

Influence of deposition conditions on structure parameters and mechanical properties of multi-element coatings based on niobium nitride

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Abstract. The paper presents the results of studies of the influence of the deposition conditions, coatings NbTiZrN, NbTiAlN on structure parameters and mechanical properties. It is shown that the changes of these parameters depend on the composition of coatings. It was found that the condensation temperature affects the phase composition of the coating. Data obtained can be used when choosing functional layers of multi-element coatings.

1 Introduction

Wear-resistant coatings boost the efficiency of cutting tools [1-5]. Multi-element coatings are increasingly applied [6-9]. To boost the efficiency of functional layers of multi-element coatings it is necessary to have data on the influence of various factors accompanying their deposition process on their mechanical properties.

Objective of this research is to study the influence of the composition and deposition conditions of coatings on their structural parameters and mechanical properties

2 Methodology of Experiment

Multi-element coatings based on niobium nitride NbTiZrN and NbTiAlN were studied. They were applied on carbide blades MK8 and plates of 20X13 and P6M5 steel using «Bulat-6» unit. Chemical composition of coatings was determined by the quantitative X-ray spectroscopic analysis method using the apparatus MAP-4 taking into consideration ZAF-modifications. Structural parameters of coatings (the lattice spacing a , the half-width of the X-ray diffraction line β_{004}) and residual compressive stresses σ_0 were studied using the X-ray diffraction meter «ДРОН-3М», sizes of coherent scattering regions (CSR) D were calculated using the method described in the paper [10]. Micro-hardness H_M , elasticity modulus E and stress intensity coefficient K_{IC} of coatings were determined using methods

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described in the paper [11]. Adhesion strength of coatings with the instrumental base was estimated by the stripping coefficient K_0 [12].

3 Research Results and Discussion

NbTiZrN coatings were applied using two cathodes of niobium and a composite cathode of titan with a zirconium insertion. Coating composition was changed by varying the area of zirconium insertions. When applying NbTiAlN coating, we used cathodes of niobium, alloy of niobium, titan and aluminum and alloy of titan and aluminum. Coating composition was changed by varying the layout diagram of the unit – the combination of cathodes used. Chemical composition of coatings is presented in Table 1.

Table 1. Chemical composition of coatings

Coating	Content of elements, % at.			
	Nb	Ti	Zr	Al
NbTiAlN (№ 1)	67.20	32.60	-	0.20
NbTiAlN (№ 2)	40.0	49.16	-	10.84
NbTiZrN (№ 1)	65.70	33.50	0.80	-
NbTiZrN (№ 2)	46.49	41.94	11.57	-

It has been established that multi-element coatings NbTiZrN and NbTiAlN are single-phased ones. They have a tetragonal lattice with predominant texture (004) compared to nitride NbN having the hexagonal lattice [13, 14]. As Table 2 shows, coatings NbTiZrN and NbTiAlN are characterized with higher parameter values of the lattice, smaller value of the X-ray line half-width and substantially smaller compression residual stresses (by 1,6...2,7 times smaller compared to NbN), slight increase of CSR block sizes.

Table 2. Influence of the coating composition on structural parameters and residual stresses

Instrumental base	Coating	a , nm	c , nm	D , nm	β_{004} , grad	σ_0 , MPa
20X13	NbN	0.2994	0.5594	9.24	1.13*	-2893±94
	NbTiZrN (№ 1)	0.4415	0.8764	10.35	0.93	-2085±84
	NbTiAlN (№ 1)	0.4417	0.8684	13.76	0.71	-1828± 124
P6M5	NbN	0.3020	0.5751	8.66	1.20*	-4716±348
	NbTiZrN (№ 1)	0.4470	0.8764	11.65	0.83	-2904±312
	NbTiAlN (№ 1)	0.4394	0.8704	13.76	0.70	-1742±15

Note: * – measured by peak (100)

Study of mechanical properties (Table 3) showed that micro-hardness and elastic module of three-element coatings do slightly differ from niobium nitride. NbTiZrN coating is characterized with higher values of micro-hardness and elastic module. Stress-intensity factor of multi-element coatings is higher compared to NbN coating by 8.4...23 %. This indicates higher crack resistance. Resistance to abrasive wear H_μ / E and plastic straining H_μ^3/E^2 of multi-element coatings and NbN differ slightly. Adhesion strength of multi-element coatings is lower compared to NbN. It is evidenced by higher values of the delamination coefficient.

