Peculiarities of the structure formation of nanoscale coatings from the vacuum arc discharge plasma

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Abstract. In this paper features of the structure formation of nanoscale coatings (TiN)–(AlN)–(Ti–Al–N) in the vacuum arc discharge plasma are considered. The composition and structure of the formed nanoscale coatings are studied. The main factors influencing the quality of the formed coatings are shown.

Nanoscale and nanocomposite coatings represent a new type of materials obtained by ion-plasma technological devices. Nanocomposite materials, due to the small dimensions of the grains, exhibit very different performance properties compared to the conventional materials.

As the first nanostructured multilayer coating can be considered a combination of layers Ti:TiN, because titanium nitride is the most used reinforcing coating. For multilayer coatings was obtained a hardness level of 3700 kg/mm^2, which is higher than the hardness of homogeneous films.

The wear resistance of the workpiece increases due to the layer-by-layer deposition of nitrides of various metals [1, 2] generated using the plasma of a vacuum arc discharge while sputtering the cathode material by a cathode spot [3, 4]. Coatings consisting of multiple layers have a high hardness while maintaining the viscosity as a result of brittle fracture energy dissipation on the intergranular and interlayer interfaces formed by the layers.

Currently, one of the possible types of such coatings is alternating layers of nanocrystalline nitrides of titanium (TiN) and aluminum (AlN), with an intermediate layer of complex composition (Ti–Al–N). Nitride compounds are metal-like formations which have high hardness, melt without decomposition at a high temperature and are able to possess superconductivity.

For the plasmachemical synthesis as the reaction gas is used a chemically reactive molecular nitrogen N_2 ($2s^2\ 2p^3$), which has a strong triple bond with $d_{\text{N–N}}$ = 1.095 Å [5]. The destruction of the triple N–N bond prevents unusually strong first of the breaking bonds in the N_2 molecule (~ 1250 cal/mole).

Due to the small values of the threshold energies of excitation for vibrational and rotational levels of molecules particles are already excited at small values of the average energy, and by the electron collisions the processes of vibrational relaxation and dissociation of molecules not only through the main, but also through the electron excited states are accelerated.

Therefore, in the discharge gap charged particles not only cause the dissociation of N_2 molecules, but also excite higher energy vibrational levels of N atoms contributing to the occurrence of the reverse reaction N + N → N_2 with the allocation of the energy spent on decomposition. Chemical transformations of the neutral particles affect the ionization balance in the plasma flux and the distribution function of the electron energy and as a result all the plasma characteristics.

Increasing the strength of the films is possible due to the structural changes associated with the variation of the deposition conditions and also can be obtained by reduction of their thickness. Films with nanometer thicknesses have hardness several times higher than the micrometer films. Their durability is influenced by the structure of the free surface and the interface film–substrate, formed in the process of condensation of atoms.

The increase of the negative bias potential that is set on the substrate and consecutive increase in the power of the sprayed particles, and also the variation of the product temperature lead to a change in the phase structure of the formed coating and the percentage content of the elements in the coating due to the sputtering of the light elements with increasing energy of ions bombarding the substrate. For deposition of the coating can be used technological devices, which enable simultaneous spraying of different materials (figure 1), and also the spraying of the alloy cathode consisting of various materials in different proportions.

