Coating Formation in SHS-Regime During Thermal Treatment of Material by Moving Energy Source

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Abstract – The methods of combined treatment of steel specimens with pre-deposited one and two layer coatings by electron beam were experimentally studied. The investigations were carried out for the Ti–Ni, Ni–Al, Al–Ti systems. The mathematical model of the coating formation under the conditions of self-sustaining high-temperature synthesis (SHS) were suggested for the treatment of material (with pre-deposited layer of exothermic composition) by moving energy source. The difference between physical properties of the coating and substrate as well as between melting temperatures, the kinetics and heat release for exothermic chemical reaction leading to coating properties formation were taken into account. The various conditions of SH-synthesis were numerically investigated and could be realized depending on technology parameters.

1. Introduction

The SHS methods possess an extensive potential to obtain the materials of various types. The use of electron beam (EB) energy is perspective for thermal treatment of materials and coatings. It must be expected that combined method of EB treatment of parts with previously deposited layer of powder material that involves SH-synthesis of the coating would allow realizing (with correct organization) the advantages of EB treatment and solid-phase synthesis with the purpose of obtaining the coatings with required properties.

2.Experiment

The coatings of the Ni–Al system have been applied to the specimen surface by the method of arc spraying. The material in the form of wire has been sprayed using EM 12M setup and deposited on the substrate prepared from Ст 3 steel (0.2%C, 0.5 Mn). On sputtering, Ni and Al react with each other to form intermetallic compounds. The coatings 0.1 mm thick consisting of one (Al or Al–Ni) or two (Al + Al–Ni) layers have lamellar structure, defective interface between the substrate and sublayer and unfused particles and substantial porosity are visible. 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 makes possible surface and volume diffusion acceleration; gas desorption occurs and the diffusion zone is formed between the coating and base. The formation of dendritic structure oriented mainly 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_2Al_3, Al_2O_3 is increased, new phases Ni_2Al, Fe_3Al, FeAl are formed and the traces of NiO and Ni are observed. The content of hard phases (NiAl, Al_2O_3, NiO) is increased on heating by source at relatively low intensity (energy density is $0.8\cdot10^3$ W/cm^2). When the heating mode is more intensive (specific power is $2\cdot10^3$ W/cm^2) the partial interaction between coating and substrate materials occurs and the portion of iron-containing Fe_3Al, FeAl phases and plastic phase Ni_2Al_3 is increased. This leads to change of coating properties depending on the heating source energy density.

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 melting by electron beam the coating – substrate adhesion strength is increased by a factor of 15 to 20 up to 140 MPa and the wear resistance of the coating-substrate system is enhanced 2.5 times as compared with an initial state.

The corrosion resistance of samples increases 3–6 times in 3% NaCl and 5% H_2SO_4 solutions. When modified coatings are subjected to blasting with SiO_2 particles at the rate of 40 m/s their wear resistance is twice that in as-deposited state. The modified Ni–Al system 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

Let as assume that the one layer coating was previously deposited on the surface of the specimen in the form of a thin plate. The coating has a stoichiometric composition. Therefore reagent is entirely converted into product (stoichiometric compound) during heating. This allows describing the reaction by summary scheme

$$A_s \rightarrow B_s .$$
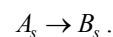
Let us neglect the temperature distribution across the depth of the coating and base (and hence, redistri-

bution of the elements in this direction) as well as change of thermal physical properties due to the reaction. Then the problem of coating formation in SHS-regime will include two-dimensional thermal conductivity equation for two-layer plate:

$$[hc\rho + h_1 c_1 \rho_1]\frac{\partial T}{\partial t} = \left[\frac{\partial}{\partial x}\bar{\lambda}\frac{\partial T}{\partial x} + \frac{\partial}{\partial y}\bar{\lambda}\frac{\partial T}{\partial y}\right] -$$

$$- \alpha_{eff}(T - T_e) - \sigma\varepsilon_0 T^4 + q_e(x,y,t) + h_1 \cdot q_i(z,T), \quad (1)$$

where T is the temperature; $\bar{\lambda} = \lambda h + \lambda_1 h_1$; c, ρ, λ and h are the heat capacity, the density, the thermal conductivity coefficient and the thickness of the base; ρ_1, c_1, λ_1 and h_1 are the thermal physical properties and thickness of the coating; T_e is the environment temperature, $h_1 q_i$ is the summary density of internal heat sources due to the volume reactions in the coating; α_{eff} is the effective coefficient of heat transfer from plate surfaces; t is the time, x,y are the space coordinates. The third term of Eq. (1) describes the radiated heat loss in accordance with Boltzmann' law, σ is the Stephan–Boltzmann' constant and ε_0 is the emissivity. The source with the energy distribution

$$q(x,y,t) = \begin{cases} q_0 \exp\left(-(x-Vt)^2/a^2\right), & y \le b; \\ 0, & y > b \end{cases} \quad (2)$$

moves along the (Ox) axis with the rate V. Such source corresponds to saw-tooth oscillations of a scanning electron beam.

