Thermodynamic model of the metal-ceramic coating formation on titanium surface by laser treatment

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Abstract. The article is concerned with mathematical modeling of the method of laser treatment of titanium surface by the finite-element method in the FlexPDE program to obtain a qualitative and quantitative picture of the heating process of the treated surface that consists of the temperature field on the surface and in the bulk.

1. Introduction
The main physical characteristic of laser action to the material is the process of treated surface heating, consisting of a temperature field on the surface and bulk, which can be determined by theoretical or experimental methods [1–5]. The temperature effect on the material depends on the energy and technological parameters of laser treatment: laser power concentration, duration of laser action, pulse-recurrence rate, diameter of the heat-affected zone, thermal diffusivity of the process material [6–10]. During the process design of laser treatment, it is necessary to have a clear idea of the basic parameters of process conditions, their interrelationships and influence on the criteria for determining the quality of the generated surface. Optimization of the parameters of process conditions according to the quality criteria is the basic principle of choosing the conditions of any technological process and the process of laser surface modification [11–14].

The correct combination of the main parameters of laser treatment and technological methods will ensure the achievement of quality criteria: stress-related characteristics, morphological heterogeneity, absence of internal and external defects, chemical and phase-structural composition of the formed coatings.

A number of physical phenomena and processes that affect the quality criteria of coatings accompanies the formation of metal-ceramic coatings on the surface of titanium during pulsed laser treatment. Review of these phenomena will allow controlling the process of modification and reasonably choosing the technological modes of formation of metal-ceramic coatings on the surface.

2. Materials and methods
Modeling of the process of laser modification of the titanium surface by the finite-element method was carried out in the FlexPDE program with obtaining the distribution of temperature fields in the treatment area and calculating the temperature in the laser impingement point according to laser fluence, laser output power, pulse duration, pulse-recurrence rate and the number of pulses applied to one point.
The following thermal and physical characteristics of treated titanium were used (density \( \rho = 4507 \) kg/m\(^3\), melting point TPL = 1668 °C, heat conduction coefficient \( \lambda = 21.9 \) W/(m\( \cdot \)K), thermal diffusivity \( a = 1.19 \times 10^{-4} \) m\(^2\)/s).

The surfaces of experimental samples made of titanium VT1-00 (GOST 19807-91) were subjected to pulsed laser treatment on Nd:YAG-laser technological complex LRS-50 with a wavelength of 1,064 microns in the air with varying technological parameters of laser treatment: the voltage at the pump lamp U from 310 to 450 V, pulse duration \( \tau \) from 3.3 to 8 ms, repetition rate \( f \) from 1 to 2 Hz and the number of pulses applied at one point \( N \) from 2 to 5.

X-ray diffractometer “Xcalibur/Gemini A” was used to carry out X-ray diffraction analysis (XRD) of the compounds formed as a result of pulsed laser treatment using an x-ray tube with a copper anode. For the analysis of diffractograms software envelope “Match! 2003-2009”, Crystal Impact (Bonn, Germany), using databases, “American Mineralogist Crystal Structure Data base” (AMCSD) and “Crystallography Open Database” (COD) was used.

3. Results and discussion
The proposed scheme of the model of interaction of pulsed laser radiation with the surface of a solid body (figure 1), is most compliant with the experiment and presents a system that consists of a titanium base with a size of 10×10×2 mm, which is effected by laser radiation moving along a reference trajectory.

![Figure 1](image)

As the profile of the temperature field in the zone of thermal action has a Gaussian distribution, the haulage distance assigned by the pulse repetition frequency and the number of pulses is selected from the condition of obtaining a rational 50 % overlap to obtain the most uniform thickness of the modified layer (figure 2).

![Figure 2](image)
When the concentrated radiation source interacts with the treated surface, in the impact spot a heat source with a normal distribution of the power and energy density appears.

In the calculation of thermal processes in the course of laser treatment, the Gaussian spatial distribution of the heat flux rate in the heating spot with radius \( r \) is usually used [1, 2]:

The thermal input \( q \) of a normally circular source is determined by:

\[
q_m (r) = q_m e^{-kr^2},
\]

where \( q_m \) is the maximum power density at the heating spot center; \( k \) is the concentration coefficient characterizing the shape of the normal distribution curve; \( r \) is the radial distance of this point from the center.

The power density for the Gaussian distribution will be determined by the formula:

\[
q = \frac{P}{2\pi \int_0^r e^{-kr^2} r dr},
\]

where \( P \) is the laser power.

The temperature on the treated surface \( T \) depends on the falling power density \( q \) and energy density \( Q \).

The relation between temperature and laser power density can be determined from the thermal conductivity equation:

\[
\frac{\partial T}{\partial \tau} = a \Delta T = \frac{Q_0 (x, y, z, \tau)}{\rho c},
\]

where \( Q_0 \) is the volume density of the absorbed light flux, \( a \) is the thermal diffusivity, \( \rho \) is the material density, \( c \) is thermal capacitance of the material.

To solve the equation (3) it is necessary to set 1 initial condition and 6 boundary conditions, and determine \( Q_0 (x, y, z, \tau) \):

\[
T_{x, y, z, 0} = T_{u}, \quad T_{x=0, \tau} = T_{y=0, \tau} = T_{z=0, \tau} = T_{u}
\]

\[
\frac{\partial T}{\partial x_{0, \tau}} = \frac{\partial T}{\partial y_{0, \tau}} = \frac{\partial T}{\partial z_{0, \tau}} = 0, \quad Q_0 = q_0 (1 - R) e^{-\alpha}
\]

After solving equations (4) and (5) we need to determine the relationship between temperature \( T \) and power density \( q \) in the form:

\[
T = f \left[ q_0 (1 - R), \rho, c, a, R, \alpha, x, y, z, \tau \right],
\]

where \( q_0 (1 - R) \) – absorbed power, \( \rho, c, a, R, \alpha \) – thermal and optical parameters, \( x, y, z, \tau \) – arguments.

