

# Coating synthesis controlled by electron-beam heating

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**Abstract.** The methods of combined electron-beam treatment of parts made of steel with one- and two-layer coatings are studied experimentally. Ti-Ni, Ni-Al and Al-Ti systems were used as the examples in the experiments. The mathematical model is suggested for coating formation in the controlled regime of high temperature synthesis during high energy source motion along the preliminarily deposited layer of exothermic composition. The study takes into account the difference in thermophysical properties of the materials of coating and substrate, heat release from chemical reaction that leads to the coating properties formation and other factors. The realization of the synthesis depends on technological parameters. Various regimes of the treatment process are investigated numerically.

## 1. Introduction

Self-propagating high-temperature synthesis (SHS) methods possess the extensive possibilities to create the materials of various types [1-3]. Coating synthesis on metals using SHS faces some difficulties and is not a widely spread technological process. A material obtained by SHS, as a rule, has the porosity comparable with initial one and has low mechanical characteristics. To obtain compact and chemically uniform material, the following treatment is necessary.

Employment of electron-beam has advantages for a broad spectrum of technology applications [4-6], including surface engineering: thermal treatment of alloys based on iron, titanium, aluminum and copper in the hardening regime from solid and liquid states, build-up welding of coatings on these alloys from materials with considerably different properties.

It is to be expected that a combined method of electron-beam treatment of material with preliminarily deposited powder alloy when the coating synthesis is realized allows for realizing the advantage of electron-beam treatment and condensed phase synthesis if the technological process will be arranged correctly for obtaining a material with anticipated properties. Preliminary investigations with green compositions of powders and composite wires of Ti-Ni, Ni-Al, Al-Ti [4] have shown that electron-beam technologies enable obtaining the smooth transition of the distribution of composition, chemical elements and mechanical properties from deposited layer to the basic detail. Intermetallic coating synthesis during laser heating was described in [7]. Here, the model was suggested taking into account the reaction retardation and controlling of the heating by moving source. However, only in [8] the heat losses from reaction zone to the substrate were taken into account, which could be the key

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factor for the realization of one or another synthesis regime. Some general consideration in conjugate and coupling models formulation were recounted in [9]. But only certain results for the simplest variant of the model (without reaction retardation by product layer) were presented in the previous work.

Note, that on the one hand, Ti-Ni, Ni-Al and Al-Ti systems, especially in the form of coatings on the base of steels and titanium alloys, are weakly examined despite enormous number of publications, and on the other hand, they are extremely promising from the practical point of view. Really, they could be applied to heighten the wear resistance and corrosion stability of details made from inexpensive engineering materials. For example, Ni-Al coating can be used for anticorrosion insulation of large vessels, reservoirs, metallic barriers and etc.  $\gamma$ -TiAl is the most perspective composite for automotive (in turbo compressors) and for aerospace applications [10-15]. This material has low density, high heat resistance and high-temperature strength. The production of blading for aviation gas-turbine engines from this material is a pretty complex problem. One of Ti-Al alloy applications can be their deposition on a titanium-based alloy using the combined method EB+SHS.

This paper briefly describes the experimental procedure for coating synthesis from Al-Ni (this system is actively studied in the applications of SLS and SLM [16, 17], and during development of new alloys [18]), shows the results of investigation of phase composition determination after electron-beam treatment and suggests the model of phase composition evolution for the coating synthesized on the substrate.

## 2. Experimental results

During experiments, Ni-Al coatings were deposited on the surface of the part by thermal spraying. The material in the form of a wire was sprayed using EM 12M setup and deposited on the substrate prepared from steel (0.2%C, 0.5%Mn). On sputtering, Ni and Al react with each other to form intermetallic compounds. The 0.1 mm-thick coatings consisting of one (Al or Al-Ni) or two (Al + Al-Ni) layers have lamellar structure; they demonstrate defective interface between the substrate and sublayer; contain unfused particles and have substantial porosity. To improve the cohesion strength and diminish the porosity, the EB energy has been used. Coating structure ordering occurs during intensive heating and fusing. The formed liquid phase enables the acceleration of surface and volume diffusion; gas desorption occurs, and the diffusion zone forms between the coating and the base. The formation of dendritic structure oriented mainly in perpendicular to the surface is typical for the coatings. This is conditioned by the heat sink direction during the melt solidification when EB action is terminated. The structure becomes more dispersed near the substrate. The diffusion zone is observed between the aluminum coating and the base.