The conversion degree z (or mass portion of the reaction product) changes in conformity with the kinetic equation

$$\frac{\partial z}{\partial t} = k_0 \varphi_1(z)\varphi_2(T), \quad (3)$$

where $\varphi_1(z)$ is the kinetic function, $\varphi_1(T) = \exp(-E/RT)$, k_0 the preexponential factor, E the activation energy of summary chemical reaction and R the universal gas constant. The value of activation energy, E, is determined by the limiting stage of a chemical reaction. The kinetic function $\varphi_1(z)$ reflects the reaction mechanism in a micro level. Then we have $q_i = Q_0 k_0 \varphi_1(z)\varphi_2(T)$. Taking into consideration that heat capacities of substances change essentially near the vicinity of melting temperatures (or other points of phase transitions), we shall write

$$(c\rho) = (c\rho)_{eff} + L_{ph}\rho_s\delta(T - T_{ph}),$$

$$(c_1\rho_1) = (c_1\rho_1)_{eff} + L_{ph,1}\rho_{s,1}\delta(T - T_{ph,1}), \quad (4)$$

where

$$(c\rho)_{eff} = \begin{cases} c_s\rho_s, & T < T_{ph}; \\ c_L\rho_L, & T \ge T_{ph}, \end{cases}$$

$$(c_1\rho_1)_{eff} = \begin{cases} c_{s,1}\rho_{s,1}, & T < T_{ph,1}; \\ c_{L,1}\rho_{L,1}, & T \ge T_{ph,1}, \end{cases}$$

δ is the delta function; L_{ph}, $L_{ph,1}$ are the melting (crystallization) heats; L_{ph}, $L_{ph,1}$ the melting (crystallization) temperatures of the base and coating, respectively. Index «L» relates to the liquid phase and «s» corresponds to the solid phase. (In the real calculations, delta function is changed for delta shaped function).

The heat sources and heat losses are absent on the butt-ends of the plate:

$$x = 0, h_x : \quad \lambda\frac{\partial T}{\partial x} = 0; \quad y = 0, h_y : \quad \lambda\frac{\partial T}{\partial y} = 0. \quad (5)$$

We have

$$t = 0: \quad T(x,y,0) = T_0; \quad z(x,y,0) = 0 \quad (6)$$

at the initial time instant.

Depending on the energy parameters characterizing the external source as well as exothermal reaction and melting, the conditions of coating formation from an initial material can be different.

So, the problem is many-parameter and their analysis demands substantial effort. To detect the possible conversion conditions we dwell in this work on the analysis of one-dimensional version of the problem, which results from the abovesaid at the conditions of $b \gg a$, $h_x \to \infty$ and $\alpha_{eff} = 0$.

In nondimensional variables typical for the combustion problems, we have

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

where $x_* = a$ is the space scale; the temperature scale, T_* is determined as the product temperature of solid phase combustion:

$$T_* = T_0 + \frac{Q_0}{c_{s,1}\rho_{s,1}}; \quad t_* = \frac{c_{s,1}\rho_{s,1}RT_*^2}{EQ_0 k_0}\exp\left(\frac{E}{RT_*}\right) -$$

is the specific time of chemical reaction in adiabatic condition and the problem takes the form

$$f_1\frac{\partial\theta}{\partial\tau} = \frac{1}{\delta}f_2\frac{\partial^2\theta}{\partial\xi^2} + \gamma\varphi_1(z)\varphi_2(\theta) + Sf_3,$$

$$\frac{\partial z}{\partial\tau} = \gamma\varphi_1(z)\varphi_2(\theta),$$

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

$$\tau = 0: \theta = 0, \quad z = 0,$$

where

$$\varphi_2(\theta) = \exp\left[\frac{\theta-1}{1+\beta\theta}\frac{\beta+1}{\gamma}\right],$$

