The structure of composite coatings based on titanium nitride, formed using condensation with ion bombardment

P M Korusenko[1], S N Nesov[1], S N Povoroznyuk [1,2], K N Poleshenko[2], P V Orlov[2], D N Korotaev[2], D A Suleymenova[1]

[1]Omsk State Technical University, Mira Avenue 11, 644050, Omsk, Russia
[2]Siberian State Automobile and Highway University, Mira Avenue 5, 644080, Omsk, Russia

E-mail: korusenko_petr@mail.ru

Abstract. The main aim of this work was to study the morphology, elemental and quantitative composition, as well as the chemical state of titanium nitride coatings obtained by condensation with ion bombardment on substrates of sintered hard alloy (VK8: WC – 92%, Co – 8%) and Hadfield steel (110G13L: Mn – 11-14.5%, C – 0.9-1.3%). Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) were used to analyze the structure and composition of the coatings. It was established that the composition of coatings formed on different substrates at the same deposition time is almost identical and consists of TiN, TiNO, and TiC. This indicates that coating formation conditions are reproducible. At the same time, it was shown that in the coating formed on 110G13L steel, an increase in the amount of titanium oxy nitrides is observed, associated with the peculiarity of the occurrence of nonequilibrium processes in the preparation of coatings. It was shown that the application of the approach based on the use of XPS and EDX data obtained from various depths makes it possible to correctly study the composition of coatings based on titanium nitride and future control their composition by changing the parameters of coating formation.

1. Introduction

The application of wear-resistant coatings based on titanium nitride on the working surfaces of various products, including elements of gas turbine engines and internal combustion engines operating at elevated temperatures and speeds, is one of the most encountered ways to increase their technological characteristics [1, 2]. One of the methods for applying TiN coatings is the condensation of a substance from a plasma in a vacuum with ion bombardment of the surface (CIB) [3]. The advantage of the CIB method compared to the magnetron sputtering method is the formation of a high adhesion of the coating to the substrate due to the sufficiently high ion energy during the preliminary cleaning process and the rate of coating formation. At the same time, the disadvantages of this method are the probability of the formation of a droplet phase of titanium metal, the presence of which reduces the operational characteristics of the coatings. In addition, residual gases containing carbon and oxygen, which are present in the vacuum chamber in addition to the main working gas, significantly affect the elemental and phase composition and, accordingly, the properties of the formed coatings [4]. These gases deposited on the surface, due to elevated temperatures lead to a change in the distribution of the phase composition over the depth of the formed coating. In this regard, it is important to analyze changes in the composition and chemical state of coatings deposited at the same formation parameters using a combination of non-destructive methods with different analysis depths.

In this work, scanning electron microscopy (Scanning Electron Microscopy - SEM) was used to obtain information on the morphology and structure of coatings formed on substrates of VK8 sintered hard alloy and 110G13L steel. To study the elemental and quantitative composition of the coatings, a combination of X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) methods with different analysis depths were used. To obtain information on the chemical and phase state of the coatings, the XPS method was used.

2. Experimental details

The formation of TiN coatings was carried out at the HHB 6.6 equipment at the Omsk Research Institute of Technology and Organization of Engine Production. Substrates of VK8 hard alloy were used, as well as steel grade 110G13L with a roughness of not more than 1.25 microns. When forming the coatings, a VT5 grade cathode was used, consisting of titanium metal (up to ~ 92-96%) with the inclusion of aluminum metal. The presence of Al in the composition of the cathode reduced the formation of titanium in the droplet phase in the coatings [5]. To form coatings with high interfacial adhesion to the substrate, the substrates were preliminarily cleaned in plasma at a voltage of ~ 1000 V and a pressure in the HHB 6.6 chamber of about $5 \cdot 10^{-5}$ mm Hg. Forming of coating was carried out in an atmosphere of dry N_2 at a pressure of ~ $3 \cdot 10^{-3}$ mm Hg. The arc discharge current was 110 A at a voltage of 210 V on the substrate. The coating time was 15 minutes, and its estimated thickness was ~ 500 nm.