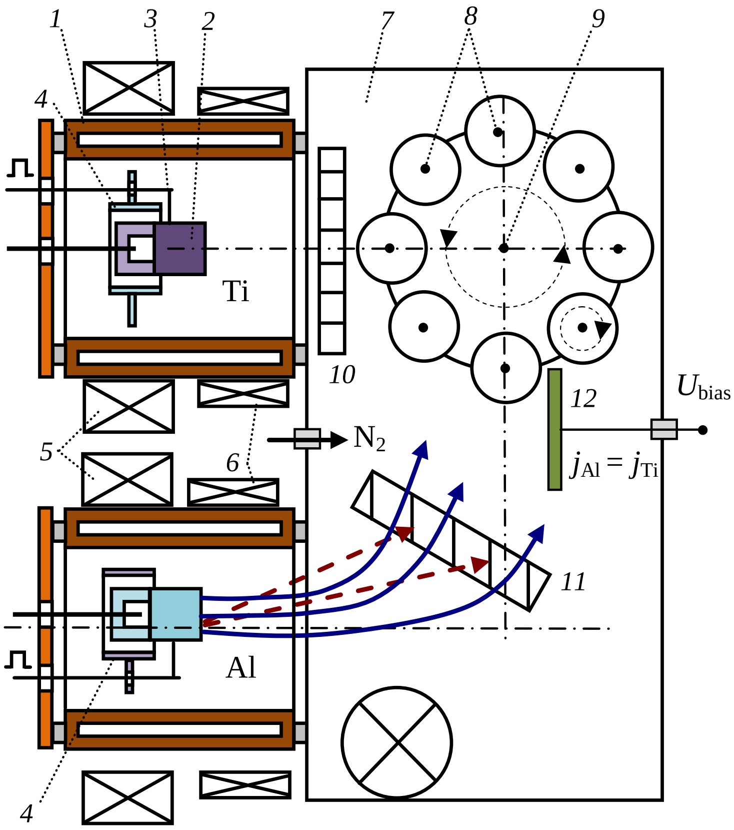

Figure 1. Scheme of the technological apparatus for producing complex composite coatings: *1* – anode; *2* – cathode; *3* – igniting electrode; *4* – screen; *5* – stabilizing solenoid; *6* – focusing solenoid; *7* – working volume; *8* – workpiece; *9* – planetary rotation mechanism; *10* – plasma attenuator; *11* – plasma separator; *12* – substrate.

During simultaneous sputtering of materials the main objective is to harmonize the density of ion currents to the sample and to clean the plasma flux from the droplet formation of the aluminum. For the purpose of weakening the flux of, for example, titanium plasma was used an attenuator *10*, and for cleaning – the separator *11*, creating a solid, impenetrable barrier to droplet formation, having the straight path of movement. In this case, their deposition is carried out on the separator surface facing the working surface of the cathode.

The change in the set bias voltage leads to a change in the content of nitrogen in the composition of the nitride coatings MeN_{1-x} in the range $x = 0.5\ldots0.9$ and the change in the lattice of the nitride phase, which is associated with an increased likelihood of the nitrides formation at growing energy of nitrogen and titanium ions [6].

When applying combined coatings it was taken into account that Ti and Al have different melting and boiling points, sputtering yields and atomic masses. The last condition leads to the fact that the plasma flux contains particles with different kinetic energy. Therefore, the main task was to harmonize ionic currents of titanium and aluminum coming to the sample.

Depending on the conditions of deposition in the coating was observed the presence of both phases of titanium and aluminum, and intermetallic compound (Ti–Al). It was noted that with growth of aluminum ion current reaching the substrate, the percentage of the intermetallic compound in the coating is increased, and the decrease of the current $I_{i\mathrm{Al}}$ leads to the predominance in the coating of the titanium nitride phase. Figure 2 shows X-ray diffraction pattern for Ti–Al–N system obtained using bias voltage –130 V.

