Deposition of Functional Coatings Based on Intermetallic Systems TiAl on the Steel Surface by Vacuum Arc Plasma

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Abstract. Laws governing the formation of intermetallic phase by sequential deposition of nano-sized layers coatings from vacuum arc plasma were studied. Mathematical modeling process of deposition by vacuum arc plasma was performed. In order to identify the structural and phase composition of coatings and to explain their physical and chemical behaviour XRD studies were carried out. Production tests of the hardened punching tools were performed.

1. Introduction
Development of new coating materials with advanced physical and chemical properties as well as technologies of their deposition are considered the potential areas of industrial development. Such materials include composite intermetallide-based multicomponent materials with unique properties and ability to maintain their ordered structure up to melting temperatures. Ti-Al system is considered to be rather promising in the field of creating layered metallic and intermetallic composites, first and foremost due to low density and advanced physical and mechanical properties.

Multiple methods are used to obtain intermetallide-based coatings within TiAl system: self-propagating high-temperature synthesis (SHS) [1], ion implantation [2], deposition of composite cathode coatings, high-current pulse electron beam irradiation of Ti-based Al coatings [3], alternate deposition of Ti and Al layers (from 5 to 500 nm) with further thermal treatment (700-1200K). However, the existing methods are technologically complex and require multiple stages of their implementation.

Main intermetallitic compounds of Ti-Al system are formed in the range of temperatures varying from 850 to 1200 °C. However, thin-film coatings are characterized by temperature variations of phase transitions depending on their thickness. Under certain conditions coatings are subject to formation and stabilization of phases, which are not observed in bulk samples [4].

The description of a method to obtain intermetallide-based coatings within TiAl system during simultaneous deposition of vacuum arc discharge plasma is presented in work [5]. The work also includes research results of layer-by-layer deposition of multilayered coatings with the thickness of layers ranging from 1 to 0.1 μm, according to which intermetallides are not formed in coatings. Nanostructured multilayered coatings with the thickness of layers less than 0.1 μm were not studied. Thus, the purpose of this work is to study regularities during the formation of coating intermetallic phases during layer-by-layer deposition of nano-sized layers from vacuum arc discharge plasma.
2. Mathematical modeling

In the course of deposition of intermetallide-based coatings within TiAl system the treated samples pass 4 areas during rotations of a table:

1. Area where only aluminum ion flux gets to the surface;
2. Area where aluminum and titanium ion fluxes get to the surface;
3. Area where only titanium ion flux gets to the surface;
4. Area where the treated surface is located in the shadow zone.

In order to predict phase composition of coatings it is advisable to use the mathematical model of deposition process from vacuum arc discharge plasma. To identify stoichiometric composition of coatings there is a need to: calculate the density of Al and Ti ions fluxes; calculate thicknesses of nano-sized layers of Ti, Al and a transition layer per single rotation of a table. All calculations for stoichiometric composition and thickness of layers were carried out using Budilov and Yagafarov’s model thus taking into account various patterns of electric-arc sources.

The following formula [5] was used to calculate the density of ion fluxes:

\[
j_i = \frac{\mu_p \cdot I_a \cdot \pi \cdot e}{2 \cdot \pi \cdot m_i \cdot R_c^2} \times \left[1 + \frac{R_c^2 - l^2 - b^2}{\left((R_c^2 - l^2 - b^2)^2 - 4 \cdot R_c^2 \cdot b^2\right)^{1/2}}\right]
\]  

(1)

where \(i\) – Ti or Al, \(\mu_p\) – coefficient of cathode erosion, \(I_a\) – arc current at the cathode, \(R_c\) – cathode radius, \(l\) – distance from the face of the cathode; \(b\) – relative displacement of cathode axis.

The thickness of coatings was defined according to the formula:

\[h = V_k \cdot t\]  

(2)

The following algorithm was used for calculations of layers thickness during deposition from two electric-arc sources with single component Ti and Al cathodes and rotation of a table round its axis: measurement of the amount of targeted points depending on the table rotation rate and definition of its geometrics (\(l, b,\) deposition angle); calculation of density of Ti and Al ions fluxes and their growth rate in every point; definition of the total thickness per one turn of the table. Calculation results of Ti, Al and transition layers thickness at various rotation rates of a table are shown in Figure 1.
Calculations show that with the increase in the rotation rate the thickness of coating decreases from 228 to 8 nm per one rotation, whereas the thickness of Ti layers changes from 60 nm per 1 rpm and at the distance of 22 cm from the center to 2.5 nm per 14 rpm and position in the center of the table. Al thickness varies within the range of 168 nm to 5 nm at the same modes.

3. Experimental methods
Deposition of intermetallide-based coatings of Ti-Al system was carried out using NNV-6.6-I1 unit. Technological modes were adjusted within the following limits: pressure in a chamber $P = 10^{-1} - 10^{-2}$ Pa; arc current $I = 40 - 120$ A; treatment time 60 - 75 min. Deposition scheme of intermetallide-based coatings of Ti-Al system and layout of samples is shown in Figure 2.