To study the morphology of the formed coatings, the SEM method was used on a JEOL JSM 6610 LV microscope at the Omsk Regional Shared Equipment Center SB RAS. SEM images were recorded at an accelerating voltage of 20 kV, with different spatial resolutions. To conduct elemental analysis in selected regions on SEM images, the EDX method was used using an INCA-350 Oxford Instruments implemented on a JEOL JSM 6610 LV microscope. The diameter of the focused electron beam in the study of coatings by the EDX method was from 1.5 to 2 μm, and the analysis depth to ~ 1-2 μm.
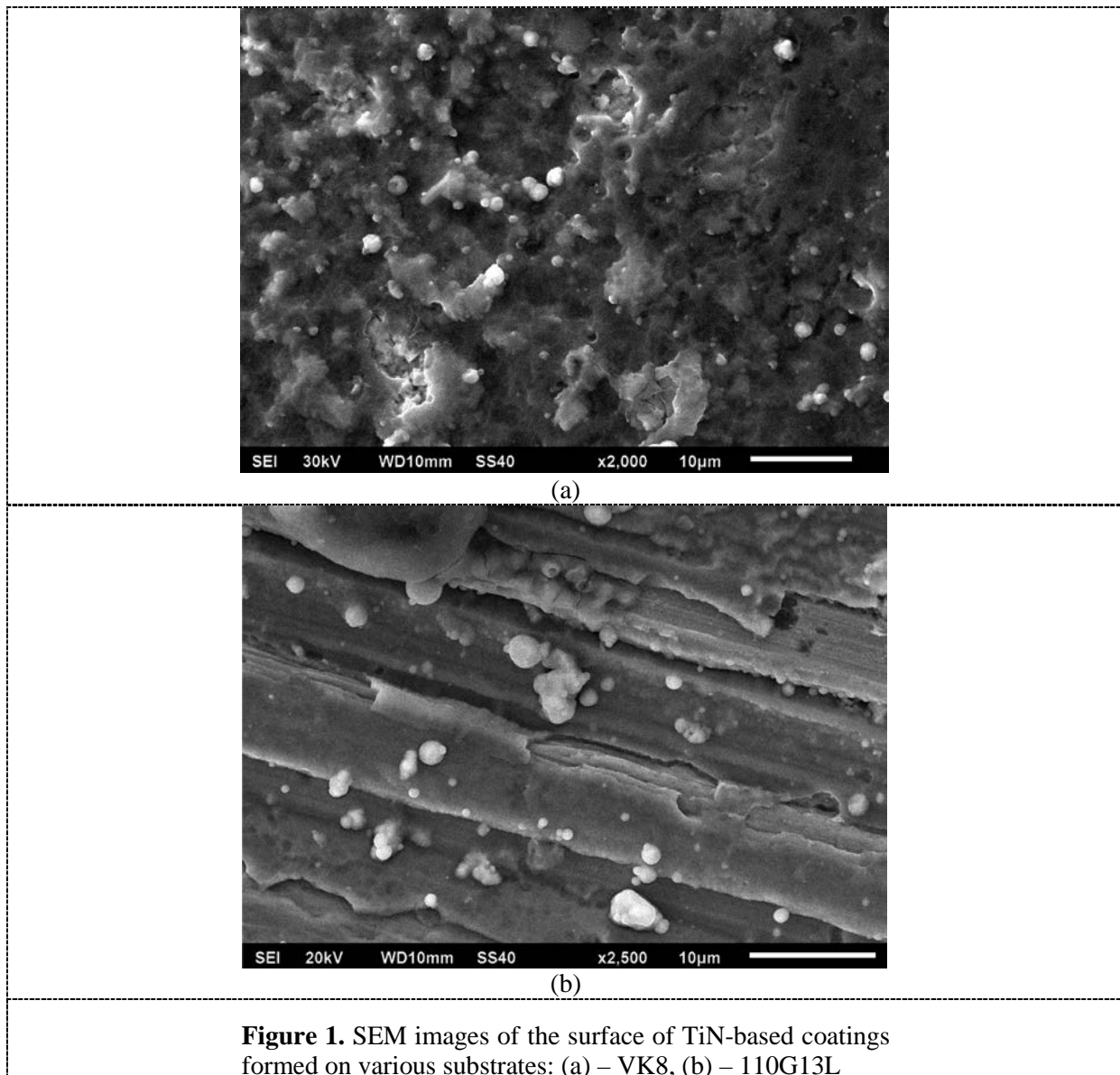
To obtain information on the structure and chemical state of coatings, the XPS method was used on a Surface Science Center (Riber) laboratory spectrometer at the Omsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences. The photoemission spectra were excited using an aluminum anticathode with a line energy of 1487 eV. The spectra were recorded on a two-stage cylindrical mirror analyzer type EA 150. XPS analysis depth was up to 3-5 nm.

