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Abstract. Structural and phase researches of the multicomponent nanocrystalline coatings synthesized by plasma-assisted vacuum arc method at high-temperature influence by method of X-ray diffraction with the use of synchrotron radiation *in situ* have been carried out. The main features of these coatings are the superhardness (39 – 45 GPa) and nanocrystalline structure (5 – 20 nm). The analysis of results of structural and phase researches, physical and mechanical characteristics after oxidation of multicomponent nitride coatings at high-temperature heating in open air is presented.

1. Introduction

Despite existence of a large amount of materials with various element composition, within technical progress of the modern industry, new materials and coatings with unique service properties are required constantly. Their preparation is one of the actual technical problems today.

It should be noted, that in many cases, the creation of product made of expensive materials is not economically beneficial, and the formation of thin modified layer or a coating with the required physical and mechanical characteristics on their working surface is more preferably. That provides long service life and high service properties of the products.

In this case multicomponent nanocrystalline coatings based on transitional metals with unique characteristics is peculiar such as super- and ultrahardness (40 – 100 GPa) [1, 2], low friction coefficient (≤ 0.2) [3], high degree of elastic recovery (80 – 94%), elastic deformation more than 10%, high tensile strength of 10 - 40 GPa [4], high thermal stability (up to 1700 ºC) [5], resistance to oxidation at high temperatures (> 1000 °C) [6, 7] possess great potential opportunities. One of striking examples – multicomponent nitride coatings based on traditional binary TiN system with addition of such elements, as Si, Al, Cu, Cr, etc. in its composition [4].

Multicomponent thin (up to 5 μm) coatings based on titanium nitride with additional elements, such as Ti-Cu-N, Ti-Si-N, Ti-Al-N, Ti-Cr-N [8 – 11] were the objects of researches in this work. These coatings were developed and obtained in Institute of high current electronics SB RAS (Russia, Tomsk) on the modern automated plasma-ion equipment for the vacuum- arc plasma-assisted deposition [11 – 12]. The synthesized coatings possess nanocrystalline structure (d = 5 - 30 nm), high hardness (up to 50

GPa), low friction coefficient (≤ 0.3), high wear resistance (in 2 - 3 times higher, than that of traditional TiN coatings), and etc. It should be noted that such superhard wear-resistant coatings are used for hardening and increase of service life of the cutting and other tools, details and products. And during operation the temperature of a working surface can increases to ≥ 600 °C (it is critical temperature for binary TiN coatings) that in turn can lead to intensive corrosion and destruction, both coatings, and the products surface protected by them. Therefore, the reveal of regularities of nanostructured coatings stability at high-temperature influence gains special relevance, both with practical, and from the fundamental point of view.

The purpose of this work was carrying out *ex situ* researches of resistance of multicomponent coatings based on titanium nitride with various additional elements to oxidation at high-temperature heating in open air by methods of modern materials science (physical and mechanical characteristics, structural and phase composition), and also *in situ* research by methods of X-ray diffraction analysis with the use of synchrotron radiation. And, in particular, that is reveal of critical temperature at which there are an essential structural and phase changes of coatings, and their degradation and destruction.

2. Equipment and procedures

The deposition of thin (3 – 5 μm) multicomponent nanocrystalline coatings based on titanium nitride was carried out on the unique automated vacuum plasma-ion QUINTA installation developed in Institute of high current electronics SB RAS [12] with the following key parameters: dimension of a vacuum chamber: 750 × 600 × 600 mm^3; working pressure: 10^{-1} – 1 Pa; negative bias voltage: up to 1000 V; arc current of gas-plasma source PINK: up to 250 A; arc current of standard arc evaporator: up to 150 A; arc current of gas-plasma PINK-P-0.4M source: up to 150 A; arc current of DI400 arc evaporator: up to 200 A [13 – 15]. The installation is completely automated for the purpose of exact reproducibility of complex technological processes and equipped with five plasma sources – three arc evaporators (sources of metal plasma based on arc discharge with a cathode spot) and two plasma sources based on non-self-sustained arc discharge with filament and hollow cathode (sources of gas-discharge plasma PINK). It allows varying elemental structure of coatings at using few cathodes of different composition or it is essential to reduce the duration of experiments at using few identical cathodes. Besides, existence of gas-discharge plasma sources allows carrying out the process of coating condensation in the mode of plasma assistance. That promotes the formation fine structure (with a size of crystallites up to ~ 1 – 10 nm) dense composite coatings with good adhesion to the substrate.

