SYNTHESIS OF LAYERED COATINGS FROM SOLID SOLUTIONS OF NIOBIUM, ZIRCONIUM AND TITANIUM CARBIDES ON HARD ALLOY TOOL USING VACUUM ARC DEPOSITION

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Layered carbide coatings were formed on a carbide tool as a result of ion exposure by niobium cathode-arc source with energy of 1 keV and subsequent cathodic arc-vacuum deposition (CAVD) of coatings using simultaneous plasma flows of Nb and Zr, Nb and Ti in a methane atmosphere. The aim of the work was to study the phase and element composition, microhardness, adhesive strength, wear resistance and microstructure of a system of layered refractory carbide coatings formed on a WC-Co hard alloy. As a result, it was established, that vacuum cathode-arc deposition with simultaneous combustion of two metal cathodes Nb and Zr, or Nb and Ti with preliminary intense ionic action of Nb forms layered coatings on the hard alloy from solid solutions (Nb,Zr)C, (Nb,Ti)C and a sublayer of (W,Nb)C. The uppermost layer a few microns thick is solid solutions of carbides (Nb,Zr)C or (Nb,Ti)C. Between it and the hard alloy there is a thinner layer (Nb,W)C with a thickness of up to 0.5 μm. The hardness, flaking critical load of these layered coatings from solid carbide solutions is very high (58-65 GPa), (110-140 N). The volumetric wear of the tool with these carbide coatings is 4-10 times less than the wear of the hard alloy without coating.

Keywords: solid solution carbide coatings; vacuum arc deposition; hard alloy; wear; hardness.

Introduction

To increase the wear resistance of cutting carbide tools used in various fields of industry, the possibilities of new types of hard coatings having a multiphase composition, a multilayer structure, the nanocrystalline structure of the entire coating or its layers are actively studied. Using various vacuum deposition methods, nanostructured coatings were synthesized, consisting of crystallites of TiN, ZrN, (Zr,Al,Cr)N nitride ceramics and others with sizes <10 nm, which are separated by disordered or amorphous nanolayers of carbon, Si3N4, etc. [1-5]. Multilayer coatings with nanocrystalline structure are also formed from such nanocomposites. Such coatings acquire high hardness values (≥40 GPa). The practical application of such nanostructured high hard coatings for increasing of tool wear resistance is still limited. This is due to the fact that increasing of a coated tool wear resistance for practical use is determined by a set of properties. Mechanical stresses (internal, residual) in the coating, cracking resistance, adhesion strength of the coating to the substrate, as well as interlayer, intergrain strength have a more significant impact on wear resistance than hardness [4, 5].

It should be noted that coatings that improve the operational properties of cutting woodworking carbide tools should have a special set of properties: low friction coefficient, high hardness, adhesion, oxidative and chemical resistance to interaction with oxygen and components of wood-containing materials [6, 7]. To implement a complex of these properties, a layered coating architecture can be used [2–4, 6-9]. The possibility of using oxide chromium, aluminum, or other types of antifriction and chemically resistant layers as upper coating layer providing a low coefficient of dry friction and oxidation resistance is studied [10-12]. The main coating layer with adhesive transition layers should provide resistance to deformation, cracking, wear. To strengthen the wood-cutting tool, it is possible to use coatings made of carbide ceramics, which are not widely used in metalworking due to an increase in the friction coefficient during the cutting of steel materials with carbides as a result of the interaction of carbon with iron, dissolution of tungsten in iron. It was shown [13] that new types of composite hard alloys based on niobium and tungsten carbide can significantly increase the tool wear resistance compared to the known alloys based on tungsten carbide and cobalt. It is also known that carbide coatings of transition metals have high hardness, chemical inertness, and thermal stability [10]. Promising coatings for increasing of carbide wood-cutting tool wear resistance could be high-hard multilayer thermostable carbide coatings formed in a single technological cycle of vacuum-arc ion bombardment and plasma deposition. Studies of the mechanical properties of niobium carbide coatings formed by the vacuum-arc method on a WC carbide tool showed the possibility of creating layered carbide coatings having a hardness of up to 50–60 GPa [14]. The hardness of these coatings exceeds the hardness of various types of nitride coatings with a nanocrystalline structure, layered coating structure those formed by the vacuum-arc method, but without creating special thick hard sublayers on the surface [15-18].

