

# Nanostructured Nitride Coatings Produced by Vacuum Arc Evaporation of Sintered Ti–Al Cathodes<sup>1</sup>

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**Abstract** – This paper discusses the possibility of nanostructured coatings formation with the use of composite powder Ti–Al system cathodes in arc low-pressure discharges. The results of sintered Ti-40 at.% material investigation, the Ti–Al–N coating synthesis processes and research of structure and properties of deposited coatings are presented.

## 1. Introduction

At present, the wear-resistant coatings are widely used to increase the lifetime of instruments, machine details and mechanisms. The main attention is devoted to the formation and investigation of nanocrystalline multi-component nitride coatings such systems as Ti–Si–N [1], Ti–Al–N [2, 3], Ti–Si–Al–N [4], Ti–Zr–N [5] formed by ion-plasma methods. Owing to introduction of additional element in coating composition during its synthesis the growth of coating structure elements cease in rage of few to few tens nanometers. Usually the coating nanostructurization results in improvement of its exploitation characteristics. The choice of additional element material is based on its possibility to assist the coating formation with stable nanosize structure which is characterized the certain features. For example, during deposition of multicomponent coatings based on TiN the additional elements such Si, Al, Zr, B etc. are used. In the case of Ti–Si–N coatings a composite structure has been formed. In the coating structure, the crystallites of TiN are embedded in amorphous matrix of silicon nitrides. The coatings with such structure have high hardness [6, 7]. Its values can reach and exceed that of diamond. Ti–Al–N system distinguishes the high corrosion stability at ordinary and high temperature [8, 9]. That system has huge potential in the view of application Ti–Al–N coatings for protection of machine and device details, instruments from negative influence of environment, wear etc.

The composite coatings are condensed from multi-component plasma generated by PVD methods. To generate the multicomponent plasma as a rule it is used the simultaneous sputtering a few monoelemental cathodes. Another way is the use of multicomponent composite cathodes produced by alloying, sintering or

by self-propagation high-temperature synthesis. At that, the main factors are selection of cathode composition and optimization of parameters of coating deposition process.

The purposes of the work were 1) the investigation of sintered Ti–Al materials developed for sputtering cathodes in the arc evaporator; 2) the deposition of Ti–Al–N coatings in plasma of arc low-pressure discharges with use of powder Ti–Al cathodes; 3) the investigation of structure and mechanical properties of the coatings formed at the different conditions of the deposition process.

## 2. Experimental technique

The cathodes for vacuum arc deposition were prepared by vacuum sintering of powder mixture: titanium (<160 μm) and TiAl<sub>3</sub> intermetallic compound (<50 μm). The regimes (temperature, time etc.) of sintering were selected to provide the minimum and uniform residual porosity of sintered material. Microstructure of sintered materials was investigated by metallurgical microscope (MIM-9) and method of X-ray diffraction (DRON-1).

The experimental works of coating synthesis were carried out on specialized setup for coating deposition [10]. It includes the arc evaporator (source of metal plasma) and plasmagenerator with filament (source of gas-discharge plasma) [11]. The use of plasma source with filament (PINK) allows 1) carrying out the previously cleaning of substrate by gaseous ions; 2) to increase the effectiveness of plasma-chemical reaction during coating growth. Ti–Al composite material sintered of Ti and Ti<sub>3</sub>Al powder mixture was used as a sputtered cathode.

The substrate samples were made of austenite steel SUS 302 and hard alloy WC–8%Co. The samples were previously polished using diamond paste up to roughness of  $R_a \sim 0.04 \mu\text{m}$  and were ultrasonically cleaned.

Directly before coating deposition the substrate surface was previously cleaned, activated and heated by argon ions at bias about  $U_b \sim -1 \text{ kV}$ . That bombardment of high-energy ions not only cleans the sur-

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face from oxide films and adsorbed gases but assists the increase of adherence of coating with substrates.

The optimization of process of deposition Ti–Al–N coatings were carried out in the atmosphere of gas mixture Ar–N<sub>2</sub> at following parameters: arc discharge current  $I_d = 25 \div 100$  A; bias voltage  $U_b = -(15 \div 600)$  V, discharge current of PINK  $I_{\text{PINK}} = 5 \div 20$  A, total pressure of gas mixture  $p \sim 0.1$  Pa. The deposition duration was influenced from discharge current of arc evaporator and required thickness of coatings and it was in range of 60–180 min. The investigations of coating structure and phase composition were carried out by the methods of scanning and transmission diffraction microscopy, X-ray diffraction analysis; mechanical properties were measured by micro- and nanoindentation, scratch test etc.

### 3. Results and discussion

#### 3.1 Investigation of sintered powder cathodes

A microstructure of sintered Ti–Al material is shown in Fig. 1.