The composite sintered cathodes of Ti-Cu, Ti-Si, Ti-Al, Ti-Cr systems obtained by the methods of powder metallurgy [16, 17] were used as material of the evaporated cathodes. The specimens made of hard alloy (WC-8%Co) which were polished on diamond paste to roughness R_a = 0.02 μm were used as substrates. The synthesis of multicomponent coatings was carried out in the range of following values of parameters: bias voltage U_b = - (100 ÷ 300) V; working gas pressure p = (0.3 ÷ 0.4) Pa; arc current of evaporator I_d = (50 ÷ 100) A; specimen temperature T = (300 ÷ 400) °C. Thickness of coatings was 3 – 5 μm at coating deposition rate of 1 – 3 μm/h.

It should be noted that at first the coating resistance to oxidation was checked *ex situ* after temperature influence. For this purpose the specimens with coatings were heated in the muffle SNOL-1,6.2,5.1/11-I2 furnace at temperatures of 300, 400, 500 and 800°C in the air atmosphere. The rate of specimen temperature increase was 10 °/min. After endurance of the specimens at a certain temperature within 20 min, these were cooled in furnace volume to room temperature during several hours.

The research of the synthesized coatings before and after thermal influence was carried out by optical microscopy (metallographic microvizor μVizo-MET-221), an optical profilometry (micro-nano-profilometer MNP-1), the scanning electron microscopy and the micro X-ray spectral analysis (scanning electron microscope Philips SEM-515 with the EDAX Genesis XM 260 SEM microanalyzer), the X-ray diffraction analysis (X-ray diffractometer Shimadzu XRD 6000), micro- and nanoindentation (PMT-3 microhardness tester and the Nano Hardness Tester NHT-S-AX-000X). The researches of structural and phase composition were carried out at stations of powder diffraction on channels of the synchrotron radiation (SR) of the VEPP-3 (Siberian Synchrotron and Terahertz Radiation Centre, Budker Institute

of Nuclear Physics (BINP), Russia, Novosibirsk) [18] and by the method of transmission electron microscopy (JEOL JEM-2100 F).

In situ experiments on research of coating resistance to oxidation at high-temperature heating in open air were carried out at the "Precision diffractometry and anomalous scattering" located on the 6th channel of synchrotron radiation extraction of the electron store VEPP-3 with the use of the high-temperature X-ray camera of the XRK-900 reactor and the position sensitive parallax-free detector OD-3M350 [19] of production BINP SB RAS. The detector allows to register X-ray pattern in the range of ~ 30 ° (range 2θ = 33.5 ÷ 64.5 ° was chosen here) with discretization ~ 0.01 °, and the record duration of one diffraction pattern is about 3 s. The fixed wavelength of 1.7135 Å was set by single reflection of radiation from a crystal of Ge (111) monochromator, and was determined by a diffraction pattern of α-Al_2O_3 standard (NIST SRM 676). In the required range of angles, the X-ray diffraction pattern of the standard was registered. According that the graduation of the detector was carried out. Further measurements were carried out at a standard position of the detector. The element composition of coatings was investigated by the method of Auger spectroscopy (Auger-electron spectrometer "Schooner-2").

