STRUCTURE AND PROPERTIES OF THE (Cr, Al)N COATINGS DEPOSITED BY PIII&D METHOD

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Cr-Al-N coatings deposited from the vacuum-arc plasma source with rectilinear macroparticle filter were investigated. Influence of the amplitude of pulsed substrate bias potential in the range of 0…2500 V on the structure and mechanical properties of the coatings was studied. It is found that in all coatings formed solid solution of (Cr, Al)N with a cubic structure type NaCl. High voltage pulsed potential bias causes formation of the coatings structure with fine grains (6…7 nm) and strong axial texture [110]. Residual compressive stress varies nonmonotonously from 2 to 7 GPa when the amplitude of the pulses increases. The coatings are characterized by high hardness 30…36 GPa, the surface roughness at the level of 40…50 nm and a low friction coefficient, which allows their use as protective coatings for tools and friction units.

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INTRODUCTION

Multicomponent nitride vacuum-arc coatings have high hardness, thermal stability and oxidation resistance [1]. Deposition from the filtered vacuum-arc plasma by PIII&D (Plasma immersion ion implantation and deposition) method under high voltage pulsed substrate bias allows to improve coatings characteristics [2-4]. To implement this method, the sources of filtered cathodic-arc plasma are usually used, and a negative pulsed bias potential with amplitude from a few hundred to several thousand volts is applied to the substrate during coatings deposition. Unlike the DC offset, in such conditions it is possible to minimize the effects associated with the sputtering of the coating surface. Furthermore, under bombardment at low substrate temperature the coating structure can be controlled, the level of residual stresses therein, and hence their properties.

The aim of the present work was to study the structure and mechanical properties of Cr-Al-N coatings, deposited from filtered vacuum-arc plasma by PIII&D method, as well as to study the influence of the value of the substrate bias potential amplitude on the coatings characteristics.

EXPERIMENTAL METHODS

Deposition of nitride coatings system Cr-Al-N was performed by vacuum arc process using $Cr_{0,5}Al_{0,5}$ cathodes made by powder metallurgy. About 2 microns thick coatings were deposited on polished substrates X6Cr17 steel with size 17 × 20 mm and 1.5 mm thick. The distance from the outlet of the filter to the samples was 210 mm. The coatings were deposited at an arc current of 100 A in the conditions of supply pulsed bias potential on the substrate. The high-voltage pulsed generator with the parameters: amplitude (A_U) in the range (0…2.5) kV, pulse duration 12 μs, repetition rate 12 kHz was used as the source of pulsed substrate bias potential. In the intervals between pulses substrate was at a potential of -100 V. Coating deposition time was 30 minutes. The reaction gas (nitrogen) was introduced into the vacuum chamber through a plasma source. The nitrogen pressure in the chamber was 0.1 Pa.

The coating composition was monitored by X-ray fluorescence analysis (XRF) on the vacuum scanning crystal diffraction spectrometer SPRUT. The phase composition, texture, substructure and the stress state of the coatings were studied by X-ray diffractometer DRON-3 in the Cu-Kα radiation. Along with X-ray, the Raman spectra of the coatings were investigated, exciting radiation wavelength was 514 nm.

The morphology of the coating surface was examined using an optical microscope Leica MTU 253 and 3D optical profilometer FRT. Hardness (H) and Young's modulus (E) coatings were measured by G200 nanoindenter by CSM method. The values of H and E were taken at a depth of indentation of 10 % of the film thickness. Adhesion properties were studied by means of a scratch tester REVETEST, a diamond indenter radius of 200 nm.

RESULTS AND DISCUSSION

The characteristics of the Cr-Al-N coatings, synthesized at different values amplitude A_U of the pulsed potential bias, are listed in Table 1. It is seen that the values of the Al concentration C_{Al} in metal sublattice (excluding nitrogen) indicate fairly good reproducibility of the cathode composition in coatings. The Al content in the cathode is 50 at.%, and in the coating Cr-Al-N, according to the results of XRF analysis, it varies within C_{Al} 49…51 at.%. This is significantly different from the results obtained for the vacuum-arc coating system Ti-Si-N [5], in which the composition of the cathode was reproduced not very satisfactorily in the coatings, the silicon content in the Ti-Si-N coatings are several times lower than in the cathode. This is mainly due to the selective silicon sputtering as a result of bombardment of the growing film surface by energetic ions. With increasing amplitude of the pulses the Al concentration in the Cr-Al-N coatings tends to decrease, but significant sputtering of aluminum is not observed. These data are consistent with those for known similar system, Ti-Al-N [6].