Table 3. Mechanical properties of coatings (base – MK8)

Coating	H_m , GPa	K_0	K_{IC} , MPa·m ^{1/2}	E , GPa	H_m/E	H_m^3/E^2
NbN	29.8	0.12	9.78	467	0.064	0.121
NbTiAlN	30.2	0.26	12.04	445	0.068	0.139
NbTiZrN	32.6	0.19	10.60	575	0.057	0.105

Change of the coating composition slightly influences its phase composition. For NbTiAlN coatings of various composition, the diffraction peak of NbN (004) of maximum intensity is observed almost at one and the same angle $2\theta=41.4$ grad. For NbTiZrN coatings, reducing Nb and increasing Ti and Zr respectively lead to displacement of the diffraction peak of NbN (004) from the angle $2\theta=41.2$ grad. to the angle $2\theta=35.4$ grad.

Comparing of data, presented in Tables 2 and 3, shows that change of composition differently influences structural parameters of coatings. For NbTiZrN coatings, parameter values of the lattice, X-ray line half-width, CSR block sizes almost do not depend on the composition. At the same time, the value of compression residual stresses in coatings with the lower content of niobium is by 2.0...2.8 times higher.

Table 4. Structural parameters of coatings and residual stresses

Coating	Base	<i>a</i> , nm	<i>c</i> , nm	<i>D</i> , nm	β_{004} , grad	σ_0 , MPa
NbTiZrN	20X13	0.4420	0.8678	11.75	0.81	-6212±235
	P6M5	0.4407	0.8747	12.39	0.77	-5860±191
NbTiAlN	20X13	0.4366	0.8744	5.73	1.66	-5950± 47
	P6M5	0.4302	0.8647	5.76	1.65	-4753± 269

Note: Data in the Table are for NbTiZrN (№2) and NbTiAlN (№2) coatings

Compared to NbTiZrN coating, change of NbTiAlN coating composition to a far greater degree influences structural parameters. Coatings with the lower content of niobium (NbTiAlN №2 coating) have higher values of the X-ray line half-width. This suggests the higher lattice deformation. Respectively, these coatings are characterized with lower CSR block sizes. Level of compression residual stresses in these coatings is by 2.7...3.2 times higher compared to NbTiAlN №1 coatings.

Influence of the condensation temperature on the chemical composition of coatings is presented in Table 5. It has been established that change of the condensation temperature slightly influences the ration of deposited elements in the coating. At the same time, if the condensation temperature in NbTiAlN coating is higher, the aluminum composition will be slightly increased provided that the titan composition is decreased.

Table 5. Influence of the condensation temperature on the chemical composition of coatings

Coating	Content of elements, % at.			
	Nb	Ti	Zr	Al
NbTiAlN*	68.17	27.23	-	4.60
NbTiAlN**	66.91	27.96	-	5.13
NbTiZrN*	46.56	41.69	11.75	-
NbTiZrN**	46.49	41.94	11.57	-

Note: *, ** - at the temperature 300 °C and 600 °C, respectively

Tables 6 and 7 show data on the influence of the condensation temperature on the phase composition of coatings. Figures 1 and 2 show diffractograms of NbTiZrN coating at different condensation temperatures.

It has been established that the condensation temperature has a great influence on the phase composition of the coating. When comparing data showed in Tables 6 and 7, it turns out that for NbTiZrN coating, obtained at the temperature 300 °C, in the diffractogram (Fig. 1, a) the diffraction peak of the highest intensity which is identified as NbN (112), common to the tetragonal structure, appears at the angle $2\theta=35.4$ grad. In the diffractogram of the coating, obtained at the temperature 600 °C (Fig. 1, b), the additional diffraction peak appears at the angle $2\theta=41$ grad. This fact is also common to the tetragonal structure and identified as NbN (200). Similar regularities of influence of the condensation temperature on the phase composition were also obtained for NbTiAlN coatings.