3. Results and discussion

After thermal influence at a certain temperature in open air the condition of specimens was fixed by means of camera and optical microscopy. After thermal influence in air at temperature of ≈ 800 ºC all coatings lost the initial color and became dark gray. Besides new formations are revealed on a surface in comparison with an initial surface (Fig. 1). At endurance of the specimens at intermediate temperatures visible changes on a surface were not observed by an optical microscope for all coatings except Ti-Si-N. The oxidation of Ti-Si-N coating surface begins already at temperature of 500 °C. On the other hand, for other coatings the degradation of properties and destruction due to oxidation takes place at higher temperatures. These conclusions are confirmed by the results of surface roughness measurements (Table 1). The values of Ti-Si-N roughness start increasing at T ≈ 500 °C, in the case of TiN and Ti-Cu-N coatings the changes occur only at T ≈ 800 °C.

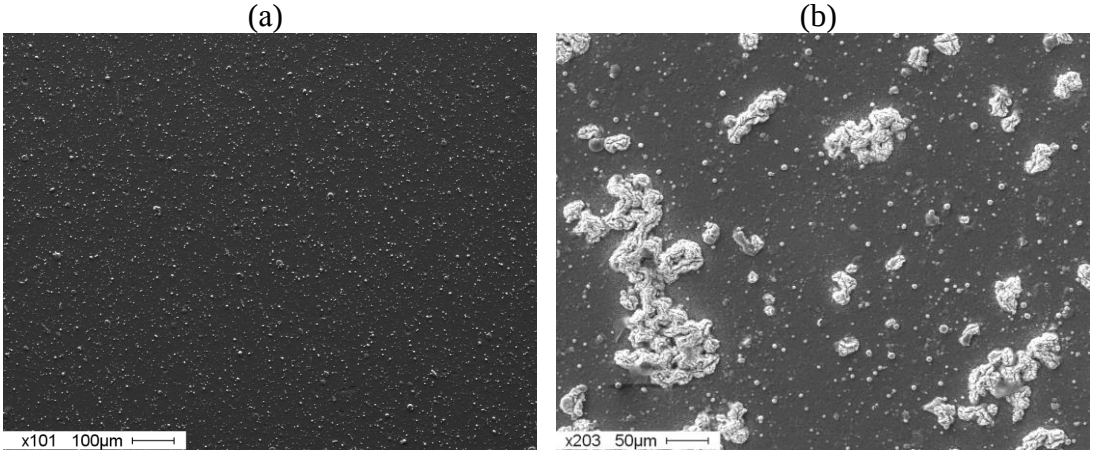

Figure 1. SEM images of specimen with deposited Ti-Cu-N coatings before (a) and after (b) high-temperature oxidation in open air at temperature of 850-850 ºC.

Table 1. Microhardness *H* and roughness R_a of the coatings before and after thermal influence in open air.

T, ºC	*H*, GPa	R_a, µm

	TiN	Ti-Cu-N	TiN	Ti-Cu-N
initial	27.6	44.8	0.4	0.4
300	32.4	43.9	0.4	0.4
400	33.8	46.9	0.5	0.4
500	38.0	48.2	0.5	0.5
800	28.1	20.4	1.0	0.8

In the Table 1 there is hardness of TiN and Ti-Cu-N coatings depending on influence temperature. It is clear that the hardness slightly increases in both cases up to 500 °C, and at achievement of T ≈ 800 °C sharply fall to the substrate hardness. That confirms full coating degradation about this temperature. All above results of researches specify that critical temperature for Ti-Si-N coatings corresponds to temperature ≈ 500 °C; for other coatings – about 800 °C.

The structural researches confirming these assumptions which are carried out by X-ray diffraction analysis are given in Fig. 2. It is clear that besides reflexes from TiN coating and a substrate the set of reflexes, such as TiO_2, WO_3, $CoWO_4$, and some reflexes which identification is complicated because of imposing, appear after thermal influence at temperature ≈ 800 °C on X-ray diffraction pattern.