The use of a complex of EDX and XPS analysis methods with different probing depths (from nanometer to micron units) allows us to obtain information about the changes in the elemental composition of coatings in depth without their destruction and modification. For XPS studies, in order to clean the surface of coatings from contaminants, the samples were preliminarily etched by argon ions with an average energy of ~ 3 keV at a pressure in the spectrometer chamber of ~ $5 \cdot 10^{-5}$ mm Hg. The rate of ion sputtering ranged from 1 to 2 nm per minute.

3. Results and discussion

3.1. Analysis of coatings by SEM

Figure 1 shows SEM images of the surface of coatings obtained on substrates of VK8 hard alloy and 110G13L steel. As can be seen (Fig. 1a), the surface of the coating on the VK8 substrate has craters and elevations, as well as spherical clusters (in the SEM image, they are observed as light colored inclusions). Comparison of SEM images (Fig. 1a, 1b) shows that the coating obtained on 110G13L steel has a smoother surface, fewer spherical clusters and does not contain craters. It should be noted that coatings on various substrates were formed in a single deposition cycle. Thus, we can conclude that the morphology of the formed coating based on titanium nitride depends on the type of substrate.

(a)

(b)

Figure 1. SEM images of the surface of TiN-based coatings
formed on various substrates: (a) – VK8, (b) – 110G13L

