Synthesis of MAX-phases, structure and phase composition of modified layers on titanium alloy VT-1 as a result of electron-beam treatment

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Abstract. The article presents the results of research and identification of optimal conditions of formation of MAX-phases during treatment of titanium alloy VT-1 by an electron beam in a vacuum. The study of strength characteristics, thermal properties of composite layers was carried out. Thermodynamic study of phase equilibrium in Ti-Si-C and Ti-B-C systems under high vacuum conditions was carried out in order to optimize conditions of formation of functional layers. A mathematical model of the thermal impact of a powerful fast-moving electron beam on the surface of a titanium alloy has been developed VT-1 under the conditions of electron beam processing in the framework of the theory of thermal conductivity using the COMSOL Multiphysics software complex. The obtained numerical results made it possible to investigate the regularity of the distribution of temperatures and their rates of change depending on the action of the electron beam.

1. Introduction

Currently, much attention is paid to the study of MAX-phases synthesized by various methods in the nanostructured state in the form of layers, ceramics, while the thermodynamic properties of MAX phases are not sufficiently investigated. The authors of the article performed thermodynamic modeling of phase equilibrium in Ti-Si-C and Ti-B-C systems under high vacuum conditions. Optimal conditions of MAX-phases formation during treatment of titanium alloy VT-1 electron beam in vacuum were revealed.

The use of an electron beam as a heating source makes it possible to significantly expand the possibilities of surface modification of alloys and metals [1]. The advantages of electron beam processing include the ability to finely control thermal processes and adjust modes; the purity of the experiment associated with the vacuum process; high efficiency (up to 90%); and the ability to automate the process [2-4].

The best operational properties of titanium alloy parts are products on the surface of which corrosion-erosion-resistant nano-coatings based on the MAX-phases of the Ti-Si-B and Ti-Al-C systems are applied. In practice, coatings of Ti and Zr nitrides are more commonly used, which is associated with satisfactory application technology [5, 6].
2. Experimental part

2.1. Mathematical model of thermal fields

To build a three-dimensional model of electron beam processing, the Comsol Multiphysics universal software complex was chosen. Comsol Multiphysics is a finite element method-based environment for numerical modeling of systems, devices, and processes, designed for computer modeling of physical tasks.

Simulation of the electron beam processing using the Comsol Multiphysics software complex included several stages. The first step was to select the dimension of the model, set geometry, global variables. Sample and processing parameters were set: electron beam power was 400 W, electron beam diameter 1 mm, sample height 7 mm, coating thickness 1 mm. The second stage was the assignment of materials for the sample and coating. To simulate the processing process, a sample of titanium alloy VT-1 was selected and its main thermophysical properties set, coating - B, lat. Borum. The next important step was grid generation. The triangular grid was selected in the model, and the grid size - fine. Adaptive mesh compaction was used in areas where the greatest error was expected.

The Heat Transfer in Solids module was used to investigate temperature change, define boundary conditions and simulate the electron beam effect on the sample surface. Using the Deposited Beam Power node, a heat source, an electron beam, were modeled. The motion of the electron beam along the x and y-axis was specified using the Analytic and Interpolation functions. The heat source was represented as a normally distributed on surface and volume:

\[
f(o,e) = \frac{1}{2p\sigma^2} \exp \left( -\frac{d^2}{2\sigma^2} \right), \quad d = \frac{\|e \times (x-o)\|}{\|e\|},
\]

where \(\sigma\) is standard deviation, \(o\) is beam movement coordinates, \(d\) is diameter of electron beam, \(p\) is electron beam power.

![Figure 1. Temperature distribution after one pass by electron beam over the surface of the simulated sample.](image1)

![Figure 2. Temperature distribution after 60 seconds of electron beam treatment of the sample.](image2)

Figures 1 and 2 show the results of simulating the temperature distribution over the surface and volume of the sample at different time intervals. After one pass by electron beam, the temperature reached 200°C.

As a result of 60 seconds of electron beam exposure to the sample surface, the temperature reached 1150°C. Maximum temperatures were reached on the surface in the central part of the sample.

Figures 3 and 4 show the temperature distribution over the depth of the sample after one pass with an electron beam and after 60 seconds of processing the sample. Within 60 seconds, the model of the
sample was heated in-depth, but the lower part of the sample remained cold, which is associated with the specified conditions of electron-beam processing.

![Figure 3. Temperature distribution by sample depth after one pass.](image1)

![Figure 4. Temperature distribution by sample depth after 60 seconds of treatment.](image2)

Figures 5 and 6 show calculations of heating and cooling rates in the electron beam exposure zone during sample processing. They reached about $10^4$-$10^5$ K/s, which proved that the process is high-speed. Temperatures were calculated at the cooling stage, after the electron beam exposure was completed at various points.