The research results [19] showed that for the formation of such high-hardness layered carbide coatings on a carbide tool, which also have significant adhesion resistance, the preliminary action of an ion flux with an energy of 1 keV created by a vacuum-arc Nb source in the range of 1-2 minutes is of decisive importance. In this case, the surface temperature of the samples increases to 1300 °C. As a result of ion incorporation, heating, and diffusion, the layers of $(Nb, W)C_{0.7}$, $Co_6W_6C_2$ carbides are formed in the hard alloy with a predominance of the metal content over carbon in these compounds. The NbC coatings were deposited onto these layers by the vacuum-arc method in a plasma mode, which made it possible to create highly hard carbide layered coatings. Previous studies [20] show the promise of creating solid-solution layered carbide layers based on NbC with a high adhesive bond with a WC-Co carbide substrate. This adhesive bond in these studies was provided by intense ion bombardment with niobium ions and the processes of formation of bonding sublayers, which were mentioned above. In this paper, we study further possibilities for improving the mechanical properties of this type of refractory carbide layered coatings to increase the wear resistance of cutting carbide tools using the vacuum-arc method and use simultaneous plasma deposition from two metal cathodes Nb and Zr, Nb and Ti. It is known that carbides of these metals form solid solutions with each other [21]. The formation of coatings from solid solutions of nitrides, metal carbides of two or more metals allows creation of materials with higher mechanical properties compared to single-phase nitride, carbide compounds and coatings [22, 23]. Thus, the aim of the work was to study the phase and element composition, microhardness, adhesive strength, wear resistance and microstructure of a system of layered refractory carbide coatings formed on a WC-Co hard alloy using vacuum-arc sources of Nb and Zr, Nb and Ti in the modes of ion bombardment and plasma deposition.

Experimental

The hard alloy on which the coatings were applied was an industrial design of the knives of a woodworking tool. A feature of the hard alloy is a low Co content (3 at.%), WC grain size is in the range of 0.2–0.8 μm. The hard alloy has a hardness of 17 GPa. The process of forming layered carbide coatings consisted of two steps. First step is ion bombardment for 1 minute with an energy of 1 keV using Nb, cathode-arc sources on a VU-2MBS installation. In this case, the ion flux density on the samples using the Nb cathode was 1.8–2.0 mA.

To increase the temperature of the samples during coating formation, the tool samples were placed at a small distance from the center of the cathodes; the special fastening of the samples reducing the heat removal from them to the sample holder was used. The temperature fields on the surface of the samples during niobium ion bombardment and the subsequent coating deposition were monitored with a high-temperature thermograph [24].

The second step is the coating deposition, was made at a methane pressure of 10^{-1} Pa for 3 minutes. The bias was – 200 V. For the deposition of two types of carbide coatings, two cathodic sources Nb and Zr, Nb and Ti were used simultaneously. The cathode arc current for Nb was 180 A; for the Zr and Ti cathodes, cathodic arc currents of 100 and 120 A were used. The study of the phase composition of the coatings was carried out with glancing incidence of X-rays on the surface with angle of 5 degree. The stress in the formed coatings were determined by X-ray diffraction studies using the Holder-Wagner technique.

To study the changes in the microstructure and concentration of elements in the coating and in underlying layers of the hard alloy, the cross–section patterns were made. SEM-images of cross-section patterns surface were obtained using a scanning electron microscope (LEO 1455 VP). Element composition of cross-section patterns surface was determined by X-ray microanalysis. The microhardness of the samples was measured by Vickers methods on a Wilson Instruments 402MVD instrument at load of 1 N, 2 N.

Scratch tests were carried out with 0.5 mm radius diamond indenter. The scratch length was about 20 mm. The track after scratching was analyzed using an optical microscope to determine the minimum load at which cracks or peeled pieces of coatings became noticeable in the track. The determined load value corresponds to the critical load of the beginning of peeling of the coating.

To determine the wear resistance of the formed coatings, tribological tests and determination of the specific volumetric wear were carried out. The tests were carried out on a scratch tester with a reciprocating movement of a diamond indenter sample with a 0.5 mm rounding on the surface under a load of 20 N, 10 mm long at a speed of 20 mm/min for 30 minutes. The wear track formed on the tool surface was measured by a profilometer (Mahr Surf SD26) and then the average specific volumetric wear was determined from profilograms in different places of wear track.

Results and discussion

The concentration of metals in the surface of the coatings of four types synthesized using two cathode sources Nb and Zr, Nb and Ti simultaneously, are shown in Table 1.

Table 1. The metal content in the synthesized coatings on the hard alloy depending on the currents of the cathode arcs of metal sources

Currents of cathode arcs of metal sources, A		The metal content in the coatings, %	
Nb	Zr	Nb	Zr
180	100	89	11
	120	66	34
	Ti		Ti
	100	88	12
	120	69	31

Figure 1 shows the diffraction patterns of samples of carbide tools with $Nb_{89}Zr_{11}C$, $Nb_{66}Zr_{34}C$, $Nb_{88}Ti_{12}C$, $Nb_{69}Ti_{31}C$ coatings.