3.2. Elemental and quantitative analysis of coatings by XPS and EDX

To determine the elemental and quantitative composition on the surface of the coatings without their destruction and modification, the XPS method was used. Figure 2 shows the survey XPS spectra of TiN coatings formed on various substrates. As can be seen, the lines of titanium (Ti 2s ~ 555 eV, Ti 2p ~ 455 eV, Ti 3s ~ 57 eV, Ti 3p ~ 31 eV), oxygen (O 1s ~ 533 eV, O KLL ~ 980 eV), nitrogen (N 1s ~ 400 eV), carbon (C 1s ~ 285 eV) are observed in all spectra. The quantitative data obtained from the analysis of the survey XPS spectra are summarized in Table. 1. Comparison of the data of a quantitative analysis of coatings obtained on various substrates allows us to conclude that the coatings have a similar composition with a titanium to nitrogen ratio of ~ 1. At the same time, a higher carbon concentration (~ 40 at.%) on the surface of the coating formed on VK8 than in the case of coating on 110G13L steel (~ 31 at.%) is observed . This may be due to the difference in the amount of carbon in the C-C, C=C, C-O groups, as well as the presence of a higher carbon content in the Ti-C bonding.
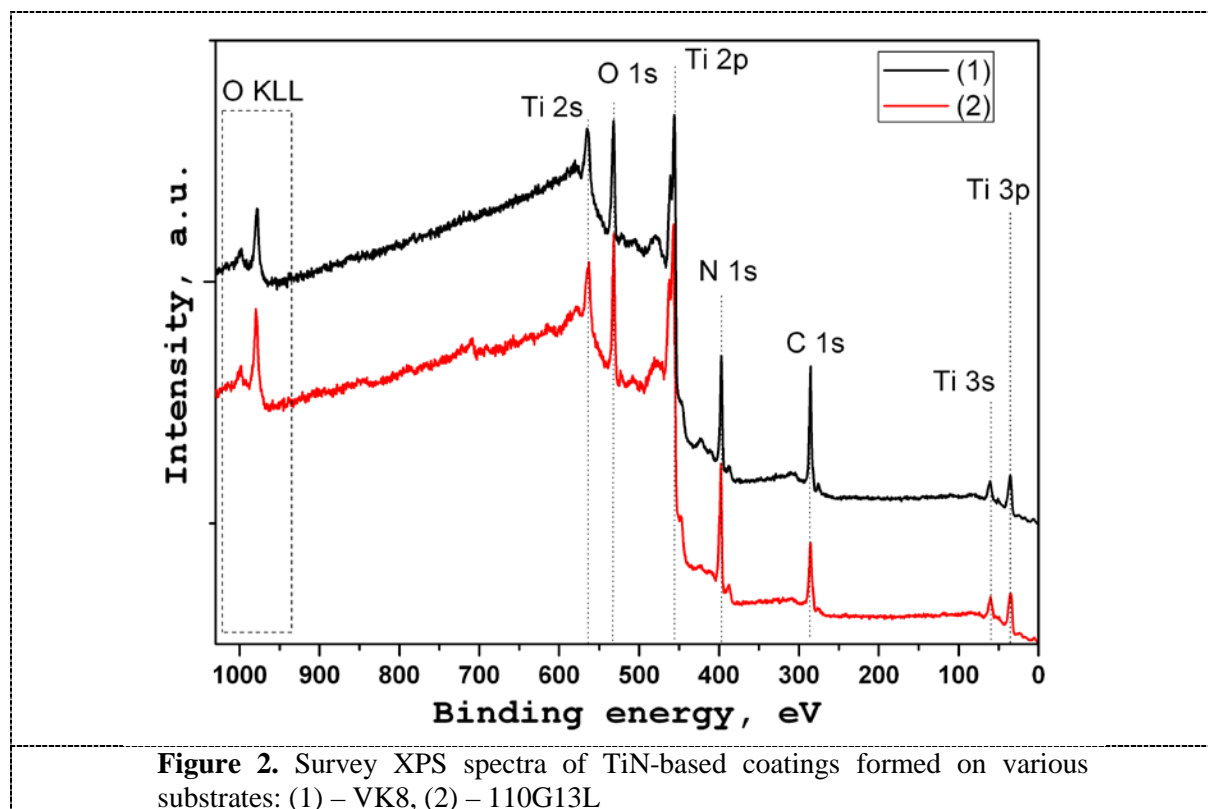
Figure 2. Survey XPS spectra of TiN-based coatings formed on various substrates: (1) – VK8, (2) – 110G13L

Table 1. Composition of coating formed on various substrates according to XPS

№ Point	Concentration, at.%			
	[C]	[N]	[O]	[Ti]
Coating on VK8				
1	41.0	20.2	19.4	19.4
2	39.7	22.5	19.1	18.7
3	40.0	23.0	18.1	18.9
Mean	40.2	21.9	18.9	19.0
Coating on 110G13L				
1	30.8	24.8	18.6	25.8
2	30.2	24.2	19.5	26.1
3	31.2	24.2	18.1	26.5
Mean	30.7	24.4	18.8	26.1