Table 1

Characteristics of Cr-Al-N coatings, synthesized at different values of the amplitude of the pulsed bias potential on the substrate

№	A_U, кV	XRA	Nanoindentation			XRD		FRT	Revetest		
		C_{Al}, %	H, GPa	E, GPa	H/E	σ, GPa	L,nm	R_a, nm	L_{C1}, H	L_{C2}, H	μ
1	0	51.4	29.6	404	0.073	2.0	18.0	38	9.0	12.4	0.15
2	0.5	51.3	33.4	390	0.087	6.1	9.2	36	5.5	7.6	0.10
3	1.0	49.2	33.1	385	0.086	7.0	6.5	56	6.5	9.8	0.10
4	1.5	49.0	36.2	436	0.083	6.1	6.0	45	5.9	10.2	0.10
5	2.0	49.2	30.5	385	0.079	3.9	6.1	50	4.0	6.8	0.10
6	2.5	49.0	30.2	373	0.071	5.3	7.2	52	1.2	2.2	0.10

Nanoindentation results indicate that all coatings are characterized by relatively high hardness in the range (30…36) GPa and a Young's modulus of about 400 GPa. High values of H / E parameter of 0.08…0.09 indicate a good stability of the coating material to plastic deformation.

Microscopic examination of coatings showed that their surface is sufficiently homogeneous with minimum amount of defects, which indicates high quality filtration of the cathodic-arc plasma flow. The area occupied by the defects does not exceed 3 % of the surface coating, and the size of the majority (~ 90 %) not greater than 1.4 microns.

According to the optical profilometry (FRT), the coatings has a cellular surface with mesh size of a few micrometers. At low values of the amplitude of potential the coatings roughness is at a level of 35…40 nm, and increases with increasing amplitude to 50 nm.

X-ray diffraction patterns of coatings are shown in Fig. 1. In all patterns except the narrow diffraction α-Fe substrate lines revealed well sufficient broad peaks of (Cr, Al)N solid solution formed by the substitution chromium by aluminum in the lattice of the chromium nitride, which has a cubic structure of the type NaCl. Wurtzite crystalline AlN phase or phase containing less nitrogen is not formed.

Line intensity ratio of the diffraction patterns indicates the formation of texture in the coatings. The calculated texture coefficients are shown in Fig. 2. At a DC bias potential (no pulses) predominates crystallite orientation with planes (111) or (200) parallel to the film surface. The size L of coherent scattering zone (CSZ) of nitride is 18 nm. When the amplitude of pulsed bias potential grows up to 1.5 kV a strong axial texture [110] is formed, and the size of the CSZ decreases to 6 nm. With further increase of the pulse amplitude to (2…2.5) kV the reflection (200) appears in the diffraction patterns along with (220). Such change of preferred orientation we observed earlier for coatings based on (Ti, Al)N [6].

An important characteristic of the coating affecting their performance properties is the level of residual stresses σ. The resulting stress values calculated from X-ray strain measurements are shown in Fig. 3. It is seen that with increasing amplitude of the potential in the range of 0…2 kV the stress changes non monotonically: first increase and then decrease, which corresponds to the Davis formula [2-4]. This behavior of (Cr, Al)N coatings is different from TiN, where the maximum stress value is 10 GPa as well as the (Ti, Al)N, where the residual stress level is almost constant in this range of amplitudes of bias potential [6].

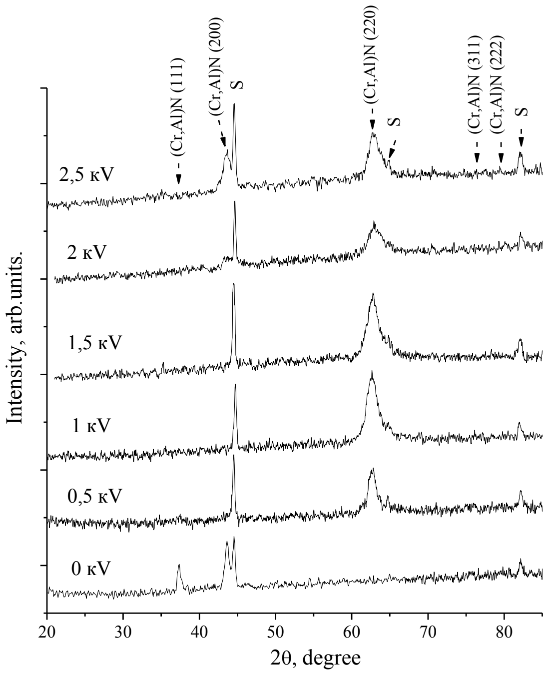

Fig. 1. X-ray diffraction patterns of coatings Cr-Al-N, deposited at different amplitude values of the pulsed bias potential on the substrate (s - substrate lines)

With further increase of the amplitude up to 2.5 kV, increase of stress is observed, which is accompanied by a decrease in the hardness of the coating.

