Model calculation of the stoichiometric composition of three-component vacuum ion plasma coatings

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Abstract. Development and creation of intermetallic materials and nanostructured, amorphous materials, coatings with high physicochemical properties and technologies for their production are priority strategic directions for the development of materials and technologies. A mathematical model has been developed that makes it possible to determine the stoichiometric composition of the Ti-Al-O, Ti-Al-C, Ti-Al-N coatings under given treatment conditions. On the basis of the model, a software was created that allows calculating the ionic saturation current for each of the cathodes and the flow of metal ions per unit area per unit time at an arbitrary point of the vacuum chamber. Using the software product, it is possible to determine the stoichiometric composition of the Ti-Al-O, Ti-Al-C, Ti-Al-N system coatings, depending on the technological modes of their deposition from the vacuum-arc plasma.

1. Introduction
Development and creation of intermetallic materials and nanostructured, amorphous materials, coatings with high physicochemical properties and technologies for their production are priority strategic directions for the development of materials and technologies (presidential decree of the Russian Federation).

In the last decade, titanium-aluminum nitride (Ti_{1-x}Al_xN) has been widely used, which increases the hardness and durability of cutting tool during high-speed processing.

Worth to mention that layered threefold carbides (Ti-Al-C) and nitrides (Ti-Al-N) show a unique combination of properties characteristic of both metals and ceramics.

Such materials have a low density, high values of electrical conductivity, thermal conductivity and hardness, excellent corrosion resistance in aggressive fluid, low modulus of elasticity, resistance to thermal shock and high-temperature oxidation, and easily machined, have a high melting point and are quite stable at temperatures up to 1000 °C [2].

One of the most promising methods for applying coatings is the deposition of coatings from the plasma of a vacuum-arc discharge, due to its special features [3]:

- Versatility of the spectrum of applied coatings.
- High productivity (deposition rate up to 40 μm·h⁻¹).
- High strength adhesive bond of the coating with the substrate.
- High ionization coefficient of evaporated particles.
- The large kinetic energy of the emitted ions.

A lot of research have been devoted to the study of the Ti-Al-O, Ti-Al-C, Ti-Al-N systems [4, 5, 6] and the development of mathematical models [3, 7, 8].
The authors of Kimura A., Hasegawa H., and others [4] found that under vacuum arc deposition conditions, the hardness of coatings gradually increases from 20 to 32 GPa with increasing x from 0 to 0.6. The author A.L. Kameneva [5] found dependencies that make it possible to predict the tribological properties of systems according to their phase and elemental composition. An improvement of the wear-resistant and antifriction properties of the system with an increase in the content of aluminum and the hexagonal phase in it has been set. The elemental composition of the system formed by magnetron sputtering, electric arc evaporation, and the combined method varies depending on the technological and temperature parameters of substrate preparation and deposition of the system in the following intervals: 8.55–33.14 at.% Al; 40.88–65.80 at.% Ti, 24.92–39.57 at.% N. In the research of O. V. Krysina [6] it was shown that, in significant extent, the potential of the substrate in the deposition process affects the composition of the coatings and concentration of elements. With a change in the substrate potential from 0 to -300 V, the concentration of aluminum considerable decreases; the ratio for also decreases by half.

Previously, the authors of N.V. Belan, V.V. Kolesnik et al [7] developed a model for calculating the component composition of a multicomponent coating. This model is proposed to be used to determine the technological parameters (current density on groups of cathodes-targets; discharge potential; magnitude of the blocking potential) of the process of formation of multicomponent coatings of different stoichiometric composition. However, there is no data confirming that this model is suitable for the process of deposition of coatings from plasma of a vacuum-arc discharge. In the work of I.I. Yagafarov [3] developed a mathematical model of coating growth in a vacuum-arc discharge plasma, in the form of a system of motion equations, growth coverage rate, and shading, that recorded in uniform coordinates, the distinctive feature of which is the configuration and kinematics of the movement of the detail. A computer program that implements a model of coating growth in a vacuum-arc discharge plasma has been developed, characterized in that it allows calculating the thickness and thickness variation of the coating, as well as shape deviation caused by coating, depending on the area of the location of parts, and details. This model does not allow to determine the stoichiometric composition of the coating under different conditions of processing. The authors E.L. Vardanyan, I.I. Yagafarov et al [8] developed a model of the coating process based on the Ti-Al intermetallic compound. On the basis of the model, a software product that allows calculating the ionic saturation current for each of the cathodes and the flow of metal ions per unit area per unit time at an arbitrary point of the vacuum chamber was created. The lack of this model is that it is designed to determine the intermetallic phases of the Ti-Al system only and only in argon.