The EDX method was used to determine the elemental composition of coatings in a bulk without their destruction and modification. The data of elemental and quantitative analysis are given in Table. 2. As can be seen, the results of the EDX analysis make it possible to obtain integral information on the entire thickness of the coatings, including the upper layers of the substrates (in the case of VK8 it is cobalt and tungsten; in the case of 110G13L it is manganese and iron). It can be seen that in both coatings the presence of aluminum is observed, the concentration of which is almost identical. In addition, the presence of iron is also observed in the coating on VK8, the presence of which can be explained by partial sputtering of the structural parts of the NNV-6.6 equipement [4]. Apparently, in the case of the coating on 110G13L, the presence of a certain amount of iron in the coating should also take place. However, a more significant signal of iron from the substrate dominates the signal of iron in the coating, which does not allow to accurately determine the concentration of the latter. It should also be noted that the determination of a reliable concentration of oxygen and nitrogen by the EDX method is difficult due to the fact that their energy ranges overlap.
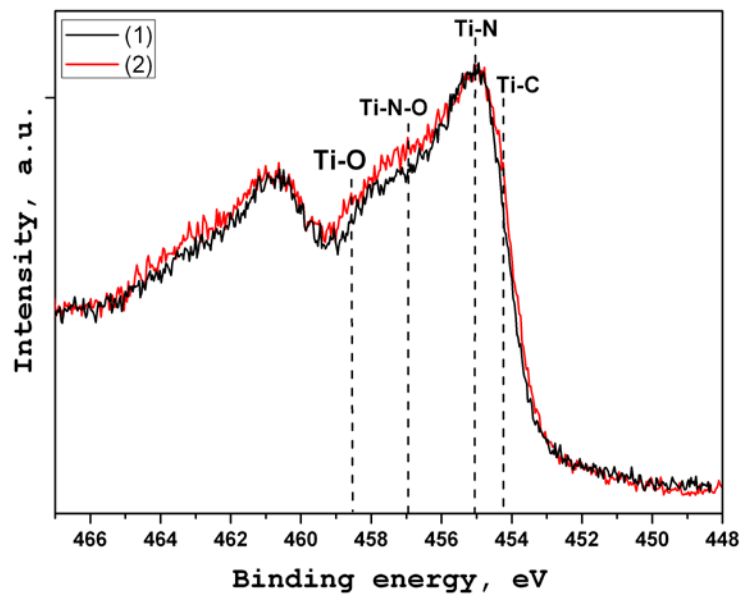
Therefore, in Tab. 2, we presented a superposition of oxygen and nitrogen concentrations. The analysis showed that the ratio of titanium to oxygen and nitrogen for coatings obtained on substrates of VK8 and 110G13L is slightly different. In the case of coating on VK8 the ratio [Ti]/([N]+[O]) = 0.6, while for coating on 110G13L – 0.9. Most likely, the low value of the [Ti]/([N]+[O]) ratio is due to the presence of a part of oxygen in bonds with carbon.

Table 2. Composition of coatings formed on various substrates according to EDX
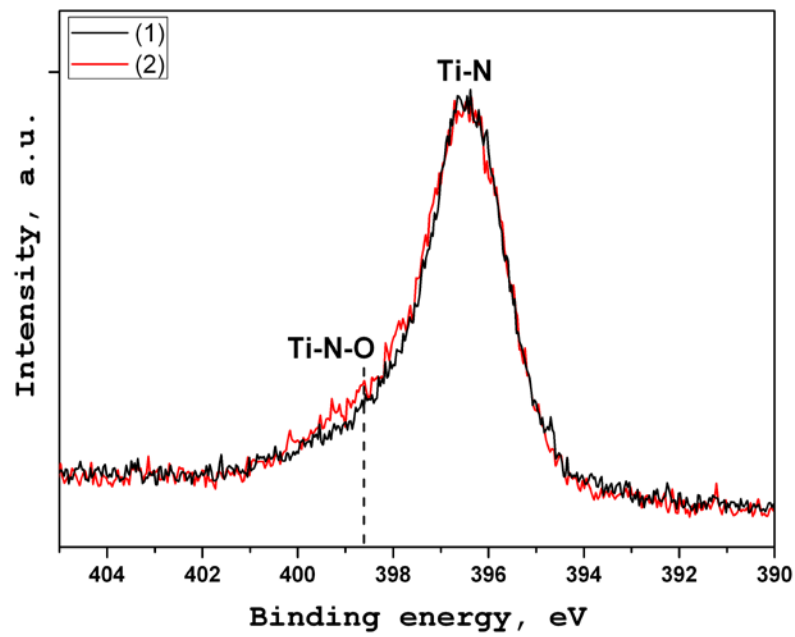
№ Point	Concentration, at.%						
	Coating on VK8						
	[C]	[N]+[O]	[Al]	[Ti]	[Co]	[W]	[Fe]
1	16.86	44.49	1.52	31.51	0.48	5.09	0.05
2	15.54	48.92	0.76	28.18	1.53	5.00	0.07
3	19.50	46.80	0.62	25.27	2.65	5.11	0.05
Mean	17.33	46.73	0.96	28.32	1.55	5.06	0.05
	Coating on 110G13L						
	[C]	[N]+[O]	[Al]	[Ti]	[Mn]	[Fe]	
1	12.18	39.54	0.68	39.56	1.54	6.49	
2	12.22	42.02	0.71	37.67	1.38	5.99	
3	12.66	41.55	0.73	37.42	1.31	6.33	
Mean	12.35	41.03	0.70	38.21	1.41	6.27	