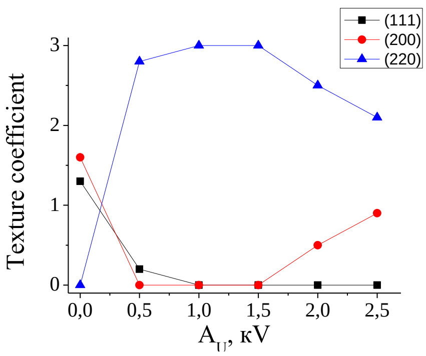

Fig. 2. The texture coefficients for the reflections (111), (200), (220) nitride (Cr,Al)N

Such changes in the system (Ti, Al)N were explained earlear by partial decomposition of the supersaturated solid solution with the cubic structure and formation of AlN hexagonal phase in the coatings.

It should be noted that the compressive stress level in the synthesized coatings (Cr, Al)N reaches high but not critical values. Usually the best operating properties show nitride coating, the stress level in which does not exceed 5 GPa [7].

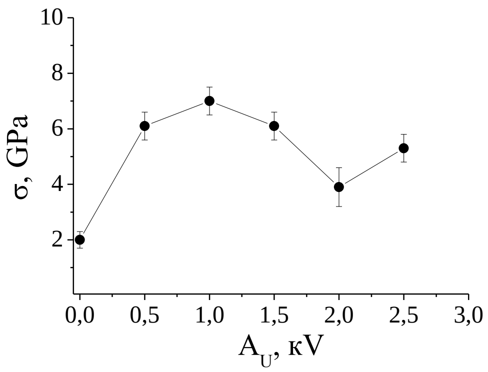

Fig. 3. The residual compressive stresses in the coatings (Cr, Al)N (XRD data)

Adhesion of the coating to the substrate was evaluated by the results of the scratch test (Revetest). The Table 1 shows the values of L_{C1} and L_{C2} loads, at which the first crack arise in the coating and delamination occurs, respectively. Coatings begin to break down at relatively low values of load (several Newtons), i.e. the adhesion to the substrate is low. This is due to the softness of the substrate steel (hardness of 2.5 GPa), on which enough thin coatings are greatly deformed even at low loads. Correlations between the adhesion of the coating and the level of residual compressive stress in it was not observed.

This test also gives information on the friction coefficient μ of the friction pair: diamond-coating material. The μ value 0.10…0.15 corresponds to the load lower than L_{C1} until the coating retains its integrity. At higher loads coating begins to break down, the friction coefficient increases somewhat, but does not exceed 0.3.

Additional information about the structure of (Cr, Al)N coatings, deposited under different values of the amplitude of the pulse bias potential to the substrate in the range of 0…2.5 kV, was obtained from the results of the study of Raman spectra. Typical Raman spectrum in a range of 100…2000 cm^{-1} is shown in Fig. 4. Deconvolution and identification of relevant phonon modes was carried out taking into account the literature data on the Raman spectra of CrAlN [8]. The peak positions were determined using the ORIGIN package with Gaussian peak shapes. The spectrum peaks detected are corresponded to the first order acoustic transverse TA mode and longitudinal LA mode in the range of 222…242 cm^{-1}, first order optical transverse TO mode and longitudinal LO mode in the range of 670…680 cm^{-1} along with second order peaks (2A, A + O, 2O), whose positions are listed in Table 2. It is known that in the perfect crystal structure of the cubic NaCl type the first order Raman scattering by phonons is not possible due to inversion symmetry of each lattice site. The presence of Raman peaks of the first order indicates the presence of defects in the crystalline structure of the coating (symmetry breaking).

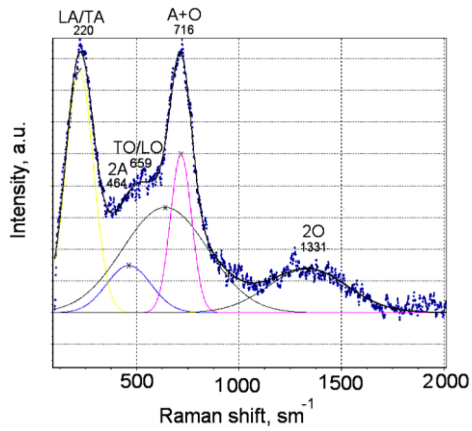

Fig. 4. Raman spectrum of (Cr,Al)N coating

Table 2

Raman peak positions (cm^{-1}) corresponding to different phonon modes of (Cr, Al)N coatings

U, kV	TA/LA	2A	TO/LO	A+O	2O
0	241.9	454.0	672.8	734.1	1375.2
0.5	220.2	445.9	676.7	715.8	1276.1
1.0	226.2	484.1	683.9	715.1	1320.4
1.5	219.5	448.8	685.0	708.9	1293.9
2	220.3	464.4	659.1	715.8	1330.7
2.5	222.4	468.5	681.8	717.6	1314.8

The spectra of all studied (Cr, Al)N coatings are similar and contain Raman peaks corresponding to the cubic crystal structure. Peaks corresponding wurtzite structure are not found in the spectra, consistent with the results of the X-ray diffraction measurements.

