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Mathematical model of deposition process of composite coatings based on intermetallic Ti-Al system by vacuum arc

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Abstract. This work is devoted to mathematical modeling of the process of deposition of composite coatings based on intermetallics of the Ti-Al system from vacuum-arc plasma, considering diffusion processes between alternating layers in order to predict the phase composition of the coating. The physical and chemical processes occurring during layer-by-layer deposition of multilayer coatings based on intermetallics of Ti-Al system by vacuum arc plasma in thin films were investigated. The processes occurring in the deposition of coatings based on intermetallic Ti-Al system by vacuum arc plasma were mathematically described. Diffusion processes were simulated using the finite element method. Diffusion processes occurring between layers of Ti and Al were modeled using Fick equations. Software based on mathematical model that allows to calculate the optimal deposition modes of coatings based on intermetallic Ti-Al system was developed. Influence of the deposition conditions on the content of intermetallic compounds in the coating was determined by X-ray diffraction methods. Results of mathematical model of deposition multilayer coatings considering diffusion processes were compared with experimental data. It is established that in the layer-by-layer deposition of titanium and aluminum, there are two mechanisms for the formation of intermetallic phases: due to diffusion processes and chemical reactions of samples running on the surface. A correlation between the percentage content of intermetallic phases in the coating and the diffusion processes between titanium and aluminum was established.

1. Introduction
Over the past 20 years, a large number of scientific papers have been devoted to the development and manufacture of coatings based on intermetallics of Ti-Al systems and to the study of mechanisms for the formation of intermetallics of Ti-Al systems. Materials based on Ti/Al multi-layer compositions are of great practical interest due to high values of corrosion resistance in aggressive media and strength characteristics [1]. These materials can be used as protective coatings in chemical industry, aerospace engineering, automotive industry, etc. [1-3]. Also, intermetallics coatings has a low friction coefficient and anti-galling properties, so can be recommended as antiadhesion coatings.

In work [4] described a new method for producing coatings based on the intermetallics of the Ti-Al system, based on the simultaneous deposition of Ti and Al from two electric arc evaporators, when the substrate was heated to 700 K. When processing products with rotation in a vacuum chamber, a layer-by-layer deposition process is realized. To predict the composition of the coating and to ensure the necessary conditions for the deposition of intermetallic coatings of a given composition, it is advisable to perform mathematical modeling of the process. To predict the phase composition of the coating, it is necessary to take into account the diffusion processes occurring between the layers of Ti and Al.

This work is devoted to mathematical modeling of the deposition of multilayer composite coatings based on intermetallics of the Ti-Al system from the vacuum-arc discharge plasma, taking into account the diffusion processes between alternating layers in order to predict the composition of the coating.
2. Experimental methods

Coatings were applied while simultaneously spraying two single-component cathodes of Al and Ti, as well as rotating the working table around its axis (figure 1). During the deposition of coatings based on intermetallics of the Ti-Al system with the rotation of the working table, the processed samples passed four regions: I – a region in which only the flow of Al ions comes onto the surface of the sample; II – the transitional region, in which the flow consists of both ions of Al and Ti; III – the region in which only the Ti ions flow comes onto the surface; IV – the region in which the processed surface of the sample is in the shadow zone, and coating does not deposit [4].

Figure 1. Experimental scheme of sequential coating deposition with rotation of the working table around the axis.

In the first region, only the flow of aluminum enters the sample surface. Aluminum layer on the surface of titanium begins to grow islands. The reaction begins at the Al-Ti interface. In the second region, when ions of both metals enter the surface of the sample, the flow ratio varies from 100% Al to 100% Ti and different intermetallic compounds Ti and Al can be formed. The formation of coatings begins with the condensation of ionized Ti and Al particles onto the substrate surface. Adsorbed atoms migrating along the surface and interacting with one another, as a result of fluctuations, are combined into thermodynamically stable nuclei of the new phase, depending on the ratio of the count of Ti and Al atoms. According to the conditions diagram of Ti-Al system the chemical reactions that can be on the surface are:

\[ \text{TiAl}_3 \rightarrow \text{TiAl} + 2\text{Al} \]
\[ \text{Ti} + \text{Al} \rightarrow \text{TiAl} \]
\[ 2\text{Ti} + \text{TiAl}_3 \rightarrow 3\text{TiAl} \]
\[ 2\text{Ti} + \text{TiAl} \rightarrow \text{Ti}_3\text{Al} \]
\[ 3\text{Ti} + \text{Al} \rightarrow 2\text{Ti}_3\text{Al} \]
\[ \text{Ti}_3\text{Al} \rightarrow 2\text{Ti} + \text{TiAl}_3 \]
\[ \text{Ti} + 3\text{Al} \rightarrow \text{TiAl}_3 \]
\[ \text{TiAl} + 2\text{Al} \rightarrow \text{TiAl}_3 \]

Figure 2. Architecture of formed multilayer coating.
In the third region, only the titanium ions flow enters the sample surface. At the same time, the lower intermetallic sublayer is saturation with titanium ions and the intermetallic phase Ti₃Al is formed in the near-surface layer. When the surface is saturated with titanium atoms, a titanium layer begins to grow. In the fourth region, the formed titanium layer is bombarded with argon ions, while the surface layer is activated.

