Nanocrystalline nitride coatings deposited by vacuum arc plasma-assisted method

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Abstract. In the given work, experiments on research of formation of titanium nitride doped with copper (≤12 at %) produced by plasma-assisted vacuum arc deposition by evaporation of sintered Ti-Cu cathodes were carried out. It was revealed that Ti-Cu-N coatings have high hardness (~40 GPa), high elastic recovery (≥50%), low friction coefficient (~0.2) and high adhesion to a substrate compared with typical TiN coatings. By methods of transmission electron microscopy of thin foils and x-ray diffraction, it was showed that the coating crystallites consist of δ-TiN with the average crystallite size of 10-30 nm and the sheath of doping elements (copper) with thickness of 2-3 monolayers is formed around of TiN crystallites.

1. Introduction

Alongside with extensive studies on the plasma-assisted synthesis of nanocrystalline coatings, investigations of their structure-phase composition, properties and of the effect of the doping element on the way by which nanostructuration of the coating occurred are carried out. Two basic models of the structure formation in these coatings depending on their phase composition have been proposed. A detailed description of the model classification is given elsewhere [1,2]. In the first case, a coating of the nc-MeN/hard phase type is formed with a-Si3N4, BN, etc., playing the part of the hard phase. For instance, in Ti–Si–N coatings, nanosized crystallites of the basic phase (TiN) are embedded in an amorphous silicon nitride (Si3N4) matrix. In the second case, when metals which do not form compounds with nitrogen, such as Cu, Ni, Y, Au, etc., are added to MeN coatings, atoms of the doped element surround crystallites of the basic element nitrides, thus restricting their growth on the nanometer scale, and a coating of the nc-MeN/soft phase system (Me = Ti, Zr, Cr, Ta, etc.) is formed. Unfortunately, the capabilities of the existing research techniques restrict the scope of investigation on nanostructured and amorphous materials. Therefore, direct verification of the proposed models of nanostructuration of multi-component coatings with a certain coating is not always possible, and the use of complex procedures, such as those based on the properties of synchrotron radiation, is required.

This paper presents a study on the structure, phase composition, and element composition of nitride coatings synthesized on metal substrates by evaporating Ti cathode and Ti-Cu composite cathode. The
goal of the study was to elucidate the effect of the doping elements on the features of the formation of nanocrystalline structure, on the basic phase crystallite size, and on the properties of the coatings.

2. The test material and the experimental procedure

The deposition of nitride coatings in low-pressure arc discharges was carried out on a plasma-ion setup equipped with a standard arc evaporator and PINK, an original gas-plasma generator developed at the Institute of High Current Electronics, SB RAS (Tomsk) [3]. Additional ionization of the working gas by means of a plasma source with filament cathode made it possible to increase the efficiency of preliminary cleaning of the specimen surface and to realize the formation of nitride compounds under the conditions of plasma assistance.

The generation of multi-component plasma and the subsequent condensation of coatings were carried out by evaporating Ti cathodes containing 12 at.% Cu in a nitrogen medium. To compare the obtained coatings and the widely used two-component coatings by their structure-phase and element composition and by mechanical properties, conventional TiN coatings were produced and investigated. Beryllium foil of thickness 0.5 mm, WC-8%Co hard alloy, and AISI 304 steel were used as substrates for x-ray diffraction analysis, mechanical and transmission electron microscopy (TEM) investigation, correspondingly. After mechanical grinding, polishing, and washing in an ultrasonic bath, the specimens were placed, on a substrate holder, in a vacuum chamber at a distance of 300 mm from the cathode. Immediately before the deposition of coatings, the surface of specimens was cleaned and activated by bombardment with accelerated argon ions at a negative substrate potential of ~1 kV. During the bombardment, the specimen surface heated up to ~300 °C.

To improve the adhesive characteristics of a nitride coating, its formation was preceded by deposition of a titanium sublayer of thickness about 100 nm by evaporating the cathode material in an argon medium. Synthesis of all Ti-Cu-N coatings was carried out in the following parameter ranges: bias voltage $U_b = -(100–300) \ V$, gas pressure $p = 0.3–0.4 \ Pa$, discharge current $I_d = 50–100 \ A$, and deposition temperature $T = 300–400 \ ^\circ C$. The coating thickness was 3–5 $\mu m$ at a coating growth rate of 1–3 $\mu m/h$.

