STRUCTURAL STABILITY OF Ti-N AND Zr-N COATINGS AT EMISSION TESTS IN MODE OF PULSES

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In this work, stability of titanium and zirconium nitride coatings deposited on steel and molybdenum was studied. The phase composition of nitride coatings was studied by X-ray method before and after emission testing in the nanosecond range of pulses. It was noted that before the testing, the titanium nitride coating was a successive alternation of α-Ti, Ti_2N, and TiN layers. After the testing, titanium was transformed into the β-phase (bcc), nitrogen was partially evaporated, and a new phase, presumably Ti_3N, with a tetragonal lattice was formed in a significant content. The Zr-N coating, obtained in the form of zirconium mono-nitride, showed structural stability during testing.

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INTRODUCTION

At present, in some areas of physics and technology, there are a number of special physical and technical tasks associated with production of electron beams. Electron beams are used in vacuum, electronic and X-ray technology, in nuclear physics, in the processing of materials or their surfaces, in the production of pure metals, etc. Some scientific and technical problems in obtaining electron beams are associated with an increase of the emissivity of cathodes. In this regard, field-emission cathodes, which made of metal substrates coated with a monomolecular layer of an electropositive material, are of interest because reducing their work function. These elements include barium, cesium, cerium, thorium, etc. As a result, a double (bipolar) electric layer is formed on the working surface of cathodes. If the work function of electron in metal is greater than the ionization potential of adsorbed atoms, then these atoms donate their valence electrons to the metal base and turn to positively charged ions. This causes the outer side of the electrical double layer on the metal surface to become positively charged. If the ionization potential of atoms deposited on metal is greater than the work function of electron in the metal, then these atoms are in the state of dipoles, which also form a double electric layer, the outer side of which is positively charged. In general, this decreases the work function of electrons in the surface of the cathodes.

Such coatings are usually deposited in a thin layer. However, this may not be sufficient for increased cathode service life. For in this case, such a resource can remain low even with a decrease in the threshold voltage. In the present work, studies have been carried out to determine the stability of nitride coatings in metal-nitride Ti-N and Zr-N coating systems with a thickness of several microns.

1. METHODS FOR OBTAINING AND INVESTIGATION OF COATINGS

Deposition of coatings from titanium and zirconium nitrides was carried out by the ion-plasma method on cylindrical cathodes made of austenitic stainless steel of the X12CrNiTi18-10 type (12Cr18Ni10Ti Rus.; is an analog of American AISI 321) with a diameter and a length of 100 mm. Simultaneously with the deposition on cylindrical cathodes, deposition of the coatings was carried out on witness samples in the form of a ferritic stainless steel plate 20×20 mm in size. On them, X-ray studies of the original structural-phase composition of the coatings were carried out. A zirconium nitride coating was also deposited on a copper cathode preliminarily coated with a molybdenum sub-layer. Before the deposition of molybdenum on the outer cylindrical surface of the cathode substrate, a screw-thread with a depth of 0.5…1.2 mm and a width of 0.5…1.2 mm was cut with a blade method. As a result, the width of the protrusions was 0.5...1.0 mm.

Before deposition of nitride coatings, ion-plasma cleaning of the surface of cathode substrates and witness samples was carried out. To do this, the bias potential on the cathode substrate was raised stepwise for 50 min every -100 to -1000 V. When -1000 V was reached, this was held for 10 min and then the bias potential was reduced to -300 V. Nitrogen was supplied to the chamber, and pressure in the reaction volume was adjusted from 10^{-6} to $5 \cdot 10^{-3}$ mm Hg during 15 min. The deposition of titanium nitride or zirconium nitride coating was carried out for 1 h. This mode of coating deposition promoted to an increase in coating adhesion and a decrease in the droplet component on the growing surface of the coating. Nitride coatings were deposited on the Bulat-6 ion-plasma installation. To deposit zirconium nitride, the Zr-1%Nb alloy was used as a cathode material in the Bulat-6 installation; to deposit titanium nitride, T1-grade titanium was used. The arc-discharge current in the plasma source was 100 A.

The appearance of the coated cathode is shown in Fig. 1.

Using a JEM scanning electron microscope, we studied the elemental composition on the surface of the coatings deposited on the witness samples. No impurities were found in the composition of the coatings. The content of niobium impurity in zirconium nitride is possible. The research results are shown in Table 1.