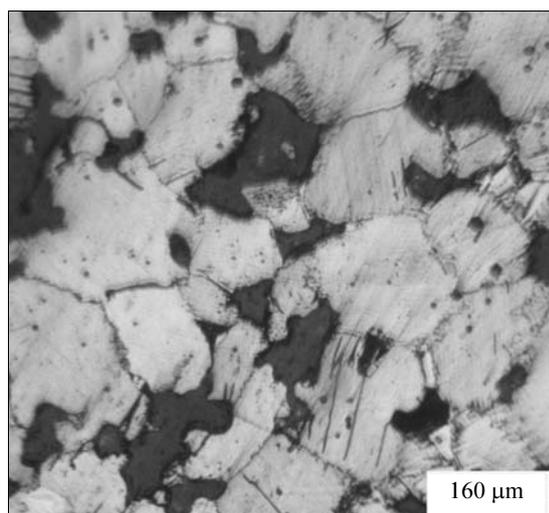


Fig. 1. A microstructure of sintered (1250 °C, 4 h) powder mixtures of Ti (< 160 μm) and TiAl<sub>3</sub> (< 50 μm)

The microstructure is composed of rounded grains and numerous pores. A size of the grains agrees with initial sizes of Ti particles in Ti powder.

According to the results of X-ray diffraction analysis (Fig. 2), the main phase in sintered material is titanium monoaluminide TiAl. There are two intensive reflexes of ordered phase Ti<sub>3</sub>Al as well.

According to the microstructure investigations (Fig. 1), the maximum possible temperature of solid-phase sintering (1280 °C) and durable isothermal temperature holding do not allow to eliminate a residual porosity, that remains rather high (up to 30%). However, residual porosity does not prohibit from stable burning of arc discharge. A stationary relief remains on the cathode surface during cathode erosion process and a roughness level depends on the residual porosity of the cathode material.

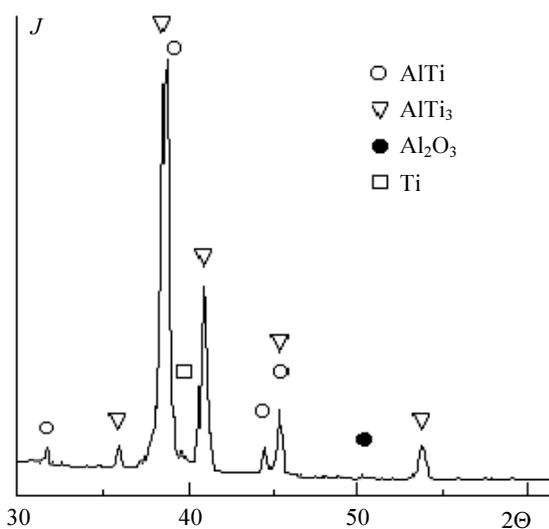


Fig. 2. X-ray diffraction pattern of sintered powder mixtures of Ti (< 160 μm) and TiAl<sub>3</sub> (< 50 μm)

#### 3.2. Coatings deposition and investigation of their properties

The structure analysis of formed coatings carried out by methods of transmission electron microscopy (TEM) shown that Ti–Al–N coating consists of fragments with size of ~ 100-200 nm. At that, they are formed by crystallites with size in range of 3 to 14 nm (Fig. 3).

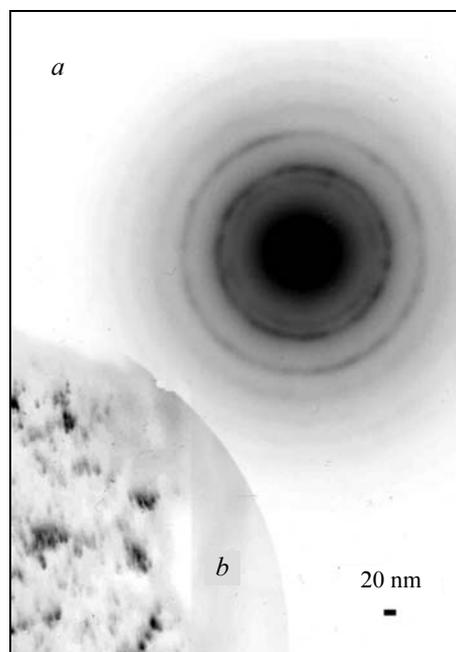


Fig. 3. Diffraction pattern (a) and bright field image (b) of Ti–Al–N coating formed by evaporation of Ti-40% at Al cathode

The analysis listed in diagram of Fig. 4 shows that the main part of volume are the crystallites with size of ~ 5–6 nm. Microdiffraction analysis of Ti–Al–N coatings carried out by TEM shown that crystallites are titanium nitride δ-TiN.

