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Structure of the local environment of titanium atoms in multicomponent nitride coatings produced by plasma-ion techniques

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Abstract. An experiment was performed to examine the X-ray Absorption Near-Edge Structure (XANES) and the Extended X-ray Absorption Fine Structure (EXAFS) near the K-edge of titanium in nanocrystalline titanium nitride coatings containing additives of copper, silicon, and aluminum. Using the observation data, the structure parameters of the local environment of titanium atoms have been estimated for the coatings. According to crystallographic data, the Ti–N distance in the bulk phase of titanium nitride is 2.12 Å and the Ti–Ti distance is 3.0 Å. Nearly these values have been obtained for the respective parameters of the coatings. The presence of copper as an additive in a TiN coating increases the Ti–N distance inappreciably compared to that estimated for titanium nitride, whereas addition of silicon decreases the bond distance. It has been revealed that the copper and silicon atoms in Ti–Cu–N and Ti–Si–N coatings do not enter into the crystallographic phase of titanium nitride and do not form bonds with titanium and nitrogen, whereas the aluminum atoms in Ti–Al–N coatings form intermetallic phases with titanium and nitride phases.

1. Introduction

Modern protective coatings should match high requirements and have high physicomechanical and operational characteristics to provide reliable operation and long service life of tools, machine parts, mechanisms, and various products. The vacuum-arc deposition technology, owing to its irrefutable advantages [1], is most reasonable to use for the production of various functional coatings. In particular, it shows promise for synthesis of superhard nanocrystalline multiphase coatings which are formed on adding conventional TiN, ZrN, and AlN binary systems and various elemental additives to the base composition [2–4].

It is well known that the operational characteristics of a hardening coating strongly depend on the coating structure-phase state, structure imperfection, and crystallite size and on the level of internal stresses in the coating. It has been found that the decrease in crystallite size in titanium-nitride-base



coatings caused by addition of Si, Cu, Al, etc. makes the coatings superhard (≥ 40 GPa) [4, 5] or even ultrahard (≥ 80 GPa), or imparts them with other useful properties [4–6].

An urgent problem in studying nanocrystalline multicomponent coatings is to reveal the mechanism of the transition of superhard coatings synthesized from multicomponent arc plasmas to the nanocrystalline state. The solution of this problem should partially or completely explain the hindered growth of crystallites on the nanometer scale in a coating during its deposition by the vacuum-arc technique.

The use of conventional X-ray methods to examine the features of the elemental composition and structure-phase state of multicomponent coatings during their synthesis is conjectural because of the specificity of the scattering of radiation beams by nanosized objects. The local crystalline structure of a nanomaterial can be different from the average structure, whereas just the local structure is responsible for the important physicochemical properties of materials, such as strength, hardness, thermal stability, etc. Therefore, to perform structure examinations of nanosized objects, XAFS (X-ray Absorption Fine Structure) spectroscopy [7] should be used alongside with high-resolution diffraction methods.

The work we present here was aimed at determining the structure parameters of the local environment of titanium atoms in titanium-nitride-based coatings containing additives of copper, silicon, and aluminum by using XAFS spectroscopy methods.

2. Equipment and procedures

The test objects were multicomponent titanium-nitride-based coatings containing no additive (TiN) and those containing additives of copper (Ti–Cu–N), silicon (Ti–Si–N), and aluminum (Ti–Al–N) [4, 8, 9]. The coatings were produced using plasma-assisted vacuum-arc deposition by evaporating sintered cathodes [10] in low-pressure arcs [2]. The plasma-assisted coating deposition was carried out on the QUINTA automated plasma-ion facility with the use of a DI-100 arc evaporator [11] and the PINK hot filament, hollow cathode plasma source [12]. Thus, the coatings were condensed from mixed metal-gas plasmas of density $\sim 10^{16}$ m⁻³. The coating thickness was 3–5 μ m. Beryllium foil of thickness 300 μ m was used for the substrates.

To examine the fine structure of the coatings by XAFS methods (X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy), the equipment of the Structural Materials Science end-station of the Kurchatov Synchrotron Radiation Source (Kurchatov Institute, Moscow) [7] was used. The X-ray beam incident on a specimen was monochromated with (111)-oriented monocrystalline silicon shaped as a cutaway monoblock ("butterfly") which was mounted on a goniometric head. The energy resolution of the monochromator, $\Delta E/E$, was 10^{-4} and the working spectral range was 5–20 keV. Measurements were carried out in the transmission mode with the use of two ionization chambers filled with nitrogen. Current signals were recorded by Keithley digital picoammeters. Besides titanium-nitride-based coatings, pure titanium coatings were produced and examined to be used as reference objects.