Investigations of the deposited coatings were carried out by the following methods: optical microscopy (OLYMPUS GX71), transmission (EM-125) and scanning electron microscopy (Philips SEM 515 equipped with EDAX ECON IV, an element composition microanalyzer), micro- and nanoindentation (PM-3, NHT-S-AX-000X Nano Hardness Tester), scratch testing (MST-S-AX-000 Micro-Scratch Tester), and the Calotest method. The phase and element composition was investigated on powder diffraction stations, on the synchrotron radiation (SR) channels of the VEPP-3 (RFA-SR, PRD SR) energy store and of the ANKA (XRPD) SR source.

3. Results and discussion

Measurements of the micro- and nanohardness of the test coatings were performed in order to investigate the influence of crystallite size on mechanical properties of the samples. The measurements performed at a normal load of 500 and 50 mN, respectively, have shown that the hardness of the coatings produced by evaporating composite cathodes is greater than the hardness of titanium nitride ($\approx 25 \ GPa$) by a factor of $\approx 1.5–2$. The coatings obtained with the use of Ti-12 at. % Cu cathodes possess superhardness ($\approx 40 \ GPa$). Analysis of the loading-unloading curves obtained by the nanoindentation method has given the elastic strain of the test coatings. The greatest residual strain of 75% was observed for a titanium nitride coating and the least of 50% for Ti-Cu-N coatings. The degree of elastic recovery of the surface shape for the coatings formed by evaporating powder cathodes was 2 times greater than that for the TiN coatings. The Young modulus of the Ti-Cu-N coatings was in the range of 500-550 GPa.

The scratch-test method was used to determine the critical load at which destruction of a coating begins. For TiN, this quantity was about 3.6 N, whereas the destruction of Ti-Cu-N coatings of $\approx 10 \ N$ begins at a critical load two times larger than that for TiN coatings.
With the use of transmission electron diffraction microscopy of thin foils it has been found that the coatings formed by evaporation of composite cathodes consist of nanosized crystallites oriented randomly relative to each other. This follows from the strongly pronounced ring structure of the electron diffraction patterns (figure 1(b)). Electron diffraction analysis has shown that the crystallites of the coatings consist of δ-TiN. The measurements of size of coating crystallites were carried out on dark-light images, the average size of crystallite was estimated by the methods of statistical analysis [4]. The size of crystallites in the coatings containing copper is equal to 10-30 nm (figure 1(a), figure 1(c)); the coatings produced by evaporating pure titanium have crystallites of average size 100 nm.

![Image of the structure of a Ti-Cu-N coating formed by evaporating Ti-12 at.% Cu composite cathode in nitrogen: dark field in the reflection of a type (111) ring of TiN (a), electron diffraction pattern (b). TiN crystallite size distribution in the Ti-Cu-N coating obtained by evaporation of Ti-12at.%Cu cathode (c).](image)

The investigations performed by the above methods gave insufficient information to construct a model of the processes responsible for the variations of the coating properties and to answer the major questions of which is the role of the impurity atoms in the formation of the nanocrystalline structure of synthesized coatings, where they are localized, and whether they form their own crystallographic phase.

It is necessary to notice that the composite cathode material was investigated earlier [5]. It was showed that copper in cathode material is situated uniformly mainly on boundary of main phase (α-Ti) or in compound with Ti (CuTi2). The size of titanium based phases is in the range of 3-20 μm for Ti-12at.%Cu cathode. The size of cathode spots of vacuum arc is in range of 50-300 μm. This fact is evidence of uniformly evaporation of composite cathode elements.

Investigations of crystalline structure and element composition of coatings based on titanium nitride with additional elements have been carried out on the stations of the store powder diffraction and x-ray fluorescence element analysis (VEPP-3) [6] and of the ANKA synchrotron radiation source [7]. We rely on the data for the construction of a model of the coatings synthesis. The results of these investigations are given in figure 2 and figure 3.