This work is devoted to the creation of a mathematical model that allows selecting the stoichiometric composition of the Ti-Al-O, Ti-Al-C, Ti-Al-N system coatings depending on the technological regimes of their deposition from the plasma of a vacuum-arc discharge. The mathematical model will make it possible to create a software for digital production, which will greatly ease the work of technologists who will no longer have to select the optimal technological coating conditions during long experiments. Recently, digital production has been increasingly used in the manufacture of any product. Digital production allows the simulation of production processes, aimed at the use of existing knowledge and optimization of technology before the release of the product. Digital production is an integral part of the product development phase, which minimizes the gap between the idea of creation and the real product.

2. Development of mathematical model
This research presents a mathematical model that allows, without conducting numerous experiments, to determine the stoichiometric composition of Ti-Al coatings deposited from a vacuum-arc discharge plasma in environment of various gases (nitrogen, oxygen, carbon).

Summarizing the results of the work of various authors, it can be confirmed that the main technological parameters affecting the stoichiometric composition (figure 1), structure and properties of multicomponent coatings from vacuum-arc discharge plasma are:

- Gas pressure.
- Current of discharge.
- Bias potential.
- Spatial arrangement of samples.

Disturbing factors are:
- Substrate temperature.
- Ion energy.

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**Figure 1.** Factors that affecting the stoichiometric composition of coatings.

The model is based on the guess that it is possible to determine the phase composition of the coating based on the calculation of the percentage of ions at an arbitrary point and comparison with the state diagrams Ti-Al-O, Ti-Al-C, Ti-Al-N [8].

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The model initiates the following assumptions [8]:
- the degree of ionization is close to 100% (the proportion of ions in the total flow of particles moving from the cathode spot of the arc in some cases reaches 90–100%);
- no drip phase.

To determine the phase composition of the coating it is necessary:
1) calculate the ion current density for Ti, Al and gas;
2) calculate the percentage of Al, Ti and gas ions;
3) compare the data obtained with the corresponding state diagram (Ti-Al-O, Ti-Al-C, Ti-Al-N) and determine the phase composition of the coating.

The formula for calculating the current density is taken from a mathematical model of the deposition process of vacuum ion-plasma coatings V.V. Budilov [8]:

$$J_{ib} = \frac{\mu_{p} \cdot I_{D} \cdot Z \cdot e}{\pi \cdot m \cdot R_{k}^{2}} \left[1 + \frac{R_{k}^{2} - l^{2} - b^{2}}{\left( R_{k}^{2} + l^{2} + b^{2} \right)^{2} - 4 \cdot R_{k}^{2} \cdot b^{2}} \right]^{1/2},$$

(1)

\(\mu_{p}\) – cathode erosion coefficient;
\(m_{i}\) – mass of condensing ion;
\(R_{k}\) – cathode radius;
\(l\) – the distance from the end of the cathode to the surface treatment;
The flow of metal ions per unit area per unit of time is determined from the following ratio [8]:

\[ n_i = \frac{J_i}{Z \cdot e}, \]  

(2)

The design scheme of geometric parameters \((l_{Ti}, b_{Ti}, l_{Al}, b_{Al})\), for the previous formulas, is presented in figures 2 and 3 [8].

**Figure 2.** Design diagram of the facility NNV-6.6-I1 for static treatment without table rotation.  
1 – working chamber; 2 – desktop; 3 – Al cathode; 4 – Ti cathode.

After calculating the ion flux per unit area per unit time using the mathematical model, the percentage of aluminum, titanium and gas is calculated at the considered point using the following formulas:

\[
N_{al} = n_{al} \cdot 100 / (\alpha_{al} \cdot n_{al} + \alpha_{Ti} \cdot n_{Ti} + \alpha_{gas} \cdot n_{gas});
\]

\[
N_{Ti} = n_{Ti} \cdot 100 / (\alpha_{al} \cdot n_{al} + \alpha_{Ti} \cdot n_{Ti} + \alpha_{gas} \cdot n_{gas});
\]

\[
N_{gas} = n_{gas} \cdot 100 / (\alpha_{al} \cdot n_{al} + \alpha_{Ti} \cdot n_{Ti} + \alpha_{gas} \cdot n_{gas}),
\]

\( \alpha_i \) – coefficient of condensation, which depends on the angle of inclination of the generator surface to the particle flow and the bias voltage. This coefficient is determined empirically.