The coating phase structure changes during EB treatment. The concentration of NiAl, Ni<sub>2</sub>Al<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> is increased, new phases of Ni<sub>2</sub>Al, Fe<sub>3</sub>Al and FeAl are formed and the traces of NiO and Ni are observed. The content of hard phases (NiAl, Al<sub>2</sub>O<sub>3</sub>, NiO) increased under heating by the source at relatively low intensity (energy density was  $0.8 \cdot 10^3$  W/cm<sup>2</sup>). When the heating is more intensive (specific power is  $2 \cdot 10^3$  W/cm<sup>2</sup>), the partial interaction between coating and substrate materials occurs, and the portion of iron-containing Fe<sub>3</sub>Al, FeAl phases and plastic phase Ni<sub>2</sub>Al<sub>3</sub> is increased. This leads to the change in coating properties depending on the density of heating source energy. By selecting the proportions of Ni and Al, one can control various properties of materials produced due to exothermic reaction.

As a result of surface coating reflow by electron beam, the coating-substrate adhesion strength is increased by the factor of 15 to 20 reaching 140 MPa, while the wear resistance of the coating-substrate system is enhanced 2.5 times as compared with initial state.

The corrosion resistance of samples increased 3-6 times in 3% NaCl and 5% H<sub>2</sub>SO<sub>4</sub> solutions. When modified coatings were subjected to blasting with SiO<sub>2</sub> particles at the rate of 40 m/s, their wear resistance doubled versus as-deposited state. The modified Ni-Al coatings can be efficiently used for protection of surfaces under the conditions of their simultaneous exposure to high temperatures and erosive media.

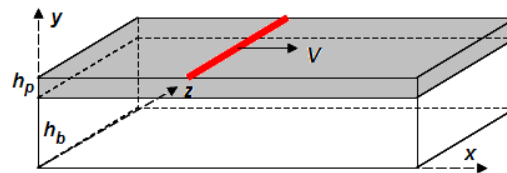
### 3. Mathematical model

A complete thermophysical model of controlled synthesis of the coating in Cartesian coordinate system includes three-dimensional thermal conductivity equation for the base (subscript  $b$ ) and thermal conductivity equation for the preliminary deposited layer (subscript  $s$ ), where the physical chemical conversions can proceed.

$$c_k \rho_k \frac{\partial T_k}{\partial t} = -\nabla \cdot \mathbf{J}_k + W_k + \Phi_k,$$

where  $k = b, s$ ;  $c_k, \rho_k$  are heat capacities and densities of materials; heat fluxes  $J_k$  obey to Fourier law;  $W_k, \Phi_k$  are total sources of heat due to chemical conversions and external heating. If external source acts only in the coating, then  $\Phi_b = 0$ .

The axis arrangement is shown in Figure 1.



**Figure 1.** Problem formulation

Under the condition of volume absorption of the energy of moving source developed to the line, the energy source for the coating can be written as

$$\Phi(x, y, z, t) = q_0 \exp\left[-\frac{(x - Vt)^2}{R_0^2}\right] \varphi_s(y, z),$$

where  $R_0$  is electron beam radius,  $V$  is its motion velocity along the  $Ox$ -axis.

The condition of ideal thermal contact is correct in the coating-base interface

$$\lambda_b \left( \frac{\partial T_b}{\partial y} \right)_{y=h_b-0} = \lambda_p \left( \frac{\partial T_p}{\partial y} \right)_{y=h_b+0}; \quad T_{b, y=h_b-0} = T_{p, y=h_b+0}.$$

The heat losses by irradiation (according to Stephen-Bolzman law) are possible in the surfaces  $y = 0$  and  $y = h_b + h_p$ . Other surfaces are insulated.

Chemical reactions can occur in the coating and lead to phase composition change. In this case,

$$W_p = -\sum_{k=1}^n h_k \frac{dy_k}{dt},$$

where  $h_k$  are partial molar enthalpies of species participating in reactions;  $y_k$  are their molar concentrations changing corresponding to kinetical equation:

$$\frac{dy_k}{dt} = \sigma_k, \quad \sigma_k = \sum_{i=1}^r \nu_{ki} \varphi_i, \quad k = 1, 2, \dots, n,$$

where  $\nu_{ki}$  is the stoichiometric coefficient of  $k$ -species in the  $i$ -reaction;  $\varphi_i$  is the rate of  $i$ -th chemical reaction;  $r$  is the number of chemical reactions. When the reactions proceed with the participation of solid phases, kinetical functions should take into account the reaction retardation by a poorly permeable layer.

In general case, chemical reactions in the base are also possible.

At the initial time moment, we have  $T = T_0, y_k = y_{k0}$ , because initial coating contains some part of the reaction product formed during deposition.