A multilayer coating is formed on the surface at transit of samples through 4 regions (figure 2).

3. Development of mathematical model

The model is based on the assumption of the possibility of determining the phase composition of the coating on the basis of calculating the percentage of ions at an arbitrary point and comparing it with the Ti-Al state diagram. The following assumptions is accepted in model:
- the degree of ionization is close to 100% (the fraction of ions in the total flow of particles moving from the cathode spot of the arc, in some cases reaches 90÷100% [7]);
- microdroplet phase is absent.

The calculation scheme of the geometric parameters is shown in figure 3.

![Calculation scheme of geometric parameters](image)

**Figure 3.** Calculation scheme of geometric parameters: \( l_1 \) – the distance to the aluminum cathode along the axis, \( b_1 \) – displacement from the axis of the aluminum cathode, \( l_2 \) – the distance to the titanium cathode along the axis, \( b_2 \) – displacement from the axis of the titanium cathode, \( \gamma \) – angle of rotation of the working table, \( r_0 \) – the center of the table, \( R \) – distance from the center of the table, 1 – vacuum chamber, 2 – Titanium cathode, 3 – Aluminum cathode.

To determine the density \( j_{i,b} \) of the ion current, the flow of metal ions, formulas are used from the mathematical model of the process of deposition of vacuum ion-plasma coatings of V.V. Budilov [7]:

\[
j_{i,b} = \frac{\mu_p \cdot I_a \cdot Z \cdot e}{2\pi \cdot m_i \cdot R_a^2} \left[ 1 + \frac{R_a^2 - l^2 - b^2}{\sqrt{(R_a^2 + l^2 + b^2) - 4R_a^2b^2}} \right], \quad (1)
\]

where \( i = Ti \text{ or } Al; \mu_p \) – cathode erosion coefficient; \( I_a \) – arc current at the cathode; \( Z \) – average ion charge; \( e \) – electron charge; \( m_i \) – mass of a condensing ion; \( R_a \) – cathode radius; \( l \) – distance from the end of the cathode; \( b \) – displacement from the axis of the cathode;

\[
n_i = \frac{j_i}{Ze}, \quad (2)
\]

where \( n_i \) – flux of metal ions, ion/m².

To determine the thickness of the layers of coatings, a formula is used from Budilov’s and Yagafarov’s coating deposition model [5], in which the possibility of taking ion flows from several electric arc evaporators:

\[
V_{ki} = \frac{m_{Al} \cdot k \cdot j_{1,b}}{Ze \cdot \rho} \cdot \sin(\alpha_{ni}) + \frac{m_{Ti} \cdot k \cdot j_{1,b}}{Ze \cdot \rho} \cdot \sin(\alpha_{ni}) \quad (3)
\]

where \( k \) – Boltzmann constant, \( \rho \) – density of materials.
To calculate the thickness of the coating using equation:

\[ h = V_k \cdot t \]  \hspace{1cm} (4)

where \( V_k \) – speed of deposition, \( t \) – processing time.

To simulate the diffusion processes between layers in the coating, Fick's equations are used. The first equation (5) describes the specific flux of the diffusing element in the metal. A minus sign means that the flow is directed from a region with a higher concentration to a region with a lower concentration.

\[ J = -D \frac{\partial c}{\partial x} \]  \hspace{1cm} (5)

where \( D \) – diffusion coefficient, m²/s; \( c \) – concentration of saturating element, mol/m³; \( x \) – coordinate, m.

The diffusion coefficients of titanium in aluminum at temperature 700K was \( 10^{-20} \) m²/s and aluminum in titanium was \( 10^{-20} \) m²/s [8, 9]:

The above formulas describe the mathematical model of the deposition of multilayer composite coatings based on intermetallics of the Ti-Al system, which was allow us to calculate the thicknesses of Ti and Al layers during vacuum arc discharge deposition from the plasma, and determine the depth of the diffusion layers between Ti and Al.

Preliminary calculations have been made for the correlation between the spatial arrangement in the vacuum chamber and the layered structure of the coatings obtained from the vacuum-arc discharge produced by the deposition of titanium and aluminum from the plasma with the rotation of the part in the chamber.

4. Results and discussion

The results of the calculations showed that when the location of the design point in the vacuum chamber changes from the center of the working table \( (r_0=0) \) to the point \( (R=22 \text{ cm}) \) located close to the arc-evaporators, the widths of (a, c) regions of deposition of pure Ti or Al are identical and remain equal to 1200. While, the region (b) in which the simultaneous deposition of titanium and aluminum occurs is reduced from 600 \( (r_0=0) \) to 0 \( (R=22 \text{ cm}) \). The angle between the normal vector of the surface being processed and the normal vectors of the cathodes of electric arc evaporators is increased.