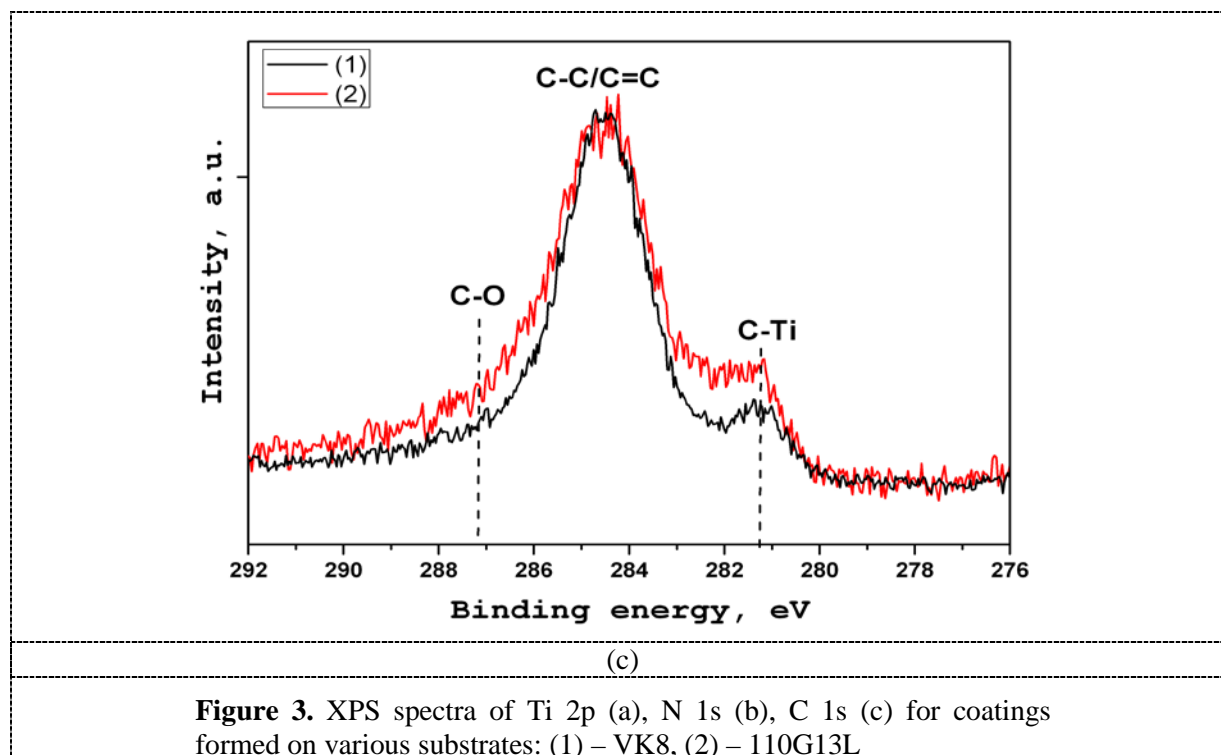*3.3. Analysis of coatings by XPS*

To study the chemical state of the coating elements, the XPS method was used. Figure 3 shows the XPS spectra of titanium, nitrogen, and carbon for coatings formed on various substrates. As can be seen from Fig. 3a, the chemical state of titanium on the coating surface is practically the same. However, for the coating on 110G13L, a slight increase in the signal intensity in the region of 456–458 eV is observed, which corresponds to the states of titanium oxynitride [6, 7]. An increase in the signal intensity in this region of the spectrum indicates the presence of a larger amount of titanium oxy nitrides in the coating on 110G13L than in the coating on VK8. This may be due to the fact that the process of coating formation is nonequilibrium. An analysis of the N 1s line (Fig. 3b) also shows a higher signal intensity from Ti-N-O in the region of high binding energies for the coating formed on 110G13L substrate. Moreover, the shape of the nitrogen spectra for both coatings is almost the same. To interpret the chemical state of carbon, the C 1s line was used. As can be seen (Fig. 3c), the carbon on the surface of the coatings is in three chemically nonequivalent states with maxima at the binding energies of ~ 281, ~ 284.5, ~ 287 eV, corresponding to carbon in Ti-C bonds, carbon-carbon bonds, and carbon in bonds with oxygen [4, 8]. The presence of C—C/C=C/C—H bonds is likely due to the presence of carbon in the form of amorphous inclusions. The presence of C—O groups on the surface of the coatings is due to the partially oxidized state of amorphous carbon. A comparison of the carbon spectra shows that in the coating formed on 110G13L, a higher value of the carbon intensity in Ti-C is observed. The decomposition of the spectra into components showed that the area of Ti-C in the coating on 110G13L is ~ 16%, while in the coating on VK8 it is ~ 12%. At the same time, taking into account the data of quantitative analysis, the carbon concentration in Ti-C for both coatings is almost identical and amounts to ~ 4.9 at.%.

(a)

(b)

(c)

Figure 3. XPS spectra of Ti 2p (a), N 1s (b), C 1s (c) for coatings