This model does not take into account explicitly the structure transformations in the coating (porosity evolution and shrinkage due to porosity change), intermixture of melts of coating and substrate in the contact area, chemical reactions between them, mechanical stresses due to high temperature gradients and properties change in the reactions etc. However, this model can give a fair idea of the heat necessary for heating, synthesis regimes and basic phases appearing during the treatment, even if we use additional simplifications [8, 9]. Assuming that the coating is thermally thin in comparison with the boundary layer width that forms due to thermal conductivity during treatment time, and the thickness of the substrate of high thermal conductivity is lesser than its width and length, we take integral of the thermal conductivity equation with  $y$ -coordinate taking into account the boundary conditions. Additionally, if we believe that scanning thickness of electron beam covers the transversal size of the part (which provides the uniform heating in this direction, Fig. 1), we come to one-dimensional thermal conductivity equation:

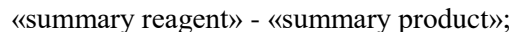
$$c_b \rho_b \left[ 1 + \frac{h_p c_p \rho_p}{h_b c_b \rho_b} \right] \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \bar{\lambda} \frac{\partial T}{\partial x} \right) - \sigma \varepsilon_{eff} (T^4 - T_W^4) + \frac{1}{h_b} \Phi'(x, t) + \frac{h_p}{h_b} \cdot W(y_k, T), \quad (1)$$

where

$$\lambda_{eff} = \lambda_b \left( 1 + \frac{\lambda_p h_p}{\lambda_b h_b} \right), \quad \varepsilon_{eff} = (\varepsilon_p + \varepsilon_b) / h_b, \quad \Phi'(x, t) = q_{eff} \exp \left[ -\frac{(x - Vt)^2}{R_0^2} \right].$$

For each system (Ti-Ni, Ni-Al, Al-Ti and etc.) we can write a detailed reaction scheme using state diagram and thermodynamical data. In this case, we should use kinetic equation system to describe the evolution of phase composition, similarly to [19, 20].

Here, we restrict the model by summary reaction:



however, the kinetic function should account the reaction retardation by the layer of reaction product.

As a result, we come to the reduced model with one equation instead of kinetic equation system:

$$\frac{dy}{dt} = \omega = k \varphi(y) \exp \left( -\frac{E}{RT} \right), \quad (2)$$

where  $y$  is the conversion degree;  $E$  is the activation energy for summary reaction;  $k$  is the pre-exponential factor,  $R$  is the universal gas constant;  $\varphi(y)$  is the kinetic function with the form depending on micro-scale processes. Then,  $W = Q\omega$ , where  $Q$  is the summary chemical heat release. Similar approach is tried-and-true method during irreversible processes modeling in the combustion theory. It allows obtaining qualitative regularities on the basis of reduced model.

In this work, we assume  $\varphi(y) = (1 - y) \exp(-my)$ .

To carry out the qualitative analysis of the problem including equations (1) and (2) and boundary conditions  $x = 0, \infty: \partial T / \partial x = 0$ , we come to dimensionless variables

$$\theta = \frac{T - T_*}{T_* - T_0}, \quad \tau = \frac{t}{t_*}, \quad \xi = \frac{x}{x_*},$$

where  $x_* = \sqrt{\lambda_b t_* / (c_b \rho_b)}$  is the spatial scale; the temperature scale  $T_*$  is determined as the temperature of product of solid-phase combustion  $T_* = T_0 + \frac{Q}{c_p \rho_p}$ ;  $t_* = \frac{c_p \rho_p R T_*^2}{EQk} \exp\left(\frac{E}{RT_*}\right)$  is time for reaction completion under adiabatic conditions. Then the reduced model turns into

$$(1 + K_c \varepsilon) \frac{\partial \theta}{\partial \tau} = (1 + K_\lambda \varepsilon) \frac{\partial^2 \theta}{\partial \xi^2} + \frac{\varepsilon K_c}{\theta_0} \varphi(y) \psi(\theta) + S \exp\left(-\frac{(\xi - \omega \tau)^2}{\delta}\right) - B[(\theta + \sigma)^4 - (\theta_W + \sigma)^4]; \quad (3)$$

$$\frac{\partial y}{\partial \tau} = \gamma \varphi(y) \psi(\theta);$$

$$\xi = 0: \frac{\partial \theta}{\partial \xi} = 0; \quad \xi \rightarrow \infty: \frac{\partial \theta}{\partial \xi} = 0;$$