Fig. 1. A sample of a copper cathode coated with zirconium nitride and an intermediate layer of molybdenum

Table 1

Elemental composition
on the surface of the coatings of witness samples

Coating	Element	wt.%	at.%
Ti-N	N	22.6	50
	Ti	77.4	50
Zr-N	N	11.97	47
	Zr	88.03	53

It follows from Table 1 that the compositions on the surface of coatings made of zirconium and titanium nitrides are close to stoichiometric norms. From this, it follows that the coatings have metallic conductivity.

Nitride-coated cathodes were tested using a powerful S-band pulsed microwave generator with a gigawatt radiation level. At the time of generator working, a voltage pulse with amplitude of 500 kV and duration of 80 ns was applied to an anode-cathode gap of 11 mm. The operating pressure in the generator when working in the mode of single pulses, as well as when working in the mode of a series of pulses with a 5 Hz repetition rate, was $6 \cdot 10^{-4}$ Pa.

For research the coatings after testing, samples were cut out of these cathodes.

The study of the structural and phase composition of the coatings was carried out by the method of X-ray diffraction phase analysis. Measurements were carried out on DRON4-07 X-ray diffractometer with a proportional counter, in CuK_α radiation and using the pair of Soller slits.

In addition to phase identification, a semi-quantitative analysis of the phase composition of the coatings has been carried out. Calculation of the molar content of the phase components of the coating was carried out on the basis of the following formula:

$$C_j = \frac{1}{v_j} \sum_i \frac{I_{ji}}{P(\theta_{ji}) f_j^2(s_{ji})} x$$

$$\left[P(\theta) = \frac{1 + \cos^2 2\theta}{2}; \ s = \frac{\sin \theta}{\lambda} \right], \quad (1)$$

where for the j-th component, I_{ji} is the integral intensity of the i-th line with reflection angle θ_{ji}; P is the radiation polarization factor; f_j is the form factor of the electron cloud of one j-metal atom (atomic reflection factor; tables of $f_j(s)$ are exist [1]); λ is the radiation wavelength (CuK_α). The molar content of the components was determined as $c_j = C_j / \Sigma C_k$.

Due to the specifics of the work, the semi-quantitative analysis was reduced to calculating the thickness of the layers of the corresponding compounds. This was done by taking into account the absorption coefficients of X-rays for the chemical elements included in the coatings [1].

2. RESULTS AND DISCUSSION

Ti-N coating. The phase analysis of the original state of the coating showed the presence in it of α-Ti (hcp structure) and nitrides – they are Ti_2N of a tetragonal structure and TiN with the fcc lattice. According to the deposition technology, pure titanium was deposited directly on the substrate. Then a mixture of titanium and nitrogen was deposited. Thus, TiN represented the outer layer of the coating, and the Ti_2N compound played the role of an interlayer between the layers of titanium and its mono-nitride.

Fig. 2 shows an X-ray diagram with the result of identifying the phases of the original Ti-N condensate on a ferritic stainless steel substrate with bcc structure.
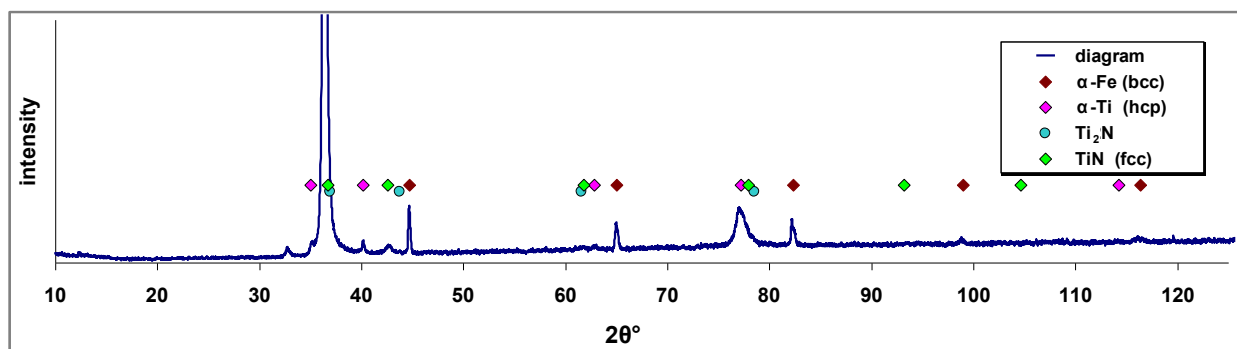

Fig. 2. X-ray diagram of the original Ti-N condensate with a ferritic steel substrate (α-Fe structure)

Table 2
Structure, lattice periods, and composition of the
original Ti-N coating with a steel substrate
in their alternation sequence

	α-Fe* (bcc)	α-Ti (hcp)	Ti₂N (th.)	TiN (fcc)
a, nm	0.2869	0.296	0.414	0.4246
c, nm	–	0.468	0.880	–
Δt, μm	–	0.5…1.0	0.4…0.8	2.5…3.5

*Substrate material.