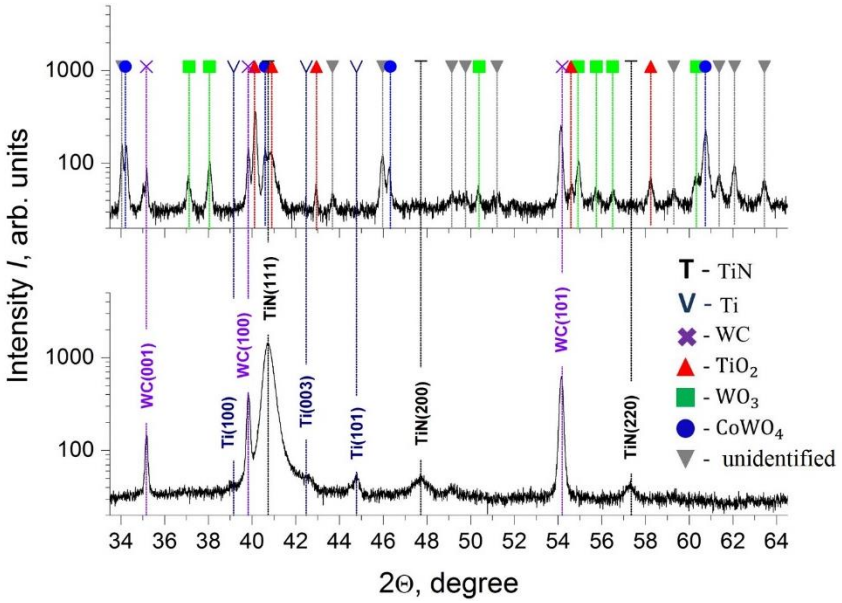

Figure 2. Diffraction pattern of a Ti–Cu–N coating before and after thermal influence in open air up to 850 °C (logarithmic scale).

In situ X-ray diffraction researches of coatings revealed that destruction of nitride phases happens not at a time (Fig. 3, 4; Table 2). The intensity of reflexes from nitride phases at some critical temperature (T_1, usually about 700 °C) starts decreasing, and they completely disappear at higher temperature which is in range of 800-850 °C for coatings based on TiN with various additional elements. Along with the decrease of the intensity of nitride phase reflexes and their disappearance, the emergence of oxides

reflexes based on coating elements (for example, TiO_2), and that based on substrate elements is observed (for example, WO_3, $CoWO_4$). And, at achievement of some second critical temperature (T_2) which is higher or it is equal about 800 °C, all reflexes of nitride phases disappear, and only reflexes of oxide compounds and reflexes of substrate (Fig. 4) are observed.

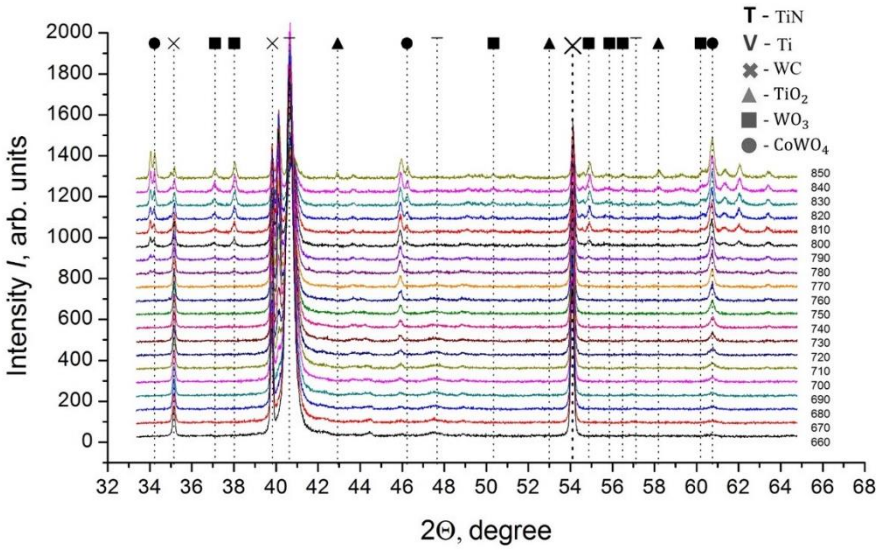

Figure 3. Diffraction pattern of a Ti–Cu–N coating at *in situ* thermal influence in open air up to 850 °C (660-850 °C).