$$\tau = 0: \theta = -1, \quad y = y_0,$$

where

$$\psi(\theta) = \exp\left[\frac{\theta \theta_0}{1 + \theta/\sigma}\right];$$

$$\delta = \frac{R_0^2 c_b \rho_b}{\lambda_b t_*}, \quad \gamma = \frac{c_p \rho_p R T_*^2}{EQ} \ll 1, \quad \sigma = \frac{T_*}{T_* - T_0} > 1, \quad \theta_W = \frac{T_W - T_*}{T_* - T_0} < 0; \quad \theta_0 = \frac{T_* - T_0}{RT_*} E \gg 1;$$

$$S = \frac{q_{eff} t_*}{h_b c_b \rho_b (T_* - T_0)}, \quad B = \frac{(T_* - T_0)^3 t_* \sigma \varepsilon_{eff}}{c_b \rho_b}; \quad K_\lambda = \frac{\lambda_p}{\lambda_b}; \quad K_C = \frac{c_p \rho_p}{c_b \rho_b}; \quad \varepsilon = \frac{h_p}{h_b} > 1; \quad \omega = \frac{V t_*}{x_*}.$$

Model contains a large number of parameters. Depending on relations between them, various conversion regimes are possible.

The problem was solved numerically. The implicit difference scheme and double-sweep method were used.

#### 4. Results of numerical investigation

We assume  $\theta_W = -1$ ;  $\sigma = 1.3$ ;  $\delta = 1$ .

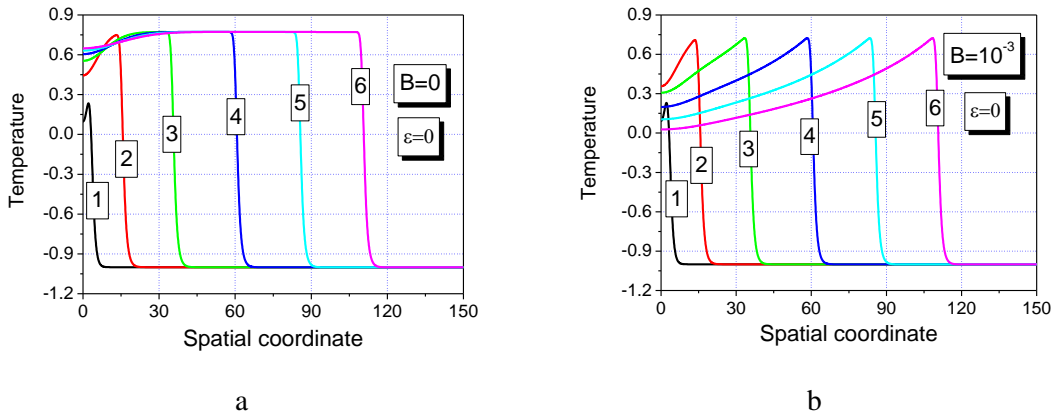
If the coating is absent,  $\varepsilon = 0$ . In this case, we shall obtain:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2} + S \exp\left(-\frac{(\xi - \omega \tau)^2}{\delta}\right) - B[(\theta + \sigma)^4 - (\theta_W + \sigma)^4]. \quad (4)$$

The scales for temperature and time are not determined here. We find them from the conditions of  $S = 1$  and  $\omega = 1$ .

Temperature distribution for this variant of the model and for  $\delta = 1$  is shown in Figure 2. For  $B = 0$  (Figure 2a) and for  $B \neq 0$  (Figure 2b), after initial non-stationary curve section, the quasistationary regime establishes in the system, when invariance of maximal temperature is typical for the process,

the value of maxima depends on  $\delta$ . However, quasistationary regime realizes when linear size of the part is larger than  $\sqrt{\delta}$ .



**Figure 2.** Temperature distribution (in a.u.) during substrate treatment for  $B = 0$  (a) and  $B \neq 0$  (b);  $\delta = 1$ . Time (in a.u.): 1) 0.3; 2) 1.5; 3) 3.5; 4) 6.0; 5) 8.5; 6) 11.0.

The limiting variant of the model of reaction initiation in plane layer without substrate accounting can be obtained when