Because of the pulse heating \( r_0 >> \sqrt{a \tau} \) is used, the surface temperature will be determined by the formula:

\[
T = \frac{2q_0 (1 - R) \sqrt{a \tau}}{k \sqrt{\pi}} + T_{u}
\]

Equation (7) allows us to calculate the liminal power density \( q_{THR} \) that is necessary for heating the surface to a given temperature. In our case, up to the temperatures of formation of metal-ceramic compounds \( TiO, TiO2 \) and \( TiN \):

\[
q_{imp}^{THR} = \frac{(T - T_0) k \sqrt{\pi}}{2(1 - R) \sqrt{a \tau}}
\]
The results of modeling the temperature distribution in the interaction of pulsed laser radiation with different energy parameters show that the temperature on the surface of the treated titanium increases because of the energy parameters of the laser radiation increases (figure 3). So the minimum temperature on the titanium surface is 730 K and is achieved on exposure to laser radiation and energy density \(Q=0.3\times10^7 \text{ j/m}^2\). The upper design temperature is 2450 K, using \(Q=3.3\times10^7 \text{ j/m}^2\).

The required temperature for the formation of titanium-based metal-ceramic compounds such as TiO, TiO\(_2\) and TiN is determined from the state diagrams Ti–O and Ti–N. Thus, the formation of TiO and TiO\(_2\) requires a temperature of 1300–1800 K at an oxygen concentration of about 45–50 %. This temperature range is achieved by using the energy density of the laser radiation from \(0.6\times10^7 \text{ j/m}^2\) to \(2.4\times10^7 \text{ j/m}^2\), the surface layer melts because surface temperature exceeds fusing point of titanium which corresponds to the modification of the titanium surface with its melting. The formation of titanium nitride requires a temperature of 1100 – 2350 K, which is achieved by using an energy density of \(1.2\times10^7 \text{ j/m}^2\) to \(3.0\times10^7 \text{ j/m}^2\).

According to the fact that it is required to obtain metal-ceramic coatings on the titanium surface with oxide and nitride phase components, the recommended ranges of energy parameters of laser treatment are power from 3 to 10 W, energy from 25 to 95 j, power density from \(0.1\times10^7\) to \(0.5\times10^7\) W/m\(^2\), energy density from \(0.8\times10^7\) j/m\(^2\) to \(3.0\times10^7\) j/m\(^2\). These values are achieved by varying the technological parameters of laser treatment: the voltage at the pump lamp \(U\) from 310 to 400 V, pulse duration \(\tau\) from 3.3 to 8 ms, repetition rate \(f\) from 1 to 2 Hz and the number of pulses applied at one point \(N\) from 2 to 5.

A further increase of the energy parameters of laser treatment is not appropriate, because such temperatures will destruct the surface layer and lead to the distortion of the samples.

XRD of the surface of the samples subjected to pulsed laser treatment (figure 4) revealed the formation of metal-ceramic coatings on the surface of titanium, such as titanium monoxide TiO and titanium nitride TiN, as well as the phase of \(\alpha\)-Ti.

Thus, at low energy exposure to \(1\times10^7 \text{ j/m}^2\), a metal-ceramic film consisting of titanium monoxide TiO and \(\alpha\)-Ti is formed on the titanium surface. With increase of the treatment energy parameters, the temperature on the surface of titanium increases, that leads to additional saturation with nitrogen and the formation of titanium nitride TiN.
The analysis of the XRD spectra shows that with the increase in the energy density supplied to the treated surface, the phase composition of the coating changes: the content of titanium monoxide increases, titanium nitride appears, the content of the $\alpha$-Ti phase decreases, which confirms the adequacy of the proposed mathematical model.

4. Conclusion
The modeling of titanium surface treatment process by pulsed laser radiation was conducted. It based on the solution of three-dimensional system of differential equations by finite element method using FlexPDE software, which allows calculating temperature fields both on the surface of the material and in its bulk. During the modeling, according to the values of the temperature fields, the ranges of variation of the energy parameters of laser processing for the formation of a metal-ceramic coating on the surface of titanium with oxide and nitride phase components were determined: laser output power from 3 to 10 W, laser energy from 25 to 95 j, power density from $0.1 \times 10^7$ to $0.5 \times 10^7$ W/m$^2$, energy density from $0.8 \times 10^7$ j/m$^2$ to $3.0 \times 10^7$ j/m$^2$. These values are achieved by varying the technological parameters of laser treatment: the voltage at the pump lamp $U$ from 310 to 400 V, pulse duration $\tau$ from 3.3 to 8 ms, repetition rate $f$ from 1 to 2 Hz and the number of pulses applied at one point $N$ from 2 to 5.

Acknowledgements
The study of the technological modes of the laser modification of the titanium surface was carried out with the financial support of the RFBR according to the research project № 18-38-00677 mol_a. The study of X-ray diffraction phase analysis of coatings was carried out with the financial support RF President stipend SP-5048.2018.4 for young scientists and graduate students. The development of a thermodynamic model of coating formation on the surface of titanium during laser processing was carried out with the financial support of RF President stipend SP-5291.2018.4 for young scientists and graduate students.

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