During rotation of the table at the rate of 1 rpm multilayered coating with subsequent Ti and Al layers is formed on the surface of a sample. During deposition approximately 120 layers are formed in the coating within 60 min. The thickness of layers decreases with the increase in the rotation rate of the table, while their quantity increases. Thus, the number of layers amounts to 360 at the rotation rate of 3 rpm, 840 - at 7 rpm, and 1680 layers at 14 rpm.
In order to determine structural and phase composition of coatings and explain their physical and chemical behavior X-ray diffraction study was carried out. The X-ray diffraction analysis of coatings was performed using DRON-3 diffractometer in Co K-alpha radiation at 30kV voltage and 20 mA current. Angular spacing of 2-theta scanning = 30-130°.

4. Results and discussion

After depositing nanostructured coatings using the developed method the following intermetallic phases of Ti-Al system were identified on XRD patterns of P6M5 steel samples surface: TiAl, TiAl3. The depth of a layer involved in the formation of a diffraction pattern makes ~ 7 µm, and the thickness of coatings varies from 3 to 5 µm. Thus, the analyzed depth during X-ray diffraction analysis of samples exceeds the thickness of coatings. Therefore, XRD patterns have iron peaks, and at quantitative analysis the percentage of iron will depend on the thickness of coatings.

Results of quantitative XRD analysis depending on spatial arrangement and number of layers are presented in Table 1.

| Number of layers | Distance from the center of a table R, cm. |
|------------------|------------------------------------------|
|                  | 22                                       | 15 | 8 | 0 |
| Fe Ti Al Ti Al 3| Fe Ti Al Ti Al 3 | Fe Ti Al Ti Al 3 | Fe Ti Al Ti Al 3 | Fe Ti Al Ti Al 3 | Fe Ti Al Ti Al 3  |
| 120              | 27 43 3 13 32 34 13 18 3 34 28 0 23 14 26 31 4 17 22 |
| 360              | 22 - 11 - 10 30 32 13 14 11 27 35 - 14 13 28 36 2 17 18 |
| 840              | 13 50 16 12 10 40 35 3 9 13 24 49 0 11 16 35 48 - - 4.8 6.2 |
| 1680             | 14 63 0 9 13 17 53 0 11 19 18 60 0 9 13 31 48 0 12 9 |

Quantitative XRD analysis made it possible to develop dependency diagrams of the percentage of Ti-Al system intermetallide content in a coating at simultaneous deposition from vacuum arc discharge plasma with two unicomponent Ti and Al cathodes in inert-gas Ar on the number of layers and spatial arrangement. The diagrams are shown in Figure 3.
The results of quantitative phase XRD analysis show that at various treatment modes (rotation rate, number of layers, thickness of layers) the percentage of Ti increases from 30 to 50% with the increase of the number of layers and decrease in their thickness, thus the percentage of Al content decreases from 4-6% when the number of layers equals 120 to 0 when their number amounts to 1680. The percentage of TiAl intermetallic also decreases from 17 to 12% with the increase in the number of layers, while the amount of TiAl\textsubscript{3} phases increases from 5 to 20%. Thus, with the increase of the number of alternating layers and decrease of their thickness almost all aluminum, being part of the coating, reacts with titanium and hence forms intermetallics of TiAl\textsubscript{3}+TiAl phases. At bigger thickness of >40 nm and a number of ~ 120 layers, not all aluminum is able to react with titanium. In order to increase the percentage of intermetallic content in a coating there is a need to increase the density of aluminum ion fluxes and to deposit a coating at high rotation rate of a table to ensure the increase in the number of layers.

The following combination of layers is suggested as a hardening multilayered composite coating to improve performance properties of punching tools: Ti-TiAl\textsubscript{3}-(TiAl)N. The thickness of multilayered wear-resistant intermetallic-based coating within Ti-Al system amounts to 4-4.5 µm.

Production test results (Fig. 4) demonstrated the increase in the resistance of punching tools with Ti-TiAl\textsubscript{3}-(TiAl) N coating by 6-7 times in comparison with the technology applied at BelZAN plant, and by 1.3-1.5 times in comparison with other coatings.

![Figure 3. Dependence of the percentage of Ti-Al system intermetallide content at layer-by-layer deposition on the number of layers and spatial arrangement: A) TiAl\textsubscript{3}; B) TiAl.](image)
5. Conclusions
The results of the undertaken study show that with the increase in the number of alternating layers up to 1680 and decrease of their thickness up to 3-5 µm the percentage of TiAl₃ phase increases from 5 to 20%. Moreover, production tests of punching tools with Ti-TiAl₃-(TiAl)N composite coating demonstrated the increase in the resistance by 6-7 times in comparison with the technology applied at the plant.

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