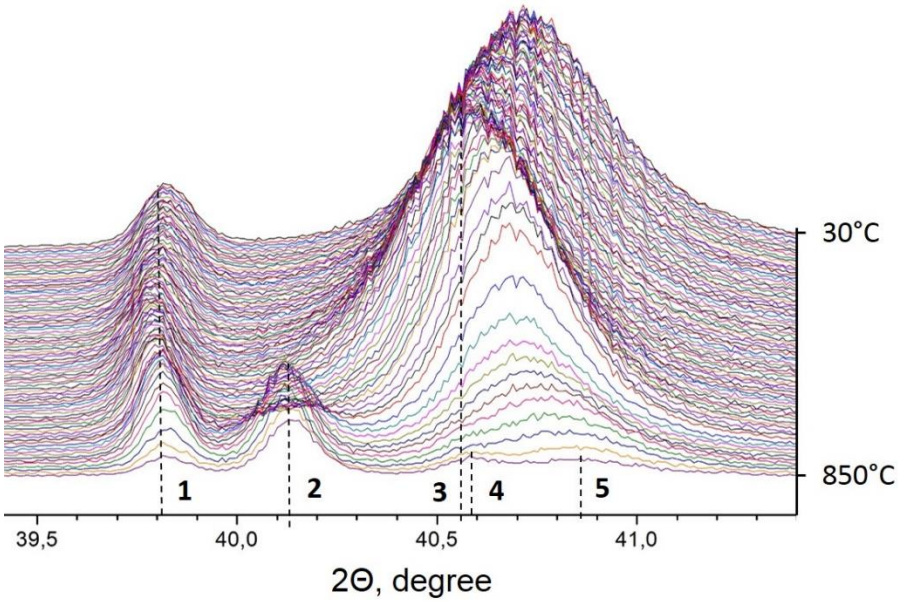

Figure 4. Diffraction pattern (2θ = 39.4 – 41.4 º) of a Ti–Cu–N coating at *in situ* thermal influence in open air up to 850 °C (30 – 850 °C, inverse temperature dependence): 1 – WC; 2 – TiO_2; 3 – TiN; 4 – WO_3; 5 – TiO_2.

The investigations of element composition (by Auger spectroscopy, Fig. 5) of coatings after high-temperature heating in open air completely confirm the conclusions based on the X-ray diffraction *in situ* researches. Namely, at achievement of the second critical temperature (T_2) which for coatings on

the basis of TiN with various additional elements is in the range of 800-850 °C (Table 2), there is a full removal of nitrogen from surface layer of coating/substrate system, and the oxygen concentration (≈ 50 at. %) in the layer is caused by formation of oxide compounds based on elements of the destroyed coating and substrate elements.

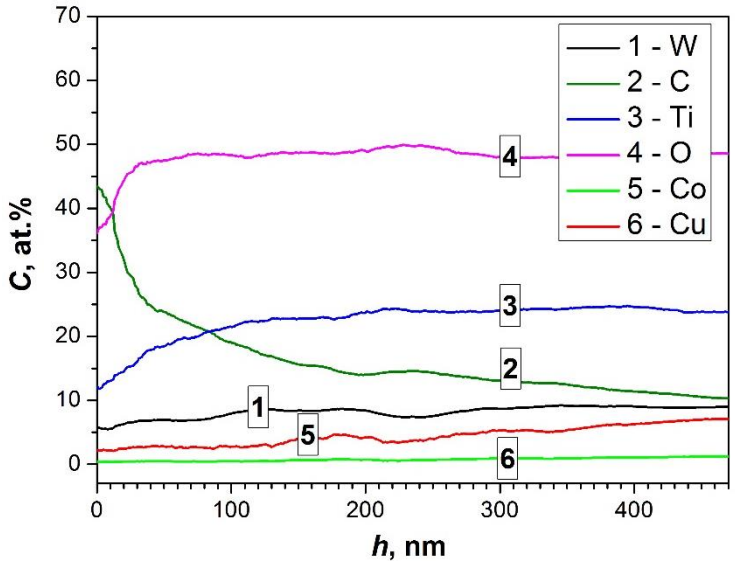

Figure 5. Distribution of element concentration (*C*) in the depth (*h*) of Ti-Cu-N coating deposited on WC-Co substrate after *in situ* high temperature oxidation up to 850 ºC (Auger electron spectroscopy)

Table 2. The main quantity changes in phase-structural composition of Ti-Cu-N, Ti-Si-N, Ti-Cr-N, Ti-Al-N coatings.