Table 2 shows the parameters of the crystal structure of the substrate and components of the original Ti-N coating with the thickness Δt of their layers.

Fig. 3 shows a diagram of the Ti-N condensate after testing it as a coating on a cathode made of austenitic stainless steel (fcc).
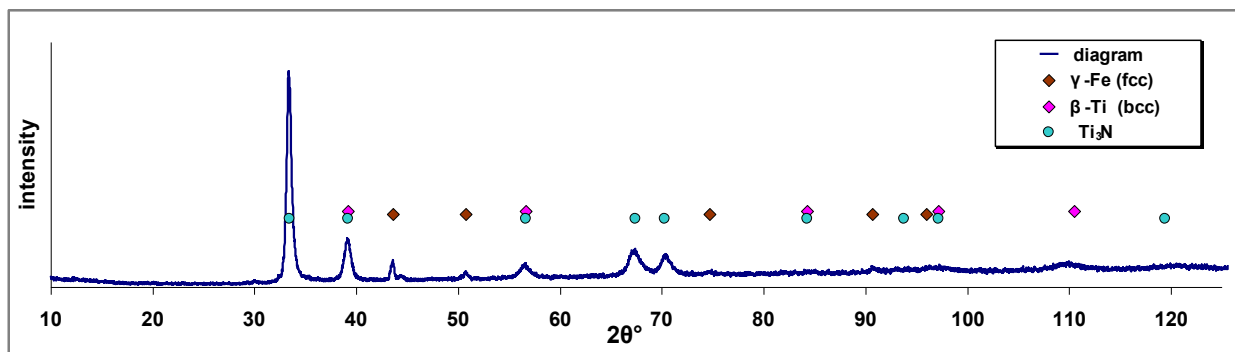

*Fig. 3. X-ray diagram after testing the Ti-N coating
with an austenitic stainless steel substrate (cathode material; γ-Fe structure)*

According to Fig. 3, after testing, the structural-phase state of the Ti-N coating has drastically changed. In particular, this was expressed in the fact that under this test mode, titanium was completely transformed into a high-temperature β-phase with the bcc structure. This structure is distinguished by a reduced lattice period a (Table 3; for pure bcc titanium, $a_0 = 0.3287$ nm [2]). It is assumed that this structure is a solution of up to 9 at.% chromium and iron. In turn, titanium in a content of ~ 2.5 at.% was dissolved into the γ-iron substrate. Traces of transformation of γ-iron into α-Fe are noted at the substrate boundary (see Fig. 3; angle 44.5°).

Significant changes in the state of the Ti-N coating as a whole expressed in the fact that, after testing, titanium nitrides with the previous structure practically disappeared from the coating, and a previously unknown phase formed in it in a significant content. Presumably, it is Ti₃N with a tetragonal lattice. In combination with data on the composition and all structures of the coating (and the substrate) after the testing, Table 3 presents its crystallographic identification by interplanar distances d, calculated on the reflection angles of lines. The nature of the intensity distribution in Fig. 3 and considerations regarding nitrogen migration give grounds to believe that the Ti₃N type compound, formed after testing the coating, was localized in its outer layer.

Table 3
Structure, lattice periods (a, c), interplanar spacings (d) of the Ti-N coating, and thickness Δt of layers
of its components in their alternation sequence. They are data after testing the cathode based on austenitic steel

	γ-Fe* (fcc)	β-Ti (bcc)	Ti₃N (th.)			γ-Fe* (fcc)	β-Ti (bcc)	Ti₃N (th.)	
a, nm c, nm	0.3593	0.326	0.324 0.535		Δt, μm	–	3.5…4.5	2.0…3.0	
d_{exp}, nm	(hkl)	(hkl)	(hkl)	d_{cal}, nm	d_{exp}, nm	(hkl)	(hkl)	(hkl)	d_{calc}, nm
0.2669			(002)	0.2676	0.1140		(220)	(220)	0.115
0.2289		(110)	(110)	0.23	0.1083	(311)			0.1083
0.2072	(111)			0.2075	0.1056			(222)	0.1053
0.2030	α-Fe				0.1037	(222)			0.1037
0.1797	(200)			0.1797	0.1028		(310)	(310)	0.103
0.1623		(200)	(200)	0.1625	0.1021	α-Fe			
0.1392			(202)	0.1386	0.0941		(222)		0.0941
0.1336			(004)	0.1338	0.0899	(400)			0.0898
0.1269	(220)			0.1270	0.0882			(321)	0.0886

*Substrate material.

