Modeling of controlled synthesis of intermetallic coatings

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Composite materials and coatings creation in modern combined technologies is perspective direction in the science when exothermic synthesis and electron beam or laser treatment are used together. Similar multifactor technologies demand the employment of mathematical modeling. In this work, two-dimensional model of the formation on the ferrous substrate of intermetallic coating from the powders Ni and Al is suggested. The model takes into account the heating by moving energy source corresponding to electron beam and the staging of chemical conversion. Due to small thickness of the treated layer temperature and composition distributions along the coating depth are not analyzed in a first approximation. However, the possibility of intermixing of materials of the coating and substrate and corresponding chemical reactions are taken into consideration for the temperature close to the melting temperature. The model was realized numerically. The distributions of the temperature and concentrations of individual species and new phases are studied for different time moments. It was shown that multi-phase coating forms in the conditions under study. It is possible to control the phase composition of the coating varying the composition of initial powders and treatment parameters. Self-sustained regime does not realize because heat losses to the substrate are high. This corresponds to experimental data. Effective properties of the coating could be evaluated for quasistationary stage that establishes quickly for each pass of electron beam.

1. Introduction

Methods of powder technology [1] possess the special possibilities for obtaining the materials and compositions with given properties, when they are combined with concentrated energy sources [2]. One of them is the method of electron beam (EB) treatment of the material with the preliminary deposited layer where the coating synthesis is carried out [3]. This method allows integrating the advantage of EB – treatment and condensed phase conversions accompanied by chemical heat release. However the substrate deducted the heat from heated zone can affect the regimes of the reaction initiation and propagation in condensed phase similarly to inert inclusions [4]; inert rood [5] or connectable materials [6]. Similar conditions for multi phase coating synthesis are realized when laser irradiation is used [7,8]. But these methods are more energy consumed. EB-technologies are characterized by more high coefficient of input energy usage [2,9]. In any case, it is not possible practically to predict the phase composition of a treated layer based only on the reversible state diagrams and the results of the solution of pure thermal conductivity problems [10,11], when the irreversible conditions for the synthesis and complex heat exchange conditions with conjugate substances, chamber walls, environment, and etc. are not taken into consideration. Even such
contemporary method as LBE (Lattice Bolzmann Equation method) does not allow to analyze the total set of physical and chemical stages and stays an illustrative one [12-14]. It is necessary to develop special models including the technology conditions and physical – chemical phenomena accompanying the EB – treatment of the surfaces. The examples of such models are contained in [15-20]. So, in the papers [15, 16], in term of the model of EB surface treatment with modifying particles, it was shown that critical conditions exist dividing the homogeneous and composite coating formation. In the works [17, 18], the examples of the modeling of the process of intermetallic coating formation for the systems Ti-Al and Ti-Ni for different conditions of EB – heating. The model of laser sintering of two-component alloy was suggested in [19,20] taking into account the shrinkage of the powder layer and dependencies of thermal and optical properties on the porosity changing in time.

Here the mathematical model is presented for the synthesis process of multi-phase coating from the powders of Al and Ni on Fe-substrate at the conditions of EB-treatment taking into account key chemical stages.

2. Problem formulation

It is assumed that one-layered coating containing the mixture of Ni and Al powders was deposited on the surface of the detail in form of thin plate. Effective energy source moves along the surface in the direction OX with some velocity $V$. Energy in the source is distributed corresponding to the law

$$ q_e(x,y,t) = \begin{cases} q_0 \exp\left(-\left(\frac{x-Vt}{a_i}\right)^2\right), & y \leq h_0; \\ 0, & y > h_0. \end{cases} $$

where $q_0$ is the maximal powder density of the source (heat flux density), $a_i$ is the effective radius of the source, $h_0$ is the scanning half-width. This effective source (1) corresponds to repetitive oscillations of electron beam [2,21], that is correct for the scanning frequency more then 50 hertz, and for the depth of the electron penetration more less then possible heated zone. For thermal thin plate or thin coating and thin surface layer of the substrate one can neglect temperature distribution along the depth similarly to [15-17]. Mass redistribution in this direction due to the diffusion is negligible small; however the melting of the substrate and coating lead to the intermixing and chemical interaction. Hydrodynamics of the melt is not analyzed explicitly. Hence the thermal part of the problem will include two-dimensional thermal conductivity equation

$$ \left[ h_i c_i \rho_i + h_2 c_2 \rho_2 \right] \frac{\partial T}{\partial t} = \left[ \frac{\partial}{\partial x} \left( \overline{\lambda} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \overline{\lambda} \frac{\partial T}{\partial y} \right) \right] - $$