The experimental spectra were processed using the IFEFFIT code [13]. The scattering phases and amplitudes of a photoelectron necessary for the EXAFS simulation were calculated by means of the FEFF code [14]. For the initial model of the local environment of titanium, crystallographic data for TiN were used (space group Fm3m, $a = 4.239$ Å; titanium atoms are in positions 4a (0, 0, 0) and nitrogen atoms in positions 4b (0.5, 0.5, 0.5) [15]). Nonlinear fitting was performed in the R space on the interval $R = 1.0$ – 3.0 Å with weight coefficient k^2 , $k = 2$ – 12 Å⁻¹.

3. Results and discussion

3.1. Ti–Cu–N and Ti–Si–N coatings

The XANES spectra measured at the K-edge of titanium for test sets of Ti, TiN, Ti–Cu–N, and Ti–Si–N specimens are given in Fig. 1 and the Fourier transforms of the EXAFS spectra are given in Fig. 2.

The absorption spectra of the coatings are similar to each other and differ substantially from the spectra measured for the reference titanium specimen. Instead of the sharp pre-edge resonance peak at

4967 eV for the metal, the absorption spectra of the titanium-nitride coatings show diffuse structure in the energy range 4965–4973 eV. The spectral maximum is observed at 4985 eV, and the point of the fastest growth (the maximum in the spectrum of the absorption constant derivative with respect to energy) corresponds to 4980 eV (4966 eV for the metallic titanium).

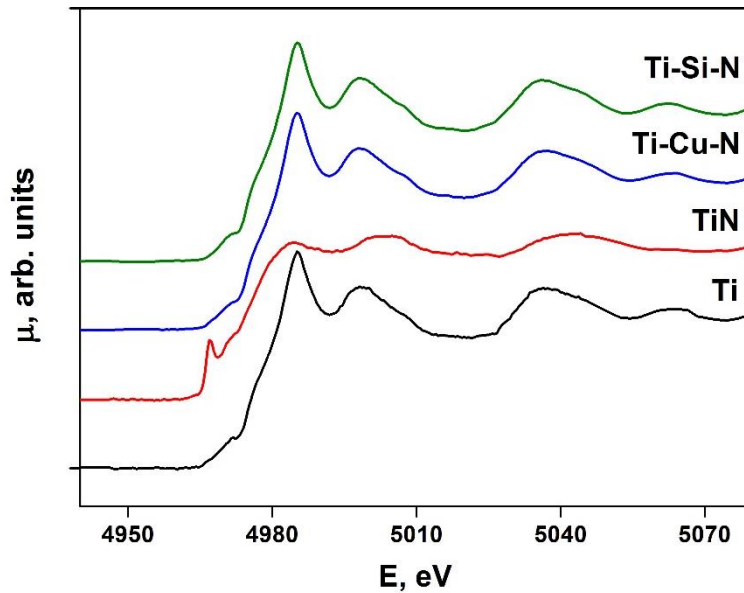


Figure 1. Experimental XANES spectra at the K-edge of titanium for test titanium-nitride coatings.

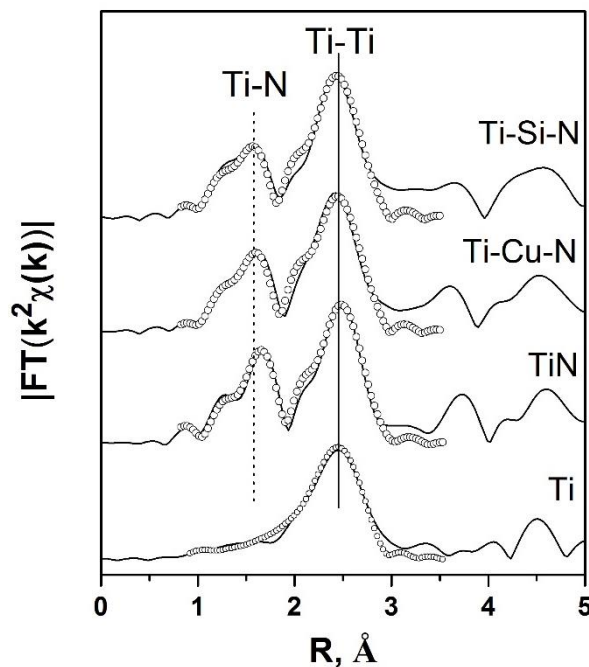


Figure 2. Fourier transforms of the EXAFS spectra for titanium-nitride coatings: the experimental and the optimized theoretical data are represented by solid lines and by circles, respectively.