$$f_1 = C\varepsilon + C_1 ,$$

$$C = \frac{rg}{s_0 \sqrt{\pi}} \cdot \exp\left[-\left(\frac{\theta - \theta_{ph}}{s_0}\right)^2\right] + \begin{cases} K_c, & \theta \le \theta_{ph}, \\ K_L, & \theta > \theta_{ph}, \end{cases}$$

$$C_1 = \frac{g}{s_{0,1} \sqrt{\pi}} \cdot \exp\left[-\left(\frac{\theta - \theta_{ph,1}}{s_{0,1}}\right)^2\right] + \begin{cases} 1, & \theta \le \theta_{ph,1}, \\ B_L, & \theta > \theta_{ph,1} \end{cases}$$

$$f_2 = 1 + K_\lambda \varepsilon , \quad f_3 = \exp\left(-\left(\xi - \bar{V}\tau\right)^2\right) .$$

We take the kinetic function

$$\varphi_1(z) = 1 - z ,$$

that corresponds to the simplest first-order reaction. The model contains many parameters

$$\delta = \frac{a^2}{\kappa_{s,1} t_*} , \quad \gamma = \frac{c_{s,1}\rho_{s,1}RT_*^2}{EQ_0} \ll 1 , \quad \beta = \frac{T_* - T_0}{T_0} > 1 ,$$

$$g = \frac{\rho_{s,1}L_{ph,1}}{Q_0} , \quad r = \frac{L_{ph}\rho_{ph}}{L_{ph,1}\rho_{ph,1}} , \quad s_0 = \frac{\sigma_0}{T_* - T_0} ,$$

$$s_{0,1} = \frac{\sigma_{0,1}}{T_* - T_0} , \quad K_C = \frac{c_s\rho_s}{c_{s,1}\rho_{s,1}} , \quad K_L = \frac{c_L\rho_L}{c_{s,1}\rho_{s,1}} ,$$

$$B_L = \frac{c_{L,1}\rho_{L,1}}{c_{s,1}\rho_{s,1}} , \quad \theta_{ph} = \frac{T_{ph} - T_0}{T_* - T_0} , \quad \theta_{ph,1} = \frac{T_{ph,1} - T_0}{T_* - T_0} ,$$

$$S = \frac{q_0 t_*}{h_1 Q_0} , \quad \varepsilon = h/h_1 > 1 ; \quad K_\lambda = \lambda/\lambda_1 ; \quad X = h_x/x_* .$$

The parameters are not all of interest for qualitative investigation of the model. So, without minimizing the importance of generality, we can assume

$$s_0 = s_{0,1} ; \quad K_C = K_L ; \quad B_L = 1 .$$

The physical sense of non-dimensional variables which are of interest for investigating the conversion conditions, is clear. δ is the ratio of effective source width to the specific heat scale (thickness of heat boundary layer formed in the coating during reaction time); S is the ratio of the heat stored in the layer of thickness h_1 during the time t_* on heating by flow q_0, to the chemical heat release; g is the ratio of the heat absorbed during the coating melting, to the chemical heat release; r is the ratio of the phase transitions heat quantities of different materials, etc. The coating formation conditions depend on the proportion between the parameters θ_{ph}, $\theta_{ph,1}$ and on closeness of these temperatures to a specific combustion temperature (product temperature) and on the values of the parameters δ, β, S, g, K_C, K_λ, ε. If phase transitions are not taken into account, the problem becomes still more simple,

$$f_1 = K_c \varepsilon + 1 .$$

The numerical solution of the problem was carried out using an implicit difference scheme and double-sweep method. The temperature and conversion degree distributions for various time instants and chemical heat release were determined with varying the problem parameters. The region of chemical heat release contained not less than 10 points of difference scheme. The subsequent mesh refinement did not affect the result. The basic calculations were realized for the parameters $K_C = K_\lambda = 1$, $\varepsilon = 10$, $\delta = 5$, $\beta = 1,5$; $\gamma = 0,03$; $\bar{V} = 2$.