	Specimen temperature *T*, °C			
	Ti-Cu-N	Ti-Cr-N	Ti-Al-N	Ti-Si-N
Decrease of TiN (111) reflex intensity	750	730	750	760
Disappearance of TiN (111) reflex	840	850	850	820
Disappearance of TiN (200) reflex	740	830	750	730
Disappearance of TiN (220) reflex	310	-	-	850
Appearance of TiO_2 reflexes	720	800	850	720
Appearance of WO_3, $CoWO_4$ reflexes	780	800	820	750

4. Conclusion

The researches and the analysis of the results on thermal oxidation of multicomponent nanocrystalline coatings based on titanium nitride were carried out. *In situ* X-ray diffraction diagnostics of multicomponent coatings at high-temperature heating (up to 850 °C) are revealed that destruction of nitride phases happens not at a time. The intensity of nitride phases reflexes at $T \approx 700$ °C (T_1) starts decreasing, and they completely disappeared at higher temperature (800 – 850 °C). Along with that, the emergence of reflexes from oxide compounds of coating and substrate elements is observed (TiO_2, WO_3, $CoWO_4$, etc.). At achievement of some second critical temperature (T_2) all reflexes from nitride phases disappeared. Thus by the results of the element analysis there is a full removal of nitrogen from surface layer of coating/substrate system, and the concentration of oxygen reaches ≈ 50 at. %.

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References
[1] Veprek S *et al* 2005 *Thin Solid Films* **476** 1
[2] Musil J 2000 *Surf. Coat. Technol*. **125** 322
[3] Musil J *et al* 2010 *J. Vac. Sci. Technol.* A **28** (2) 244
[4] Cavaleiro A and Hosson J T D 2006 *Nanostructure Coatings* (Springer Science+Business Media, LLC)
[5] Zeman P *et al* 2010 *Thin Solid Films* **519** 306
[6] PalDey S *et al* 2003 *Mater. Sci. Eng.* A **361** 1
[7] Musil J *et al* 2008 *Adv. Appl. Ceram.* **107** 148
[8] Ivanov Yu F *et al* 2012 *Surf. Coat. Technol.* **207** 430
[9] Koval N N *et al* 2007 *Russ. Phys. J.* **50** 146
[10] Krysina O V *et al* 2013 *High Temperature Material Processes* **17** (2–3) 153
[11] Koval N N *et al* 2015 *Russian Journal of General Chemistry* **85** (5) 1326
[12] Kalushevich A A *et al* 2012 *Izvestiya vuzov. Fizika* **55** (12/3) 118
[13] Vintizenko L G *et al* 2001 *Russ. Phys. J.* **44** 927
[14] Shugurov V V *et al* 2010 *Proc. 10th Intern. Conf. on Modification of Materials with Particle Beams and Plasma Flows* (Tomsk, Russia) 49
[15] Koval N N *et al* 2012 *Proceedings of the 25th International Symposium on Discharges and Electrical Insulation in Vacuum* (Tomsk, Russia) **2** 537
[16] Krysina O V *et al* 2013 *High Temperature Material Processes* **17** (2–3) 145
[17] Korosteleva E N *et al* 2009 *Powder Metallurgy and Metal Ceramics* **48** (1) 8
[18] http://ssrc.inp.nsk.su/CKP/beamlines.html
[19] Aulchenko V M *et al* 2009 *Nucl. Instrum. Methods. Phys. Res.* A **603** 76