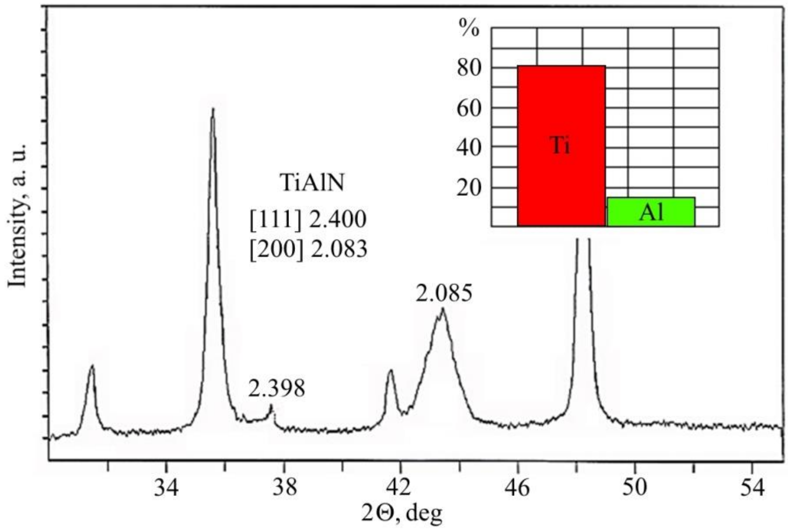

Figure 2. X-ray diffraction pattern for Ti–Al–N system.

For the Ti–Al–N system were obtained the following ratios for content of titanium and aluminum in the coating depending on the set bias voltage: 80 % Ti and 13 % Al for U_{bias} = –130 V; 63 % Ti and 31 % Al for U_{bias} = –100 V; 55 % Ti and 45 % Al for U_{bias} = –20 V.

The use of the multilayer systems in the coating formation requires to investigate and simulate not only the structure of each of the layers individually, but also to determine the thickness, type of the material and number of layers in the period, create artificial structures with unique functional properties, as the use of multilayered structures leads to the increase of the coatings hardness.

However, for multilayer nanoscale films based on Ti and Al was found that with the increase in the percentage of more solid component (Ti), the hardness of the coating decreases and, conversely, with the increase of the percentage content of the more plastic component (Al), the hardness of the coating increases. This fact shows that materials in the coating and thickness of the films must be picked up in a special way. Main parameters of the deposition process are shown in figure 3.

Conducted research of the technological peculiarities of the formation of TiN, AlN and Ti–Al–N films from a flux of metal plasma of the vacuum arc discharge showed that the main parameters influencing the structure and properties of coatings are:

- gas pressure, that is responsible for elemental and phase composition of the coating;
- discharge current, that determines the composition of the plasma flux and the growth rate of the coating;
- distance from the cathode to the workpiece, that sets a relation between the discharge current and gas pressure, determining the phase relations metal–nitrogen (Me:N) in the formed coating;
- bias potential, that provides the energy of deposited particles, and thereby the coating growth rate, and its microstructure and hardness;

- substrate temperature, that is responsible for the adhesion, microstructure and residual stress in the obtained coating.

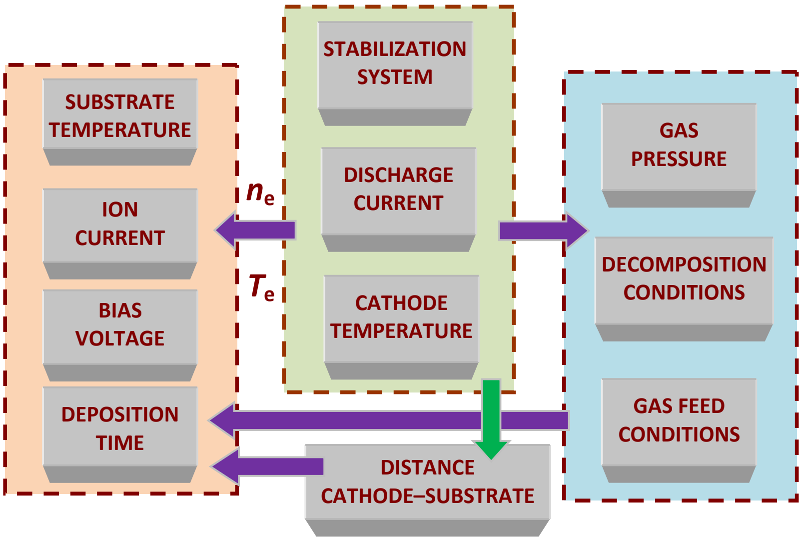

Figure 3. Factors that determine the quality of the applied coating.

It was received, that providing the cleaning of the plasma flux from the droplet formation, by varying the process parameters it is possible to effectively manage the composition and structure of the formed multilayered coating.

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