Table 6. Phase analysis of NbTiZrN coating (300 °C)

Seq. №	Diffraction angle 2θ , grad	Interplane distance d_{exp} , nm	Relative intensity	<i>HKL</i>	Interplane distance d_{tabl} , nm	Coating phases	Base phases	Coating structure
1	31.6	0.2831	0.36	002	0.2768	NbN		hexagonal
2	34.4	0.2607	1.00	100	0.2570	NbN		hexagonal
3	35.4	0.2536	1.00	112	0.2524	NbN		tetragonal
4	41.6	0.2171	0.02	004	0.2171	NbN		hexagonal
5	44.7	0.2027	1.00	110	0.2010		α -Fe	
6	61.5	0.1507	0.30	110	0.1484	NbN		hexagonal
7	65.0	0.1435	0.49	200	0.1428		α -Fe	
8	71.5	0.1320	0.05	116	0.1311	NbN		tetragonal

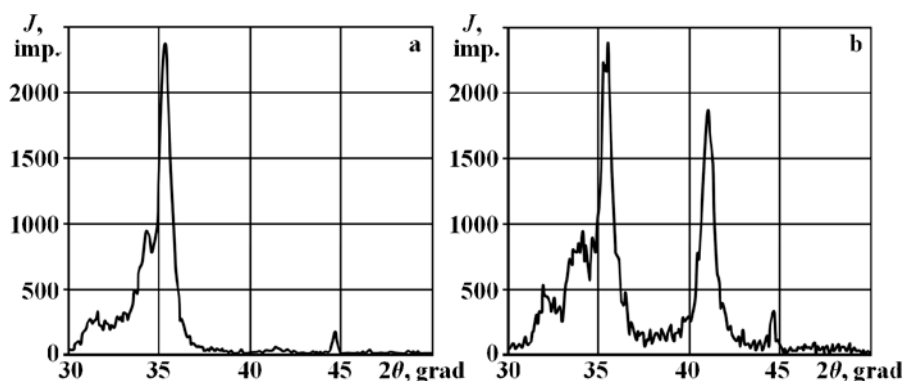


Fig. 1. Fragments of diffractograms of NbTiZrN coatings deposited at the temperature: 300 °C (a) and 600 °C (b)

Table 7. Phase analysis of NbTiZrN coating (600 °C)

Seq. №	Diffraction angle 2θ , grad	Interplane distance d_{exp} , nm	Relative intensity	<i>HKL</i>	Interplane distance d_{tabl} , nm	Coating phases	Base phases	Coating structure
1	31.9	0.2805	0.55	002	0.2768	NbN		hexagonal
2	34.1	0.2629	1.0	100	0.2570	NbN		hexagonal
3	35.5	0.2529	1.0	112	0.2524	NbN		tetragonal
4	41.0	0.2201	0.78	200	0.2193	NbN		tetragonal
5	44.7	0.2027	1.0	110	0.2010		α -Fe	
6	59.5	0.1554	0.08	220	0.1551	NbN		tetragonal
7	61.5	0.1508	0.33	110	0.1484	NbN		hexagonal
8	64.9	0.1437	0.42	200	0.1428		α -Fe	
9	67.3	0.1391	0.19	004	0.1384	NbN		hexagonal
10	71.5	0.1320	0.19	116	0.1311	NbN		tetragonal
11	75.0	0.1266	0.13	224	0.1262	NbN		tetragonal

Influence of the condensation temperature on structural parameters and mechanical properties of coatings is shown in Tables 8 and 9 and in Fig. 2-4. It has been established that decreasing of the condensation temperature from 600 °C to 300 °C changes structural parameters and the value of compression residual stresses. The X-ray line half-width is increased (by 11%...64%). CSR block sizes are decreased (by 1.2...1.6 times). Compression residual stresses are increased (by 1.1...1.4 times). Maximum change of abovementioned parameters is common to NbTiAlN coatings.

Table 8. Influence of the condensation temperature on structural parameters of coatings

Base	Coating	a , nm	c , nm	β_{112} , grad	D , nm	σ_0 , MPa
20X13	NbTiZrN	<u>0,4417</u>	<u>0,8684</u>	<u>0,81</u>	<u>11,7</u>	<u>-6555±317</u>
		0,4403	0,8671	0,73	13,04	-5147±801
P6M5	NbTiZrN	<u>0,4362</u>	<u>0,8983</u>	<u>0,79</u>	<u>12,03</u>	<u>-5211±589</u>
		0,4403	0,8741	0,7	13,71	-4980±574
20X13	NbTiAlN	<u>0,4417</u>	<u>0,884</u>	<u>1,02</u>	<u>9,41</u>	<u>-5962±516</u>
		0,4382	0,8680	0,84	11,58	-5249±330
P6M5	NbTiAlN	<u>0,4372</u>	<u>0,8791</u>	<u>1,19</u>	<u>7,98</u>	<u>-5273±290</u>
		0,4382	0,8543	0,73	13,4	-3834±548