To determine the phase composition of the coating, modeling of the diffusion processes was carried out using the finite element method. At the first stage, a simplified model of the coating architecture is created, consisting of several rectangles whose height corresponds to the calculated thicknesses of the Ti and Al layers.

Based on the results of calculations of diffusion processes, it is established that the thickness of the diffusion layers of titanium in aluminum and aluminum in titanium at a deposition temperature of \( \sim 700 \text{ K} \), regardless of the thickness of the Ti and Al layers, is the same and is on the order of 2-2.2 nm.

To check the adequacy of the developed mathematical model and estimate the reliability of the calculated results, coatings of the Ti-Al system were deposited according to the calculated technological regimes on samples from stainless steel materials. The thickness of coatings on all samples was in the range 3-3.5 \( \mu \text{m} \).

![Figure 4](image-url)

**Figure 4.** Results of simulation of diffusion processes: a) Simplified model of the coverage architecture, b) mesh for calculated diffusion processes; c) calculation results.
After deposition of the coatings, X-ray diffraction studies were performed to determine the phase composition. The results of quantitative X-ray diffraction analysis depending on the spatial arrangement and number of layers are given in table 1.

**Table 1. Results of quantitative diffraction analysis of coatings.**

| Number of layers | Ti  | Al  | TiAl | TiAl3 | R  |
|------------------|-----|-----|------|-------|----|
| 120              | 43  | 3   | 10   | TiAl  | 34 |
|                  | 13  | 18  | TiAl3| TiAl3 | 14 |
|                  | 8   | 0   | 23   | 14    | 31 |
|                  | 0   | 17  | 22   |       |    |
| 360              | 50  | 12  | 10   | TiAl  | 35 |
|                  | 35  | 9   | 13   | TiAl3 | 14 |
|                  | 9   | 0   | 11   | 13    | 36 |
|                  | 0   | 2   | 17   | 18    |    |
| 840              | 63  | 9   | 13   | TiAl  | 53 |
|                  | 0   | 11  | 19   | TiAl3 | 60 |
|                  | 0   | 9   | 13   | TiAl3 | 48 |
|                  | 0   | 12  | 9    |       |    |
| 1680             | 63  | 9   | 13   | TiAl  | 53 |
|                  | 0   | 11  | 19   | TiAl3 | 60 |
|                  | 0   | 9   | 13   | TiAl3 | 48 |
|                  | 0   | 12  | 9    |       |    |

Analysis of the XRD results shows that the maximum percentage of intermetallic phases, at different layer thicknesses, is observed for samples located at the center (r0) of the table. As the sample attachment radius increased, the total content of intermetallic phases decreased, which was due to a decrease in the width of the (b) region of simultaneous deposition of Ti and Al. On the samples (R=22 cm), intermetallic phases are formed only due to diffusion processes, because the region of simultaneous deposition of titanium and aluminum is absent. For example, according to the calculated data for samples with the number of layers 120, the total thickness of the diffusion layers is hΣ120 = ΔDifTi-Al120 = 2.2 nm, which is 8.5% of the total coating thickness (3.0 µm). The experimental results showed that the total volume of intermetallic compounds is 10%. For example with a number of layers of 360, the percentage of intermetallic compounds increased to 13% and hΣ360 = ΔDifTi-Al360 = 2 nm ·360 = 720 nm (of the total coating thickness (3.4 µm) is 20%). With the entrainment of the number of layers, the deviation of the calculated and experimental data increases, which is associated with a decrease in the thickness of the aluminum layers. On samples with the number of layers 840 and 1680, the percentage of aluminum is 0. This indicates that the entire volume of aluminum diffused into the titanium layers, and intermetallic phases were formed with a total percentage content of up to 22%. To increase the percentage of intermetallic phases, it is necessary to increase the number of layers, and the thickness of the layers for aluminum 3-5 nm and for titanium 1-2 nm. Thus, it has been experimentally proven that by increasing the attachment radius of parts, the width of the region of simultaneous deposition of Ti and Al decreases, which leads to a decrease in the percentage of intermetallic phases in the coating composition.

### 5. Conclusion

The physicochemical processes taking place in the layer-by-layer deposition of coatings based on intermetallics of the Ti-Al system from the vacuum-arc discharge are investigated. A mathematical model has been developed that takes into account the diffusion processes occurring during the deposition of coatings based on intermetallics of the Ti-Al system from the vacuum-arc discharge plasma. The influence of technological deposition parameters (arc current, voltage) on the growth rate of layers of titanium and aluminum has been studied experimentally. A correlation between the percentage content of intermetallic phases in the coating and the diffusion processes between titanium and aluminum was revealed. It is established that in the layer-by-layer deposition of titanium and aluminum, there are two mechanisms for the formation of intermetallic phases: due to diffusion processes and chemical reactions of samples running on the surface.

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