For the test coatings, two dominant contributions corresponding to the first two coordination spheres of titanium atoms, Ti–N and Ti–Ti, are clearly identified. The parameters of the local environment of titanium atoms for the specimens, obtained by simulating the EXAFS spectra, are given in Table 1.

Table 1. EXAFS data on the parameters of the local environment of titanium atoms in copper- and silicon-containing titanium-nitride-based coatings produced by plasma-assisted vacuum-arc deposition with evaporation of composite cathodes.

Specimen	Ti–N		Ti–Ti	
	$R, \text{Å}$	$\sigma^2, \text{Å}^2$	$R, \text{Å}$	$\sigma^2, \text{Å}^2$
Ti	–	–	2.93	0.0089
TiN	2.09	0.0032	2.98	0.0070
Ti-Cu-N	2.10	0.0040	2.99	0.0061
Ti-Si-N	2.07	0.0054	2.98	0.0056

According to the crystallographic data for the bulk phase of titanium nitride, the Ti–N distance is 2.12 Å and the Ti–Ti distance is 3.0 Å. The respective parameters obtained for three specimens have nearly these values. Addition of copper to the composition of a titanium nitride coating slightly increases the Ti–N distance compared to the data obtained for pure titanium nitride, whereas addition of silicon decreases the bond distance.

The data obtained suggest that the titanium and nitrogen atoms in the synthesized Ti–Cu–N coatings are not related to the copper atoms, and this agrees with the previously obtained results [4].

3.2. Ti–Al–N coatings

As can be seen from Figs. 3 and 4, the XANES spectra at the K-edge of titanium for the Ti–Al–N coatings are substantially different from those for the coatings containing no additive and for the coatings containing copper. We see a smeared fine structure in the XANES spectra and no peaks associated with long-range coordination spheres in the EXAFS spectra. This points to amorphization of the coating material or to a great amount of aluminum in the coating (approximately 1:1 in proportion with titanium). In this case, the contributions of Ti–Al and Ti–Ti to the spectra could destructively interfere with each other.

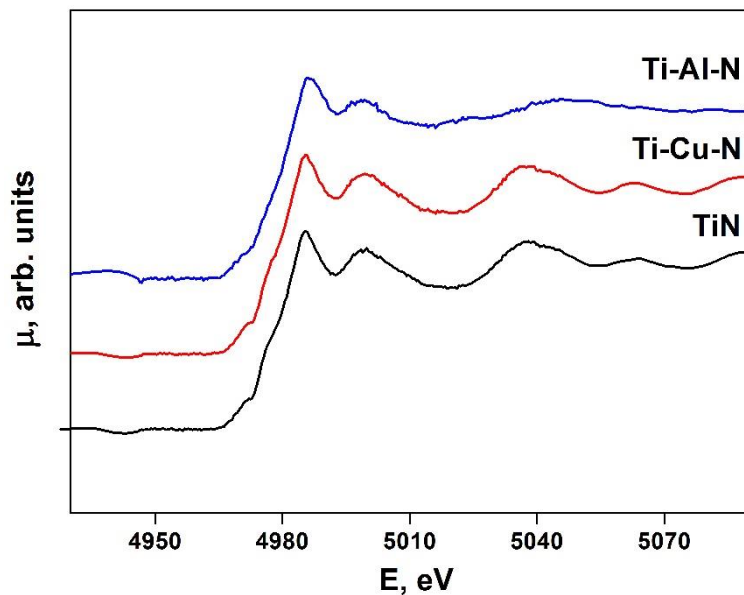


Figure 3. Experimental XANES spectra at the K-edge of titanium for TiN, Ti-Cu-N, and Ti-Al-N coatings.