Note: data in the numerator – for 300 °C, in the denominator – for 600 °C

Table 9. Influence of the condensation temperature on mechanical properties of coatings

Coating	Condensation temperature T_k , °C	E , GPa	H_μ / E	H_μ^3 / E^2
NbN	-	467	0.064	0.121
NbTiAlN	300	455	0.071	0.160
NbTiAlN	600	426	0.072	0.158
NbTiZrN	300	496	0.066	0.145
NbTiZrN	600	474	0.067	0.144

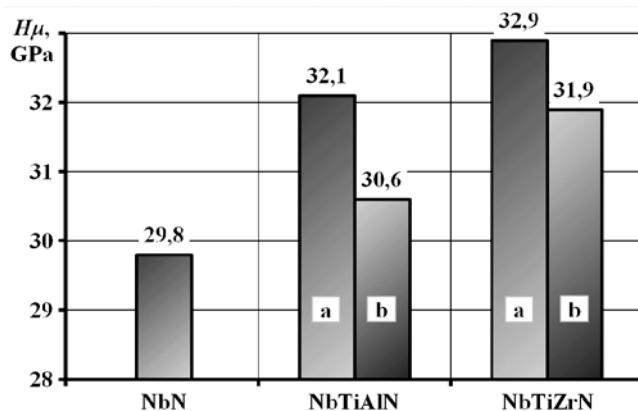


Fig. 2. Influence of the condensation temperature on the micro-hardness of wear-resistant coatings (condensation temperature: a – 300 °C, b – 600 °C)

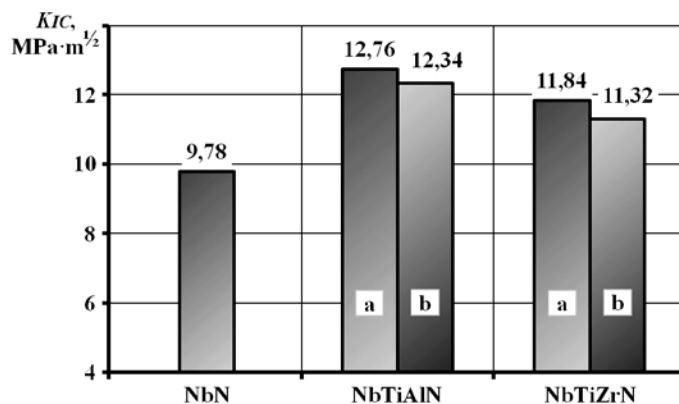


Fig. 3. Influence of the condensation temperature on the stress-intensity factor of coatings (condensation temperature: a – 300 °C, b – 600 °C)

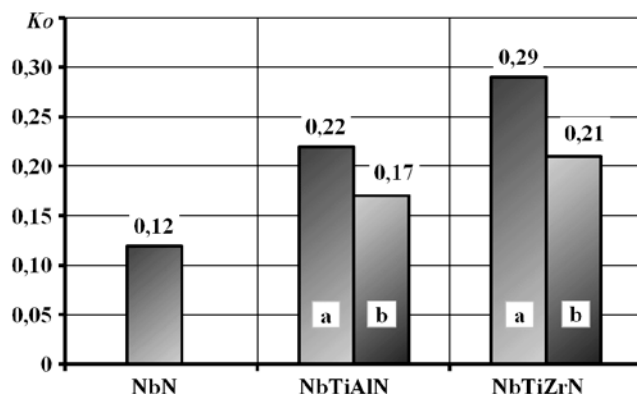


Fig. 4. Influence of the condensation temperature on the delamination coefficient of coatings (condensation temperature: a – 300 °C, b – 600 °C)

Decrease of the condensation temperature leads to increase of mechanical properties of coatings. Coatings obtained at the low condensation temperature are characterized with higher values of the micro-hardness, elastic module, stress-intensity factor provided that the adhesion strength is decreased. Condensation temperature has the maximum influence on the adhesion strength. Delamination coefficient, characterizing the adhesion strength, of coatings obtained at the high temperature, is lower by 1.3...1.4 times. This fact suggests that their adhesion strength is higher. Results obtained are well within data of works [15, 16].

4 Conclusion

It has been established that deposition conditions of coatings based on niobium nitride influence the phase composition, structural parameters, residual stresses and mechanical properties. It is testified that changes of parameters mentioned above depend on the coating composition. Data obtained can be used when choosing functional layers of multi-element coatings.

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