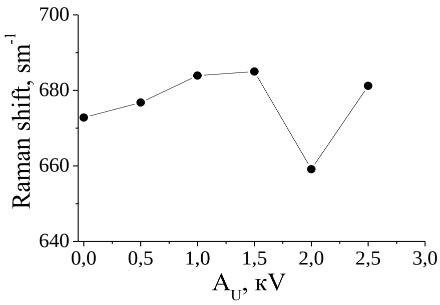

Fig. 5. The dependence of the Raman shift of the phonon mode TO / LO lattice vibrations (Cr,Al)N on the amplitude of the pulsed substrate bias potential

Raman spectra of the coatings contain information on the degree of ordering of the crystal lattice, defect density and elemental composition. In addition, certain frequency bands corresponding to the interaction with optical phonons, are sensitive to the level of residual stress in the coating. Based on this effect, the authors [9] determined the stress value in TiAlN coatings based on measurements of Raman peak position corresponding to the optical phonon mode in the vicinity 650 cm^{-1}.

In the Raman spectra of the investigated CrAlN coatings the position of the peak, identified as the LO/TO in the range (660…85) cm^{-1}, depends on the amplitude of the pulsed bias potential on the substrate during deposition, and is similar to the dependence obtained from X-ray measurements (see Figs. 3,5)

Thus, the results of X-ray and Raman measurements of structural characteristics of the (Cr, Al)N coatings are correlated with each other.

CONCLUSIONS

Using powder $Cr_{0.5}Al_{0.5}$ cathodes in a filtered vacuum-arc plasma source the (Cr, Al)N coatings with a cubic NaCl type structure were synthesized by PIIID method. The ratio of the metal components in the coatings corresponds well the cathode elemental composition.

The coatings are characterized by high hardness (30…36) GPa, the surface roughness at the level of (40…50) nm and a low friction coefficient, which allows their use for protection the tools and friction units.

High voltage pulsed bias potential with amplitude up to 2.5 kV causes formation of the coatings structure with fine grains (6…7 nm) and strong axial texture [110]. Residual compressive stress varies nonmonotonously from 2 to 7 GPa when the amplitude of the pulses increases. It is shown that the results of Raman spectroscopy measurements correlate well with x-ray analysis.

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СТРУКТУРА И СВОЙСТВА ПОКРЫТИЙ (Cr, Al)N, ОСАЖДЁННЫХ PIII И D-МЕТОДОМ

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Исследованы Cr-Al-N-покрытия, осаждённые из источника вакуумно-дуговой плазмы с прямолинейным фильтром. Изучено влияние амплитуды импульсного потенциала подложки в диапазоне 0…2500 В на структуру и механические характеристики покрытий. Установлено, что во всех покрытиях формируется твёрдый раствор (Cr, Al)N с кубической структурой типа NaCl. Подача высоковольтного импульсного потенциала смещения вызывает формирование структуры покрытий с мелкими зёрнами 6…7 нм и сильной аксиальной текстурой [110]. С ростом амплитуды импульсов остаточные напряжения сжатия немонотонно изменяются в пределах от 2 до 7 ГПа. Покрытия характеризуются высокой твёрдостью 30…36 ГПа, шероховатостью поверхности на уровне 40…50 нм и низким коэффициентом трения, что позволяет использовать их в качестве защитных покрытий для инструмента и узлов трения.

СТРУКТУРА ТА ВЛАСТИВОСТІ ПОКРИТТІВ (Cr, Al)N, ОСАДЖЕНИХ PIII І D-МЕТОДОМ

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Досліджено Cr-Al-N-покриття, осаджені з джерела вакуумно-дугової плазми з прямолінійним фільтром. Вивчено вплив амплітуди імпульсного потенціалу підкладки в діапазоні 0…2500 В на структуру та механічні характеристики покриттів. Встановлено, що в усіх покриттях формується твердий розчин (Cr, Al)N з кубічної структурою типу NaCl. Подача високовольтного імпульсного потенціалу зміщення викликає формування структури покриттів з дрібними зернами 6…7 нм і сильною аксиальної текстурою [110]. З ростом амплітуди імпульсів залишкові напруження стиску немонотонно змінюються в межах від 2 до 7 ГПа. Покриття характеризуються високою твердістю 30…36 ГПа, шорсткістю поверхні на рівні 40…50 нм і низьким коефіцієнтом тертя, що дозволяє використовувати їх в якості захисних покриттів для інструменту і вузлів тертя.