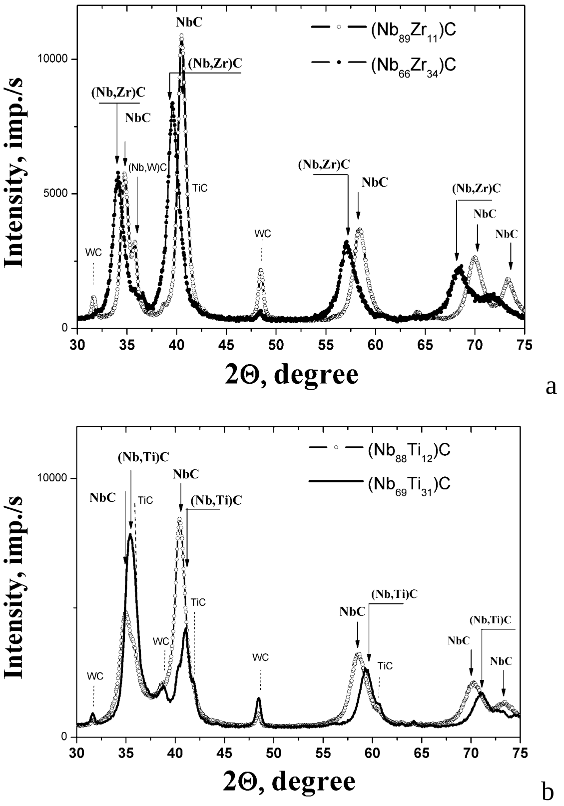

Fig. 1. XRD pattern of instrument samples with: (a) $Nb_{89}Zr_{11}C$, $Nb_{66}Zr_{34}C$; (b) $Nb_{88}Ti_{12}C$, $Nb_{69}Ti_{31}C$ coatings created by ion exposure to niobium and plasma deposition using simultaneously two cathode sources Nb and Zr; Nb and Ti

Table 2 presents the experimental values of the crystal lattice parameters of the created coatings from carbide solid solutions and the literature data for simple carbides.

Table 2. Crystal lattice parameters for synthesized (Nb,Zr)C, (Nb,Ti)C coatings and the literature data for simple carbides [21]

Type of coatings	Crystal lattice parameter, nm (± 0.0005)
$Nb_{89}Zr_{11}C$	4.4672
$Nb_{66}Zr_{34}C$	4.5435
$Nb_{88}Ti_{12}C$	4.4490
$Nb_{69}Ti_{31}C$	4.3959
NbC	4.4476
TiC	4.3282
ZrC	4.4702

Cross-sectional scanning electron microscopy images of samples with coatings formed by Nb ion bombardment and plasma deposition by Nb and Zr (arc current 120 A); Nb and Ti (arc current 120 A) and the distribution of elements over cross-section patterns are presented in Fig. 2. The initial microstructure of the hard alloy is presented in the upper area region of the images. Light areas of SEM images correspond to WC grains. The crystallite size of WC does not exceed 0.2 μm. There are thinner darker layers containing cobalt between WC crystals. From the data of Figure 2 it follows that the synthesized coatings are a layered system of carbide coatings. The uppermost layer a few microns thick is solid solutions of carbides (Nb,Zr)C (Fig. 2a) or (Nb,Ti)C (Fig. 2c). Between it and the hard alloy there is a thinner layer (Nb,W)C with a thickness of up to 0.5 μm. This is evidenced by data on the distribution of elements over the cross section of the samples (Fig. 2b, 2d). Its formation occurs as a result of exposure to an ion stream of niobium with an energy of 1 keV created by an arc source. The synthesis this of carbide layer (Nb,W)C occurred by ion exposure by Nb at a surface temperature of the hard alloy of at least 1300 °C, controlled by an optical thermograph [20].

Table 3 shows the mechanical properties and stress of layered carbide coatings on a hard alloy formed by Nb ion bombardment and plasma deposition by Nb and Zr, Nb and