4. The Results of Numerical Investigation

If $S < S_*$, the chemical reaction is not initiated in the heated region or it runs very slowly. If $S \ge S_*$, the chemical reaction zone propagates following a moving source and the quasi-stationary process develops. The maximum temperature in the heated zone does not exceed $0,8$, $S = 10$; it is more than 1.5, when $S = 18$ (Fig. 1, a), which is enough to maintain the stationary conversion conditions (Fig. 1,b). The temperature and conversion degree curves are presented for successive time instants. The heat source moving at the rate of $\bar{V} = 2$ is located in the point $\xi = 22$ by the time instant $\tau = 11$ and heats the substance in front of the conversion zone. The chemical heat release $Q_{ch} = \gamma\varphi_1(z)\,\varphi_2(\theta)/f_1$ behaves analogously to the temperature. The heated zone is much more extended than chemical reaction zone.
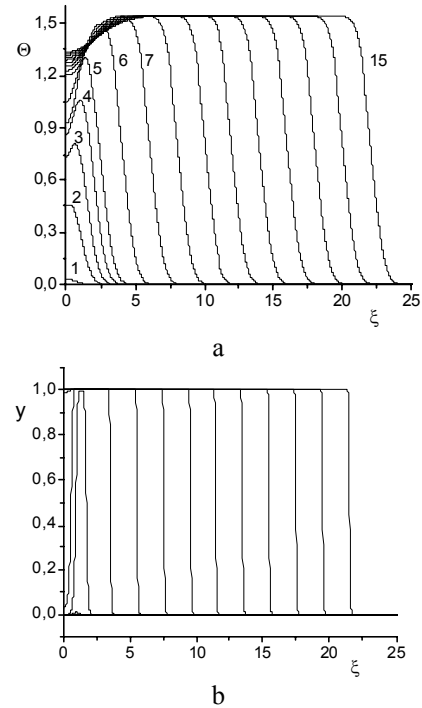

a

b

Fig. 1. Temperature and conversion degree distributions for successive time moments $\tau = 0.02, 0.3, 0.6, 0.9, 1.2, 2.0, 3.0, 4.0, 5.0 \ldots 11.0$

The chemical heat release diminishes and the reaction zone increases, if the parameter S decrease ($S = 16, 15, 14$) (Fig. 2).

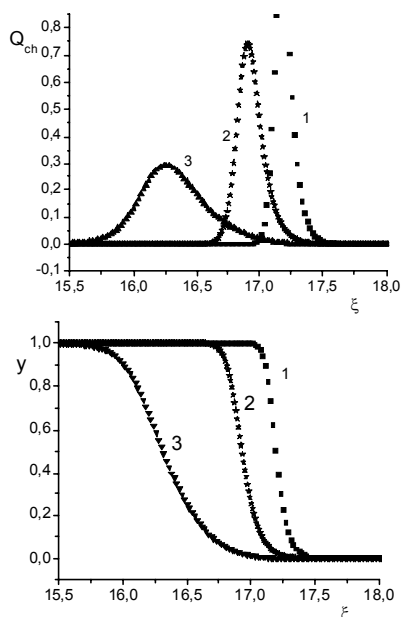
Fig. 2. Temperature and conversion degree distributions for a time instant $\tau = 9$; $S = 16$ (1), 15 (2), 14 (3)

The stationary picture and nonstationary stage of process development for these values of energy density are similar to the picture obtained for $S = 18$ Reaction starts at some distance from the surface $\xi = 0$ and than propagates to the right and to the left with different velocities (Fig. 3). The more the value S, the closer the reaction initiation to the surface $\xi = 0$.
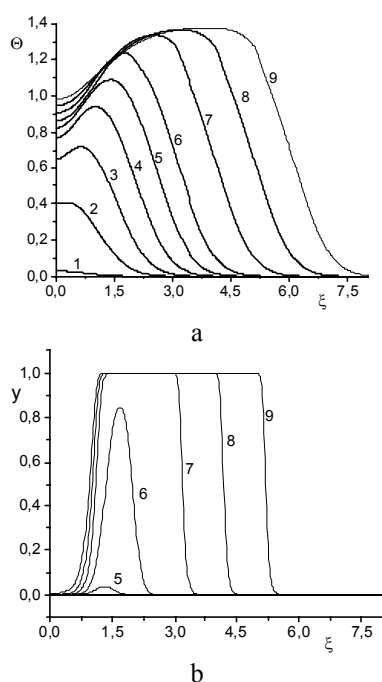

Fig. 3. Temperature and conversion degree distributions for time instants $\tau = 0.02, 0.3, 0.6, 0.9, 1.2, 1.5, 2.0, 2.5, 3.0$ and for $S = 16$