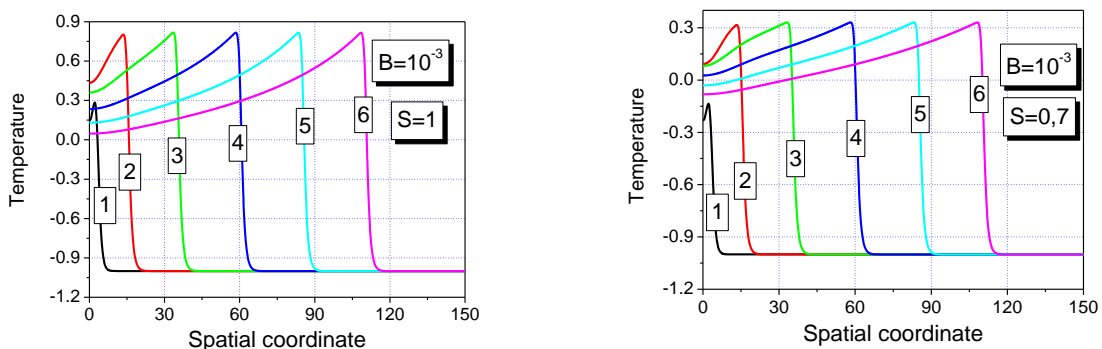
$$x_* = \sqrt{\lambda_p t_* / (c_p \rho_p)}; S = \frac{q_{eff} t_*}{h_p c_p \rho_p (T_* - T_0)}; B = \frac{(T_* - T_0)^3 t_* \sigma \epsilon_{eff}}{c_p \rho_p}; \epsilon_{eff} = 2\epsilon_p / h_p.$$

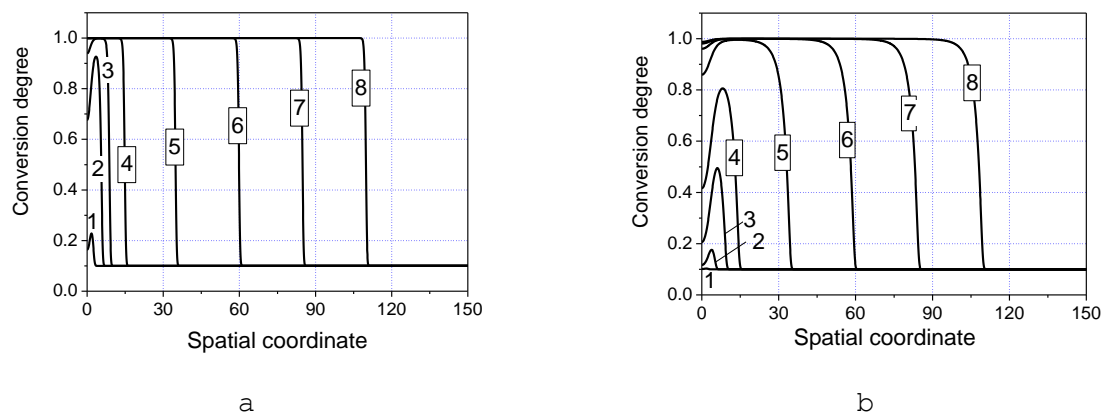
Then the thermal conductivity equation takes the form of

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\theta_0} \varphi(y) \psi(\theta) + S \exp\left(-\frac{(\xi - \omega \tau)^2}{\delta}\right) - B[(\theta + \sigma)^4 - (\theta_w + \sigma)^4] \quad (5)$$

and boundary conditions stay the same in any case.

Figure 3 demonstrates that, similarly to [8, 9], the chemical reaction starts at some distance from surface  $\xi = 0$ , and then the process continues in quasistationary regime. When capacity density of the source decreases, the velocity of its travel along the surface increases; the reaction near the surface  $\xi = 0$  is completed when external source leaves this area. The lower the capacity density of the effective external source, the lower the temperature and extension of the reaction zone.





**Figure 3.** Temperature and conversion degree distribution for different time moments during reaction initiation on thin layer without heat losses to substrate. Time for temperature curves coincides with the data from Figure 2. Time for conversion degree: 1) 0.3; 2) 0.6; 3) 0.9; 4) 1.5; 5) 3.5; 6) 6.0; 7) 8.5; 8) 11.0.

When synthesis is realized on the substrate, its properties affect the process characteristics.

On the one hand, the substrate requires the major part of the heat for heating. On the other hand, if the substrate is characterized by high thermal conductivity, it will promote the reagent heating in front of the moving external source. These effects were not taken into account in the simplest models described in [7].

The calculations have shown that the critical conditions exist in the problem. They separate the process of treatment accompanied by initiation of chemical conversions and the process of treatment without chemical reactions. Critical conditions were demonstrated by varying different parameters. Figure 4 shows different conversion degree when  $S$  changes. Different technological conditions give different composition of the coating. If we take into account the detailed reaction scheme, different coating composition will be expected in the numerical model varying the composition of green powders, similarly to [19, 20].

## 5. Conclusion

Since the Ti-Ni, Ni-Al and Al-Ti systems, especially in form of the coatings, are promising for practical implementation, the preliminary experimental data and suggested reduced model give a good start for further investigations. The model, despite the simplicity, reflects qualitatively basic regularities and will be used for prognostic model construction. The critical conditions should be taken into account to predict the technology conditions providing a given composition of the coating.

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