$$ - \sigma c_0 (T^4 - T_0^4) + q_e(x,y,t) + (h_2 + h_1) W - \alpha_{eff} (T - T_0), $$

where $\overline{\lambda} = \lambda_{eff} h_2$; $\lambda_{eff} = \lambda_1 + \lambda_2 h_2/h_1$ is effective thermal conductivity of material with the coating; $\lambda_i$, $c_i$, $\rho_i$, and $h_i$ are the thermal conductivities, densities, heat capacities, and thicknesses of the surface layer of the substrate $i = 1$ and coating $i = 2$. Second term in (2) describes the heat losses from the surface according to Stephen-Boltzmann law; third term corresponds to the external heating, fourth term is the summary chemical heat release, and fifth term gives the effective heat losses to the depth of the substrate. Heat capacity changes sharply near the melting temperature that is taken into account by following way

$$ \left(c_i \rho_i\right) = \left(c_i \rho_i\right)_{eff} + L_{m,i} \rho_{s,i} \delta(T - T_{m,i}), $$

where

$$ \left(c_i \rho_i\right)_{eff} = \begin{cases} c_{s,i} \rho_{s,i}, & T < T_{m,i}; \\ c_{L,i} \rho_{L,i}, & T \geq T_{m,i}, \end{cases} $$
δ is Dirac delta-function; $L_{m,i}$ and $T_{m,i}$ are the heats and temperatures of the melting (crystallization) for substrate and coating; $i = L,s$; index «L» relates to the liquid phase; «s» relates to the solid phase.

Boundary and initial conditions

$$x = 0, H_y: \lambda \frac{\partial T}{\partial x} = 0; \quad y = 0, H_y: \lambda \frac{\partial T}{\partial y} = 0$$

(4)

$$t = 0: \quad T(x, y, 0) = T_0.$$  

(5)

close to the thermal problem formulation.

To calculate summary heat release due to chemical conversions it is necessary to solve kinetical sub-problem. Corresponding to state diagrams for the systems Fe-Al and Ni-Al [22,23] key reactions in the transient zone and in the coating are written as

$$3\text{Ni} + \text{Al} \rightarrow \text{Ni}_3\text{Al} \quad (I); \quad \text{Ni} + \text{Al} \rightarrow \text{NiAl} \quad (II)$$

$$3\text{Fe} + \text{Al} \rightarrow \text{Fe}_3\text{Al} \quad (III); \quad \text{Fe} + \text{Al} \rightarrow \text{FeAl} \quad (IV)$$

Reactions III and IV are possible in the case of intermixing above melting temperature of substrate.

With designations of molar concentrations $y_1 = [\text{Ni}]$, $y_2 = [\text{Al}]$, $y_3 = [\text{Fe}]$, $y_4 = [\text{Ni}_3\text{Al}]$, $y_5 = [\text{NiAl}]$, $y_6 = [\text{Fe}_3\text{Al}]$, $y_7 = [\text{FeAl}]$, mol/cm$^3$, kinetical equation’s system will include

$$\frac{\partial y_k}{\partial t} = \omega_k$$

for the reagents and for the reaction’s products. Here

$$\omega_1 = -3\varphi_1 - \varphi_2, \quad \omega_2 = -\varphi_1 - \varphi_2 - \varphi_3 - \varphi_4, \quad \omega_3 = -3\varphi_3 - \varphi_4, \quad \omega_4 = \varphi_1, \quad \omega_5 = \varphi_2, \quad \omega_6 = \varphi_3, \quad \omega_7 = \varphi_4$$

Chemical reaction’s rates are:

$$\varphi_1 = k_{01} \exp(-E_{a1}/RT) y_1^3 y_2, \quad \varphi_2 = k_{02} \exp(-E_{a2}/RT) y_1 y_2,$$

$$\varphi_3 = k_{03} \exp(-E_{a3}/RT) y_3^3 y_2, \quad \varphi_4 = k_{04} \exp(-E_{a4}/RT) y_3 y_2,$$

where $k_{0i}$, $E_{a,i}$ are pre-exponential factors and activation energies for reactions.

Initial concentrations for elements are $y_{01} = 0.035$; $y_{02} = 0.035$; $y_{03} = 0.141$ mol/cm$^3$.

The problem was solved numerically. Parameters were found in the literature or are calculated based on thermodynamics.

