-phase transformations in WC–Co alloys, *Trudy 6-go mezhgosudarstvennogo seminara "Strukturnye osnovy modifikatsii materialov metodami netraditsionnykh tekhnologii"* (Proc. Sixth Int. Conf. "Structural Fundamentals of Material Modification by Non-Traditional Technologies), Obninsk, 2001, pp. 85.
56. Petrenko, P.V., Grabovskii, Yu.E., Gritskevich, A.L., and Kulish, N.P., Structural-phase transformations in WC–Co hard alloys irradiated with a low-flux electron beam, *Fiz. Khim. Obrab. Mater.*, 2003, no. 3, pp. 29–39.
57. Mamontov, A.P., Chernov, I.P., and Ryabchikov, S.Ya., RF Patent 2092282, 1997.
58. Korshunov, A.B., Shamaev, B.V., Shorin, A.M., Shesterikov, S.A., Pikunov, D.V., Shchurkova, V.V., and Danilov, S.L., RF Patent 93057445, 1996.
59. Timoshnikov, Yu.A., Klopotov, A.A, and Ivanov, Yu.F., Change in structural-phase state of VK8 alloy under the influence of gamma-ray flux, *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, 2001, no. 4, pp. 40–43.
60. Puchkareva, L.N., Poleshchenko, K.P., and Poletika, M.F., RF Patent 1707997, 1997.
61. Oskolkova, T.N., Budovskikh, E.A, and Goryushkin, V.F., Features of structure formation of the surface layer in the course of electroexplosive alloying tungsten carbide hard alloy, *Russ. J. Non-Ferrous Met.*, 2014, vol. 55, no. 2, pp. 196–200.
62. Oskolkova, T.N. and Budovskikh, E.A., Pulse plasma treatment of the surface of alloy VK10KS, *Met. Sci. Heat Treat.*, 2012, vol. 53, no. 11, pp. 608–610.
63. Oskolkova, T.N. and Budovskikh, E.A., Electric explosion alloying of the surface of hard alloy VK10KS with titanium and silicon carbide, *Met. Sci. Heat Treat.*, 2013, vol. 55, no. 1–2, pp. 96–99.
64. Oskolkova, T.N. and Budovskikh, E.A., Change in structure of the surface of VK10KS alloy after electroexplosive treatment with boron, *Tekhnol. Met.*, 2012, no. 3, pp. 13–18.

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