Ti₃N phase exhibits a certain similarity to bcc titanium, coinciding with it in period a (see Table 3).

Such a coincidence may be the result of high-speed transformations of the bcc lattice, in which the crystal

structure may not be completely transformed and, as a result, inherit coherence and some elements of similarity. When refining the cell size of this phase, the principle of integer filling of its crystal cell was used. As a result, this cell is defined in such a way that three titanium atoms fit into it with a small remainder of the volume.

Zr-N coating. The original state of the Zr-N coating after its deposition on a substrate made of ferritic steel (bcc structure of α-Fe) has been studied. After the tests, the condensate deposited on the cathode of the X12CrNiTi18-10 steel (fcc), as well as the same condensate on the copper cathode preliminarily coated with a molybdenum layer, was studied. Fig. 4 shows the corresponding X-ray diagrams with reflection identification. In all cases, pure zirconium (without nitrogen) was practically not found.
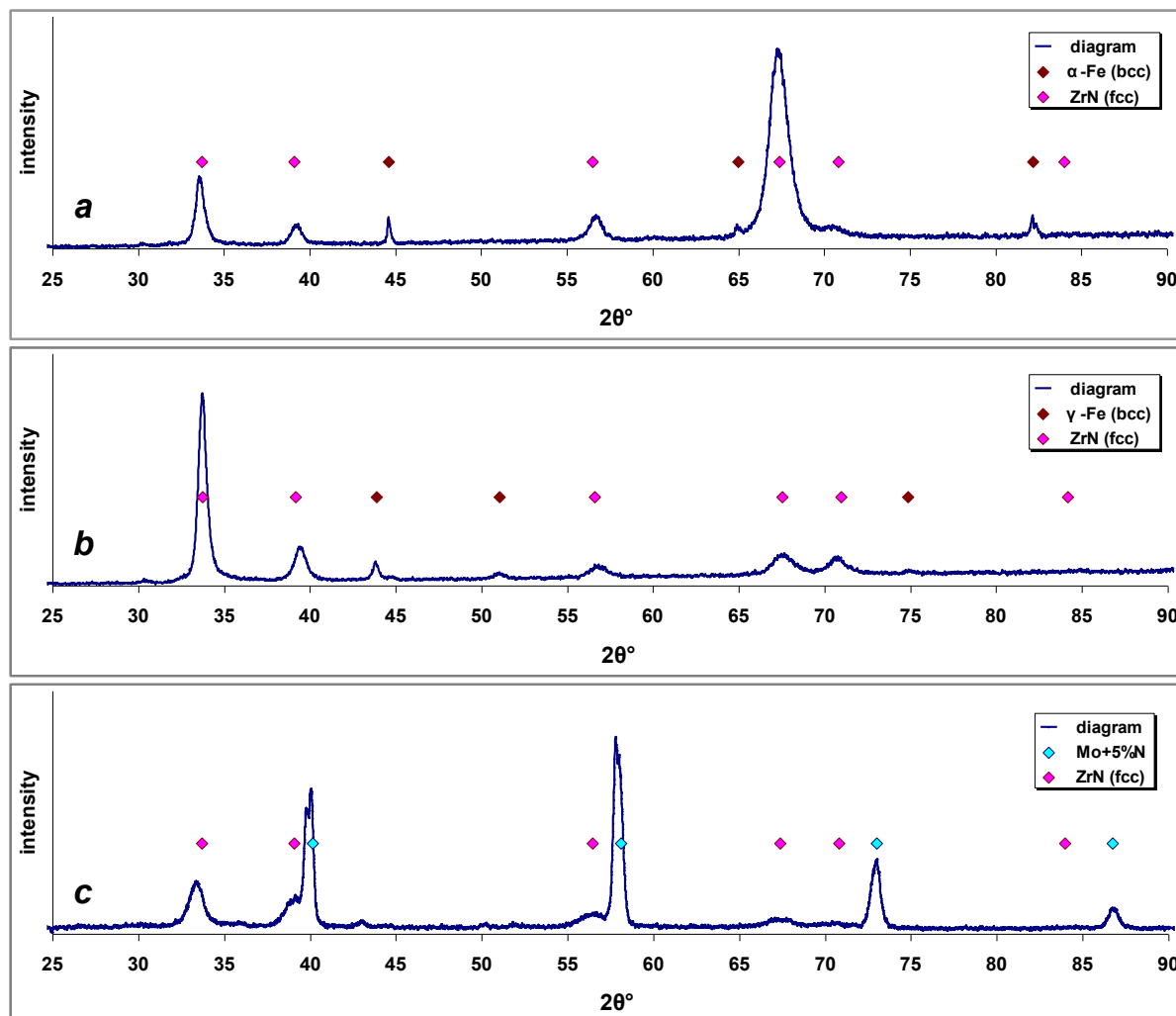