3. Results

The analysis of the results of numerical investigation shows that quasistationary regime establishes with time after some short non stationary stage together with source motion along the treated surface. This regime is characterized by the practically constant temperature (Fig.1) and shaped melting pool and heat affected zone (Fig.2). Melting pool is painted by dark gray color. Maximal size of the area of light gray color in the direction $y$ corresponds to the size of heat affected zone. It corresponds to the temperature $T = 900 K$. Plateau on the temperature curves corresponds the melting temperature. Maximal temperature value, sizes of melting pool and heat affected zone depend on the powder density $q_0$, source velocity $V$, and sizes of layers. The cooling after the source passing goes slowly. In some area of technological parameters ($q_0$, $V$, $a_t$, $h_0$), the external heating is accompanied by chemical conversions. Example of concentration distributions $C_j(x,0)$ for different time moments $t$ and various values $q_0$ is shown from Fig. 3. The reaction zone propagates with constant velocity equal to source velocity. In quasi stationary stage, maximal values of new phase concentrations and maximal temperature are registered depending on $q_0$. 


Figure 1. Spatial distribution of the temperature $T(x,0)$ along the treated surface for sequential time moments: 1. $- t = 0.06$, 2. $- t = 0.24$, 3. $- t = 0.8$, 4. $- t = 1.6$, 5. $- t = 3.7$, 6. $- t = 5.4$, 7. $- t = 7.4$, 8. $- t = 9.4$ sec. a) $- q_0 = 9 \cdot 10^4$, b) $- q_0 = 1.1 \cdot 10^5$ W/cm$^2$.

Figure 2. Influence of power density on the form and size of the melting pool (dark gray) and heat affected zone (light gray) to the quasi stationary regime establishment, $t = 9.4$ sec; a) $- q_0 = 9 \cdot 10^4$ W/cm$^2$, b) $- q_0 = 10^5$ W/cm$^2$, c) $- q_0 = 1.1 \cdot 10^5$ W/cm$^2$.

Figure 3. Spatial distributions of some mass concentrations of phases for different time moments: 1. $- t = 1.6$ sec, 2. $- t = 3$ sec, 3. $- t = 5.4$, 4. $- t = 7.4$ sec, 5. $- t = 9.4$ sec; solid lines$- q_0 = 10^5$, dotted lines $- q_0 = 9 \cdot 10^4$ W/cm$^2$; $V=0.5$ cm/sec.

Relative molar concentrations in the boundary of heat affected zone depending on the time are demonstrated in Fig. 4 for various $q_0$. Using these data one can evaluate the interval of effective properties change for obtained multi phase coating [24,25]. It is possible to use the existing analytical models for effective physical properties of heterogeneous materials, including thermal conductivity, coefficient of thermal expansion, electric conductivity, and mechanical modulus. These different physical properties obey the same regularities and general expressions of governing laws.
A substantial number of theoretical (or analytical) models for effective physical properties have been proposed in the past of more than one hundred years, however the theoretical prediction of effective properties for multiphase material systems is very important nowadays to analysis and optimization of material creation. For example, using the simplest approach one can find the Voigt–Reuss bounds for the elastic modulus $E$ and thermal conductivity coefficient $\lambda$

$$\lambda \langle b \rangle = \sum_{i=1}^{n} b_i x_i, \quad \langle \frac{1}{b} \rangle = \sum_{i=1}^{n} \frac{x_i}{b_i}$$

where $b = E, \lambda, ...$ and $x_i = y_i / \sum_{k=1}^{n} y_k$ - volume fractions of phases. Index "a" in the Fig.5 corresponds to above estimation, and index "b" relates to below estimation.

![Figure 4](image)

**Figure 4.** Phase concentration change in time in the point with coordinates $x=1$ cm, $y=0$ cm. Solid lines-- $q_0 = 10^5$, dotted lines -- $q_0 = 1.1 \cdot 10^5$ W/cm²; $V=0.5$ cm/sec;

1. – NiAl, 2. – FeAl, 3. – Fe$_3$Al, 4. – Ni$_3$Al

![Figure 5](image)

**Figure 5.** Thermal conductivity coefficient (a) and elasticity modulus (b) versus time. Solid lines-- $q_0 = 10^5$, dotted lines -- $q_0 = 1.1 \cdot 10^5$ W/cm²

As a result for this case, for the flux $q_0 = 10^5$ W/cm² we have $189 \leq \langle E \rangle \leq 211$ GPa; $0.35 \leq \langle \lambda \rangle \leq 7.5$ W/(cm·K); and for $q_0 = 1.1 \cdot 10^5 - 196 \leq \langle E \rangle \leq 224$ GPa; $0.22 \leq \langle \lambda \rangle \leq 0.59$ W/(cm·K)

**4. Conclusion**

So the model of surface layer formation on the ferric substrate from nickel and aluminium was suggested. It was shown that new phase’s formation affect the temperature, melting pool and heat affected zone formation. The composition of surface layer depends on all technological parameters. It was suggested using known theoretical models to evaluate the effective properties of forming under electron beam action composites.

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