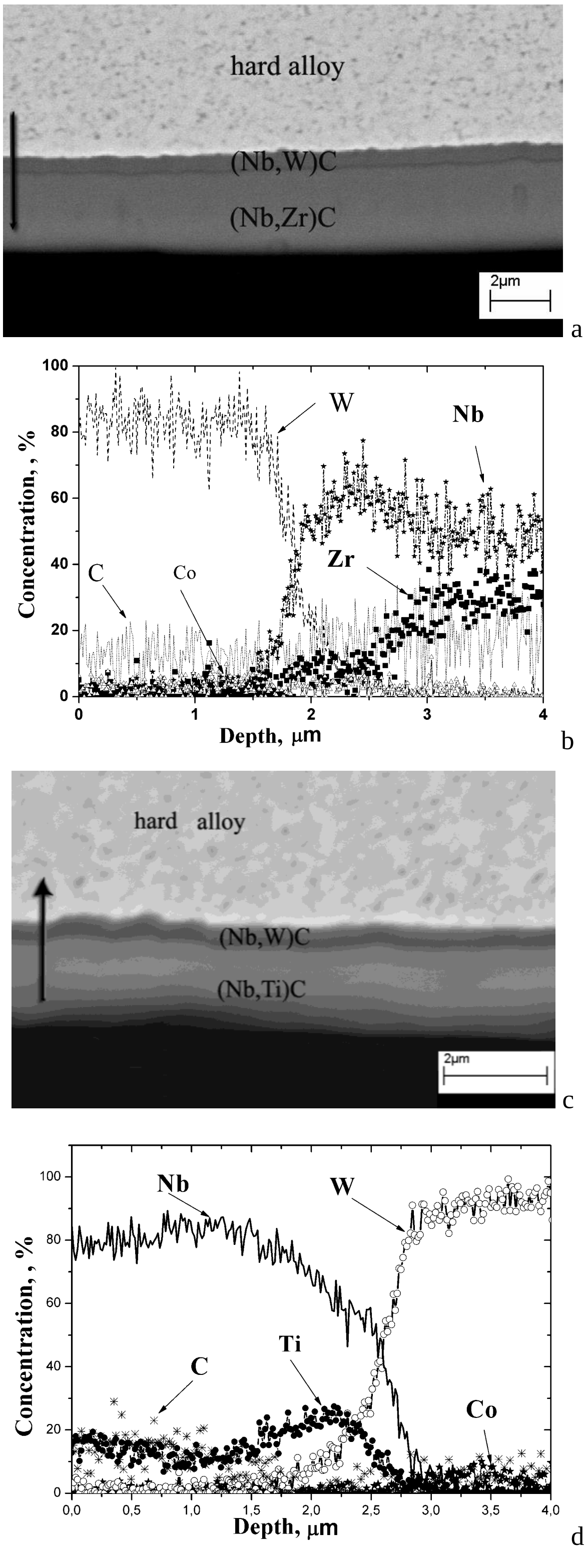

Fig. 2. Cross-sectional scanning electron microscopy images of samples with coatings formed by Nb ion bombardment and plasma deposition by: (a) Nb and Zr (arc current 120 A); (c) Nb and Ti (arc current 100 A); (b, d) vacuum-arc sources and their corresponding intensity distribution of characteristic x-ray radiation of W, Co, C, Nb, Zr, Ti along the arrows indicated in the figures (a, c)

Ti. The hardness of these layered coatings from solid carbide solutions is very high (58-65 GPa), but does not exceed the hardness of layered coatings from NbC and (Nb,W)C, obtained under similar conditions of ion exposure and plasma synthesis (table 3). Volumetric wear of these layered coatings from solid carbide solutions (Nb,Zr)C, (Nb,Ti)C less of volumetric wear NbC and (Nb,W)C coatings. Perhaps this is due to an increase in flaking critical load of carbide solutions (Nb,Zr)C, (Nb,Ti)C in comparison NbC and (Nb,W)C coatings.

Table 3. Mechanical properties and stress of layered carbide coatings on a hard alloy formed by Nb ion bombardment and vacuum arc deposition using one (Nb) [21] and two metal cathodes Nb and Zr, Nb and Ti

Sample	Load		Flaking critical load, N (error: 20 N)	Wear, (10^{-16} m^3/N·m) (error rang: (0.2-0.3) 10^{-16} m^3/N·m)	Stress, GPa (error range: 0.3-0.4 GPa)
	Hardness, GPa (error range: 2-4 GPa)				
	1 N	2 N			
Hard alloy	17	17	-	4.1	-
NbC/ (Nb,W)C	66	61	110	1.0	1.0
$Nb_{89}Zr_{11}C$	62	60	140	0.4	1.4
$Nb_{66}Zr_{34}C$	65	62	140	0.5	2.3
$Nb_{88}Ti_{12}C$	61	42	120	0.8	2.1
$Nb_{69}Ti_{31}C$	58	39	110	0.9	2.8

Conclusion

Vacuum cathode-arc deposition with simultaneous combustion of two metal cathodes Nb and Zr, or Nb and Ti with preliminary intense ionic action of Nb forms layered coatings on the hard alloy from solid solutions (Nb,Zr)C, (Nb,Ti)C and a sublayer of (W,Nb)C. The uppermost layer a few microns thick is solid solutions of carbides (Nb,Zr)C or (Nb,Ti)C. Between it and the hard alloy there is a thinner layer (Nb,W)C with a thickness of up to 0.5 μm. The hardness, flaking critical load of these layered coatings from solid carbide solutions is very high (58-65 GPa), (110-140 N). The volumetric wear of the tool with these carbide coatings is 4-10 times less than the wear of the hard alloy without coating.

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