In figure 2 the beryllium substrate shows up in all diffraction patterns in the form of very narrow strongly pronounced reflections. The reflections from the synthesized coating structure are wider owing to their nanocrystalline structure.
The diffraction patterns of the layers of titanium nitride and of titanium nitride doped with copper are identical [see figure 2]. The location of reflections testifies to the presence of TiN, TiN$_{0.3}$, and Ti phases in the coatings. The reflections from (111), (200), (220), (311), (222) TiN planes were revealed. The reflection from (101) plane corresponds to TiN$_{0.3}$ phase. The rest peaks belong to Be and BeO phases. Shifts of reflections and new reflections are not observed in the diffraction patterns obtained for specimens doped with copper. These data allow the conclusion that copper atoms do not form compounds with titanium or nitrogen and, equally, do not form their own crystalline phase. As the data of x-ray fluorescence analysis presented in figure 3 confirm the presence of copper in the test coating in amounts corresponding to its content in the composite cathode evaporated in an arc discharge (Ti-12at.%Cu), it can be concluded that copper is in the amorphous state at the crystallite boundaries. No signal from heavy elements is present in fluorescence data. A stand alone peak at 85 keV is attributed to Be windows. (The presence of Fe-peak is connected with insignificant evaporation of cathode holder material (stainless steel) during ignition of arc discharge). Therefore, we conclude that the only time it takes for copper atoms to form a closed sheath around a growing TiN crystallite determines the time of growth of the crystallite and, hence, its size.

In order to explain the observed phenomenon we developed an intuitive model of the growth process. The model assumes that a layer of finite thickness should be formed around a growing grain in order to prevent further growth of the grain. Spherical form of the grain is chosen as a statistical approximation. For a given grain radius $R$ the volume of the grain is calculated as $V = (4/3)\pi R^3$, similarly the volume of a cover layer with thickness $dR$ is calculated as $dV = (4/3)\pi((R+dR)^3-R^3)$. The concentration of doping material can be deduced as:

$$x = 1 - \frac{R^3}{(R + dR)^3} \tag{2}$$

Plot of the grain size dependence on the doping material concentration required to completely cover a growing grain for different cover layer thicknesses shown in figure 4. From the figure it is easy to see that the grain size will grow with decrease in the dopant concentration until other processes start to dominate limiting the size of the grain. In the case of grain sizes below 5 nm the dependence might be slightly modified by triangulation correction.
Figure 3. X-ray fluorescence spectra of Ti-Cu-N specimens near the K-edges of Ti and Cu obtained for the excitation with 20 keV photons.

Figure 4. Simulation of maximum grain size at a given doping concentration. The lines correspond to different coverage needed to prevent further crystallite growth in [nm]. Our experimental conditions are indicated by a cross.

If the grain sizes and doping concentrations are known the cover layer thickness is expressed as:

$$dR = R\left(\frac{1}{\sqrt{1-x}} - 1\right)$$  \hspace{1cm} (3)$$

For our experimental conditions, with 18 nm average grain size and 12at.%Cu concentration we find 0.74 nm cover layer thickness (cross in the figure 4) corresponding to 2.8 single atomic layers coverage of the grain (Atomic radius of copper is equal to 132 pm).
4. Conclusion
By method of transmission electron microscopy of thin foils in diffraction mode the formation of the nanocrystalline coatings produced by evaporating Ti-Cu composite cathodes in low-pressure arc discharges in the presence of nitrogen plasma was revealed. The coating crystallites consist of $\delta$-TiN. For the copper-containing coatings the average crystallite size is 10-30 nm; the coatings produced by evaporating pure titanium have crystallites of average size 100 nm.

With the powder diffraction method using synchrotron radiation it has been found that copper does not participate in the formation of crystalline phases in the coating; that is, they are in the amorphous state. It has been revealed that the copper concentration in the Ti-Cu-N coatings synthesized by the vacuum-arc method coincides with that in the evaporated cathode (12at.%).

The obtained data confirm the following model of nanostructuration of coatings based on titanium nitride. The nanocrystallization of these materials occurs when an amorphous sheath of doping elements (copper) is formed around of TiN crystallites, thereby preventing their further growth.

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