![Figure 5. Heating rates.](image3)

![Figure 6. Cooling rates.](image4)

2.2. **Research method**

Samples made of titanium alloy VT-1 were selected for the experiment. Layers of saturating or reaction coatings were formed. The saturating coatings contained a reaction component (Si:2C) and an organic binder. A solution of 1:10 of BF-6 adhesive in acetone [7] was used as the organic binder.

Electron beam processing of samples was carried out at a vacuum plant with an axial electron gun EPA-60-04.2 with a control unit for 1-3 minutes at a power of 250-450 W, electron beam diameter 1 mm. Technical parameters of high-voltage rectifier: acceleration voltage is 30 kV, direct current is 100 A, electron beam current is 2 mA, direct heating voltage is 10 V and electron beam voltage is 2 kV. The maximum operating pressure in the vacuum chamber did not exceed $2\times10^{-3}$ Pa [8]. The microstructure of transverse thin sections of the samples was examined on a METAM RV-21 metallographic microscope equipped with a VEC-335 digital camera and NEXSYS ImageExpert Pro.
3.0 software for quantitative metallographic analysis. X-ray phase analysis (XPA) was carried out on a Phaser 2D Bruker diffractometer (Cu Kβ1 - radiation).

The TERRA software system simulated phase equilibrium in the Ti-B-Si-C system [9]. The temperature range of the calculations was 300-4500 K. The total pressure in the system ranged from $10^5$ to $10^3$ Pa. Particular attention was paid to the Ti-Si-C system.

3. Result and discussion

Layers of composites 80-100 μm thick are formed (figure 7). The structure of the layers is eutectic.

![Figure 7. Structure of Ti-Si-C layer on titanium alloy VT-1.](image)

A study of the structure and chemical composition of the formed composite layers revealed that the formation process is very complex. The layers contain individual particles of titanium silicides, double carbides of titanium, and silicon (MAX-phase Ti$_3$SiC$_2$).

According to X-ray phase analysis (figure 8), the composite layer contains 76.5% crystalline and 23.5% amorphous phases. The metal base consists of 84.06% titanium with a hexagonal cell and 4.06% with a cubic cell. The layer contains double carbide Ti$_3$SiC$_2$ and silicon carbide $\beta$-SiC (PDF 01-073-1665), Pg. F43m, with cubic cell $a = 0.4358$ nm.

![Figure 8. X-ray diffraction pattern of a layer Ti-Si-C on titanium alloy VT-1.](image)
Figure 9 shows the Ti-Si-C-B concentration tetrahedron. Silicides Ti\textsubscript{3}Si, Ti\textsubscript{5}Si\textsubscript{3}, Ti\textsubscript{5}Si\textsubscript{4}, TiSi, and TiSi\textsubscript{2} took part in the calculations; carbides B\textsubscript{4}C, SiC, TiC; borides TiB, TiB\textsubscript{2}, and double carbides (MAX phases) Ti\textsubscript{3}SiC\textsubscript{2}, Ti\textsubscript{5}Si\textsubscript{3}C\textsubscript{x}.

Figure 9. Concentration tetrahedron Ti-B-C-Si.

The processes of formation of titanium carbides and borides occur with the release of a significant amount of energy, thereby increasing the temperature in the system to 2000-2150 K ($P = 10^5$ Pa) and 1600-1725 K ($P = 10^{-3}$ Pa).

The introduction of thermodynamic properties on titanium silicides and carbides into the base made it possible to clarify the crystallization fields of coexisting phases, which is very important when analyzing the sequence of chemical transformations and the interaction in a system involving titanium, silicon, and carbon.

The data presented are in accordance with the phase equilibrium in the Ti-Si-C triple system at total atmospheric pressure ($P = 0.1$ MPa).

**Conclusion**

A three-dimensional model of the electron beam treatment on the sample surface was modeled. Features of the introduction of the intensively focused electron beam into titanium alloy VT-1 were investigated. A model of electron beam impact on the surface of a metal alloy has been developed. The motion of the electron beam along the x and y-axis was specified using the Analytic and Interpolation functions. The temperature distribution is obtained over the surface and deep into the sample in the direction of electron beam movement at the stage of heating and cooling. Calculations of heating and cooling rates in the electron beam exposure zone - $10^4$-$10^5$ K/s are presented.

A thermodynamic study of phase equilibrium in Ti-Si-C systems under high vacuum conditions was carried out. Physical and chemical processes occurring during electron beam exposure were identified and analyzed. Thermophysical and thermochemical models of the formation of composite layers and coatings based on silicon carbides/borides and titanium on the surface of titanium alloy VT-1 under the influence of intensive electron beams have been developed.

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