**Figure 3.** Design diagram of the facility NNV-6.6-I1 for static treatment without table rotation.  
1 – working chamber; 2 – desktop; 3 – Al cathode; 4 – Ti cathode.
Consider the calculation of the percentage of aluminum, titanium and gas in the case of coating with the rotation of the desktop.

In this case, the concentration of Al, Ti and gas is calculated in a certain number of points located along the entire circumference. The accuracy of the result depends on the number of points. All points are located relative to each other at the same angle.

\[ \varphi = \frac{360^\circ}{K_t} \]

\( K_t = 1000 \) – the number of calculation points located along the entire circumference. The percentage of aluminum, titanium and gas will be calculated by the following formulas:

\[
\begin{align*}
N_{Al} &= \sum_{i=0}^{K_t} n_{Al} \cdot 100 \left( \alpha_{Al} \cdot \sum_{i=0}^{K_t} n_{Al} + \alpha_{Ti} \cdot \sum_{i=0}^{K_t} n_{Ti} + \alpha_{gas} \cdot \sum_{i=0}^{K_t} n_{gas} \right); \\
N_{Ti} &= \sum_{i=0}^{K_t} n_{Ti} \cdot 100 \left( \alpha_{Al} \cdot \sum_{i=0}^{K_t} n_{Al} + \alpha_{Ti} \cdot \sum_{i=0}^{K_t} n_{Ti} + \alpha_{gas} \cdot \sum_{i=0}^{K_t} n_{gas} \right); \\
N_{gas} &= \sum_{i=0}^{K_t} n_{gas} \cdot 100 \left( \alpha_{Al} \cdot \sum_{i=0}^{K_t} n_{Al} + \alpha_{Ti} \cdot \sum_{i=0}^{K_t} n_{Ti} + \alpha_{gas} \cdot \sum_{i=0}^{K_t} n_{gas} \right),
\end{align*}
\]

The calculated values of \( N \) are compared with the state diagram, and the phase composition of the coating is determined.

According to the model, a program has been developed (figure 4), which allows determining the stoichiometric composition of the coatings under various processing conditions. The program is configured to work with the three reaction gases.

The software allows to calculate the ion saturation current for each of the cathodes and the ion current density at an arbitrary point of the vacuum chamber. Possible adjustment of the coating. Based on these calculations, a triple state diagram with an indication of a point with a certain stoichiometric composition is automatically constructed.

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**Figure 4.** Interface of the program “Determination of the stoichiometric composition of coatings based on an intermetallic Ti-Al system deposited from a vacuum-arc discharge plasma in a medium of various gases.”

## 3. Study results and discussions

To determine the concentration of chemical elements in the surface area of the samples under study, quantitative micro X-ray spectral analysis (MRCA) was performed on a JEOL JSM-6490 LV scanning
electron microscope equipped with the Oxford Instruments (United Kingdom) prefix INCA Energy for energy dispersive analysis (EDS).

To determine the effect of the deposition process parameters on the stoichiometric composition of the coatings, samples were obtained at various numbers of table turns (1, 3, 7 and 14 turns) and different locations from the centre of the table (0, 8, 15 and 22 cm) under the following technological modes:

- Pressure in the chamber 0.01 Pa.
- Arc current 60–90 A.
- Substrate voltage 200 V.

![Ti-Al-C](image1.png)

**Figure 5.** The results of EDS with an error indication.

The results of energy dispersive analysis (figure 5) show that a change in the number of turns of the table and the location of the samples relative to the center of the table do not significantly affect the concentrations of elements.

Comparing the obtained calculated data with the experimental results obtained during the experiments, and the results of other authors, it can be argued that the results are the same.
4. Conclusions
A mathematical model has been developed that makes it possible to determine the stoichiometric composition of the Ti-Al-O, Ti-Al-C, Ti-Al-N coatings under given treatment conditions. On the basis of the model, a software was created that allows calculating the ionic saturation current for each of the cathodes and the flow of metal ions per unit area per unit time at an arbitrary point of the vacuum chamber. Using the software product, it is possible to determine the stoichiometric composition of the Ti-Al-O, Ti-Al-C, Ti-Al-N system coatings, depending on the technological modes of their deposition from the vacuum-arc plasma. Experimental results confirmed the adequacy of the mathematical model. The use of the developed model and computer program will allow at the stage of development of the technological process to choose the modes of coating the system Ti-Al-O, Ti-Al-C, Ti-Al-N of a given phase composition.

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