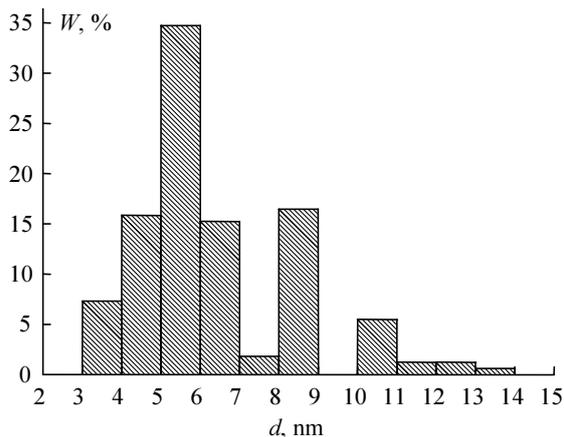


Fig. 4. Size distribution of crystallites of Ti–Al–N coatings

The coating has columnar structure. Every column is polycrystalline assembly which consists of nanosize crystallites. They are oriented chaotically relative to each other.

This fact follows from pronounced ring structure of diffraction pattern (Fig. 3, *a*). Consequently, formed coating can be rank to the class of random-orientation coatings.

The evaporation of Ti-40 at % Al system cathode in the atmosphere of the ionized nitrogen supposes an opportunity of aluminum nitrides formation. The traces of aluminum nitride (a volume fraction of ~ 1%) have been revealed by methods of X-ray diffraction analysis with the use of a technique of a sliding beam. In addition, by the method of X-ray diffraction analysis, such phases as  $Ti_2N$ , TiAl, and  $Ti_2Al_3$  had been revealed.

It is possible to assume that the given phases form by droplet fraction of the coating which arrives on a substrate in the form of microdroplets of the melt material of the cathode at generation of metal plasma from a cathode spots of the arc discharge on a surface of the composite cathode.

Measurements of micro- and nanohardness have shown that values of Ti–Al–N coating hardness strongly depend on parameters of deposition process and change in a range of 31–40 GPa. In particular, the strong influence on strength characteristics of coatings renders a bias voltage on a substrate. As follows from the analysis of the results presented in Fig. 5, the hardness of coatings increases in a range of bias voltage  $U_b = -(100-600)$  V and reaches the value of 40 GPa at bias of  $U_b = -600$  V.

Besides the increase of negative bias voltage and hence the increase of energy of nitrogen ions bombarding a surface of a substrate influences on decorative properties of a coatings.

Color of Ti–Al–N coatings in an investigated range of bias voltage varies from violet ( $U_f = -15$  V) up to gold ( $U_f = -600$  V). It can be concerned with various element structure of a coatings and requires the further research.

By the method of nanoindentation on a course of load-unloading curves had been carried out an estimation of a elastic deformation level of TiN and Ti–Al–N coatings.

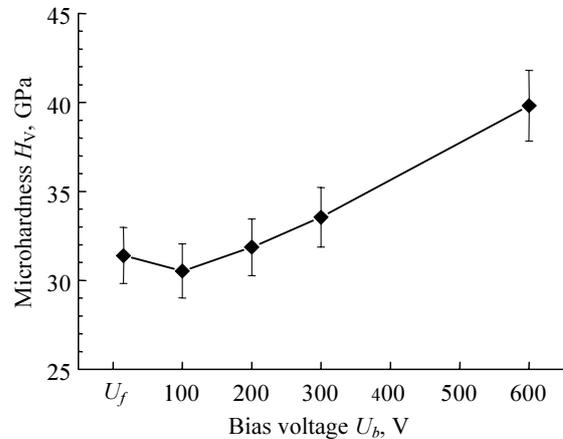


Fig. 5. Microhardness of Ti–Al–N coatings vs. bias voltage ( $I_d = 25$  A,  $I_{PINK} = 10$  A,  $t = 1$  h)

As a result of the given researches it has been revealed that the maximum residual deformation (~75%) is observed in the coating synthesized at evaporation of the pure titanium cathode, minimal – in the coating synthesized at evaporation of the Ti-40% at Al system cathode (~35%) (Fig. 6).

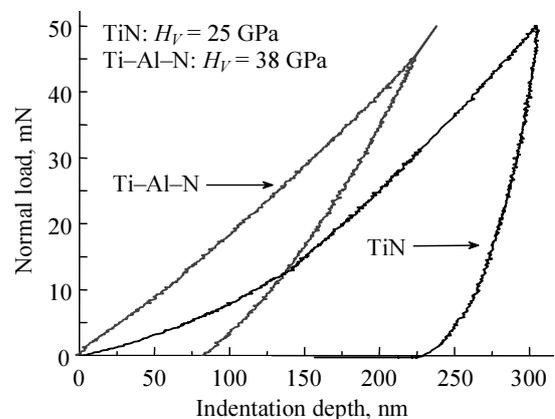


Fig. 6. Load-unloading curves for TiN and Ti–Al–N coating deposited in the arc discharge plasma.

#### 4. Conclusion

1. Sintered titanium-aluminum materials were investigated to develop two component Ti-40 at % Al cathodes for vacuum arc evaporation.
2. The possibility of formation nanostructured Ti–Al–N coatings is shown by vacuum arc method at evaporation of sintered Ti–Al system cathode in atmosphere of mixture of ionized gases.
3. The advantages of multicomponent Ti–Al–N coatings (nanocrystalline structure, high hardness, the minimal level of residual deformations) in comparison with traditional TiN coatings are shown.

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