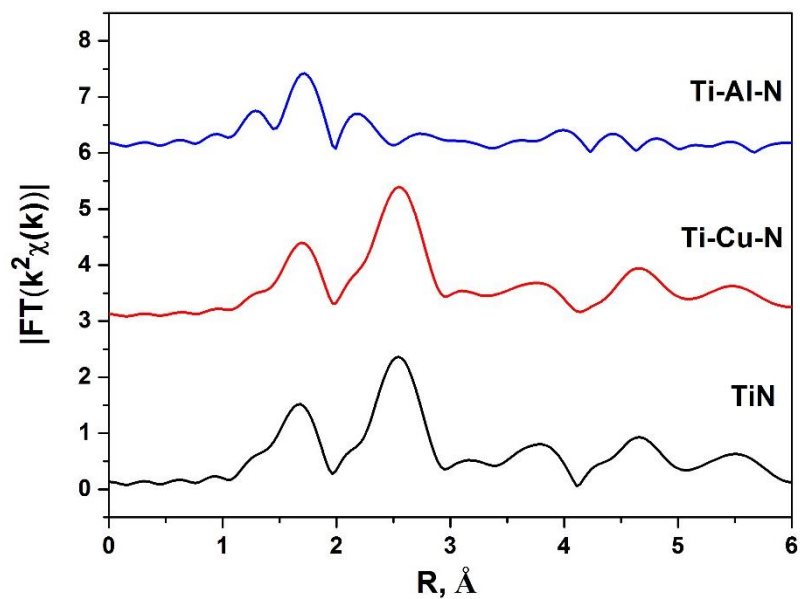


Figure 4. Fourier transforms of the EXAFS spectra for the test TiN, Ti-Cu-N, and Ti-Al-N coatings.

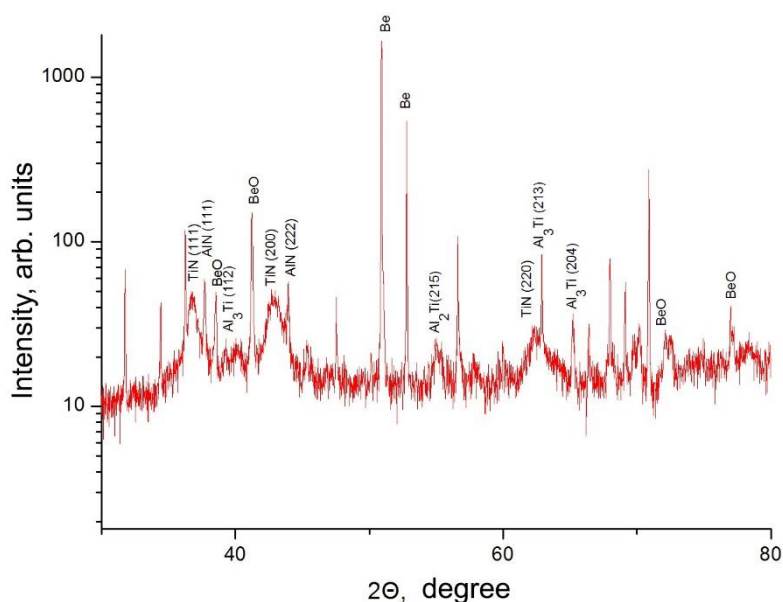


Figure 5. Diffraction pattern of a Ti–Al–N coating measured at a photon energy of 8 keV.

These data well correlate with diffraction investigations (Fig. 5), which have revealed the presence of TiN, AlN, Al₃Ti, and Al₂Ti phases, and point to a multiphase composition of the synthesized Ti–Al–N coatings.

4. Conclusion

X-ray absorption (XANES/EXAFS) spectra have been measured at the K-edge of titanium for titanium nitride coatings containing additives of copper, silicon, and aluminum. From the measured spectra, the structure parameters of the local environment of titanium atoms have been estimated for the test nanocrystalline coatings. It has been revealed that copper and silicon atoms in Ti–Cu–N and Ti–Si–N coatings do not enter into the crystallographic phase of titanium nitride and do not form compounds with titanium and nitrogen, whereas aluminum atoms in Ti–Al–N coatings form intermetallic phases with titanium and nitride phases. This is confirmed both by the XAFS spectroscopy data and by the structure-phase composition of the coatings revealed by X-ray diffraction analysis using synchrotron radiation, and these results agree with previous data of transmission electron microscopy and X-ray diffraction analysis [4, 9].

Acknowledgments

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