The temperature, conversion degree and chemical heat release for the point $\xi = 0$ as well as the maximum value of temperature for the quasi stationary stage are presented in Fig. 4 for various values of parameter S.
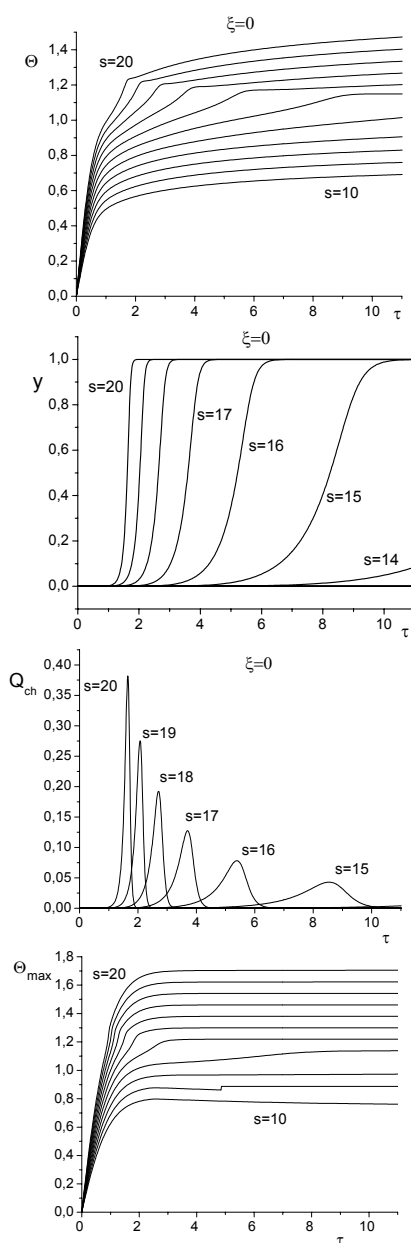

Fig. 4. Temperature, conversion degree and chemical heat release distributions in the point $\xi = 0$ and maximum value of temperature for various values of parameter S

If the value S is small, the reaction is not initiated and maximum temperature does not exceed $\theta = 1$. For a given set of problem parameters, if $S > 13$, the bending is observed in the curves $\theta(\tau)$ that is typical for the problems of ignition and combustion and allows introducing the conception of "ignition time". Then, as the source moves forward, the maximum temperature tends to some limit, and we come to the picture described above.

The time at which the maximum value of heat release associated with the chemical reaction exceeds the maximum heat release due to external heating would be named the ignition time

$$\max_{\xi \geq 0} \left[\gamma \varphi_1(z) \varphi_2(\theta) \right] \geq S$$

or

$$Q_{ch} \geq S / f_1.$$

The ignition time thus determined is presented in Fig. 5 depending on the parameter S for two different values of motion velocity of the source $\bar{V}$.
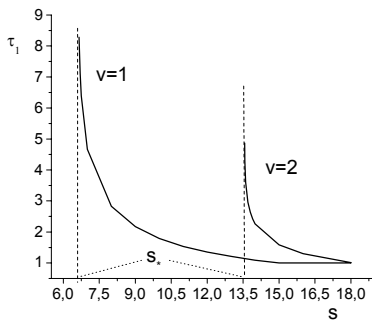

Fig. 5. The ignition time depending on parameter S for the two values of the source motion velocity

When S tends to critical value S_*, the ignition time τ_1 is sharply increased. If the source motion velocity diminishes, the values τ_1 and S_* decrease which is attributed to heated zone expansion. The critical value S_* insignificantly depends on parameters δ, β, but changes when parameters K_C and K_λ are varied. The qualitative picture of the process development also changes.

If S tends to critical value, the phenomena observed are close to critical. The chemical reaction zone essentially expands and exceeds the region with sharp temperature changing. Hence, heat release zone due to the chemical reaction is also broad. The slow chemical reaction expands along the substance with a significant delay as compared to an external source. The bending in the "temperature – time" curve is not observed in this case.

Thus, the experimental investigations have been carried out on electron beam heating and surface melting of one (Al or Al–Ni) and two (Al + Al–Ni) layer coatings previously deposited on steel substrate.

In the work, the model is proposed of coating formation using self-sustaining high-temperature synthesis together with electron beam heating. The investigations have allowed revealing the phenomena typical for the processes of non-gaseous combustion that can be used for the processes optimization of electron beam coating deposition.