formed on various substrates: (1) – VK8, (2) – 110G13L

4. Conclusion

Using the SEM, XPS, and EDX methods, we studied the morphology, elemental composition, and chemical state of titanium nitride-based coating elements formed on substrates of VK8 sintered hard alloy and 110G13L steel using method the condensation with ion bombardment. Elemental and quantitative analysis performed using the XPS (thin surface layer) and EDX (bulk layers, including the upper layers of the substrates) methods showed that the composition of the coatings on the surface is practically the same, while the volume ratio of titanium to nitrogen and oxygen for coating on VK8 is reduced to 0.6, compared with the coating on steel 110G13L - 0.9. In addition, using the EDX method, it was shown that a small amount of aluminum is also present in the coating composition, the presence of which prevents the formation of a droplet phase of titanium metal. An analysis of the chemical state of the coatings showed that the bulk of titanium in the coatings is part of TiN. At the same time, oxynitrides and carbides titanium are present in the coatings.

Thus, the study of the morphology, elemental and chemical composition, as well as the chemical state of the coatings suggests that coatings formed on various substrates have a similar composition. The analysis showed that the application of the approach based on the use of data from non-destructive analysis methods obtained from various depths allows us to correctly study the composition of coatings based on titanium nitride. It is shown that the morphology of coatings formed on various substrates is somewhat different. Therefore, under identical conditions for the formation of coatings, their mechanisms are noticeably different. This allows us to conclude that, by varying the type of substrate, it is possible to control the morphology of the formed coating.

At the same time, the presence and distribution of titanium carbides and oxynitrides in coatings requires further study, since they can significantly affect the performance of coatings.

Acknowledgement

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