Fig. 4. X-ray diagrams of Zr-N coating on steel substrate of α-Fe (a) and γ-Fe (b) structure, as well as on copper cathode with Mo layer (c) – before tests (a) and after tests (b, c)

Table 4 shows data on the structure and composition of the studied materials before and after testing.

Table 4

Structure and thicknesses of Zr-N coating on steel substrate and cathodes

Material	Without testing		After testing		
	ferr. steel* (bcc)	coating ZrN (fcc)	aust. steel* (fcc)	–	coating ZrN (fcc)
a, nm	0.2871	0.461	0.3576	–	0.460
Δt, µm	–	2.0…3.0	–	–	3.5…6.5
material	–	–	Cu* (fcc)	interlayer Mo (bcc)	coating ZrN (fcc)
a, nm	–	–	0.3639	0.3175	0.461
Δt, µm	–	–	–	4.5…6.0	1.0…2.0

*Substrate material.

According to Table 4 data, at the boundary with the molybdenum interlayer, the increased lattice period of the copper base of the cathode (for pure copper, $a_o = 0.3615$ nm [2]) indicates the dissolution of 6 at.% molybdenum into it. The increased lattice period of the molybdenum interlayer (for pure molybdenum, $a_o = 0.3147$ nm [2]) gives grounds to believe that at least 5 at.% nitrogen was dissolved into the interlayer.

By their combination, the data in Table 4 fundamentally differ from the results for Ti-N coatings (see Tables 2, 3). In the first case, titanium nitrides, as well as titanium itself, turn out to be structurally unstable to pulse tests in the nanosecond range. Under such a test mode, the phase $\alpha \leftrightarrow \beta$ transition ($t_t° = 885$ °C) actually works up in titanium. As for zirconium, its phase-transition temperature, $t_t° = 862$ °C, differs little from titanium. Meanwhile, unlike titanium nitride, zirconium nitride turned out to be highly resistant to testing. A significant role in this is seen in the increased atomic mass of zirconium: A = 91.22, whereas for titanium A = 47.9.

CONCLUSIONS

The ion-plasma method was used to obtain Ti-N and Zr-N coatings deposited on cathodes and witness samples made of stainless steel. The Zr-N coating was also deposited on a molybdenum layer previously deposited on the copper cathode. Titanium nitride coatings consisted of alternating layers of α-Ti (hcp structure), Ti_2N with a tetragonal lattice, and TiN with fcc lattice. Zirconium nitride coatings were formed in the form of a mono-nitride with fcc structure. During emission tests by series of pulses with a load of 500 kV and a duration of 80 ns, titanium nitride coatings showed stoichiometric and structural instability. Unlike it, zirconium nitride coatings showed stability.

We suppose to obtain zirconium nitride with the composition Zr_3N_4 and test it under similar conditions.

REFERENCES

1. L.I. Mirkin. *Handbook of X-ray diffraction analysis of polycrystals*. M.: "Gos. izd. fiz.-mat. lit.", 1961, 864 p. (in Russian).
2. G.V. Samsonov. *Properties of elements. Reference guide. Part I: Physical properties.* M.: "Metallurgy", II ed., 1976, 599 p.

СТРУКТУРНА СТІЙКІСТЬ ПОКРИТТІВ Ti-N І Zr-N ПРИ ЕМІСІЙНИХ ВИПРОБУВАННЯХ В ІМПУЛЬСНОМУ РЕЖИМІ

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Досліджено стійкість нітридних титанових та цирконієвих покриттів, осаджених на сталь і молібден. Рентгенівським методом досліджено фазовий склад нітридних покриттів до та після емісійних випробувань у наносекундному імпульсному діапазоні. Зазначено, що до випробувань покриття з нітриду титану є послідовним чергуванням шарів α-Ti, Ti_2N і TiN. Після випробувань титан перетворився на β-фазу (ОЦК), азот частково випарувався, і в значному вмісті сформувалася нова фаза з тетрагональною решіткою – імовірно Ti_3N. Покриття Zr-N отримано у вигляді мононітриду цирконію, який у процесі випробувань виявив структурну стійкість.