Coating combustion synthesis controlled by moving electron beam

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Abstract. The model of the coating synthesis on the substrate is suggested at the conditions of electron beam controlling. The detailed reaction scheme in the treated layer is taken into account. Reaction kinetics is described based on mass action law. Reaction retardation by solid reaction products is taken into consideration. The review of similar models, simple and coupled, is made. Asymptotical solution of the particular coupled problem with summary reaction scheme is obtained. It was found that self sustaining mode is possible when the coating is synthesized on the substrate. The example of maximal temperature establishment is illustrated for the detailed reaction scheme in the Ti-C-Al system when the conversion is initiated by electron beam.

1. Introduction

The methods of materials synthesis using combustion (Self propagating High temperature Synthesis (SHS) and Thermal Explosion (TE)) allow obtaining the materials with different properties [1, 2]. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times [3]. This is interested for the technologies of intermetallic or composite coating deposition. Today this is interested for the development of Additive Manufacturing (AM) technologies [4-6]. When electron-beam is used for intermetallic coating or detail formation, the features appear [7, 8]. The technology of electron-beam melting (EBM) was developed by Arcam of Sweden. In this technology, preliminary distributed layer of metal powder is preheated to reduce the concentration of residual stresses. The process is carried out in vacuum chamber. Different materials are used for the electron beam melting process. Steel, tantalum, pure titanium and titanium alloys, composite materials, and etc. are between them [9-11]. EBM is more energetically effective technology then laser beam melting (LBM) [12, 13].

Some models were suggested in [14, 15] to study the physical features of electron beam melting of metals forming intermetallic phase. It was shown that coupling phenomena between strain and temperature field can promote reaction front stabilization and can be cause of irreversible composition formation. When composite coating is synthesized, the electron beam energy spends on inert inclusion heating that is taken into account in [16, 17] that is favorably for quasi stationary mode establishment.

In this paper, we discuss the possibility for SHS-mode realization under conditions of composite coating synthesis on substrate and demonstrate the dynamics of coating formation under electron beam controlling. The ideas of [18, 19] are used here.
2. The general relations

In the suggestion of small thickness of treated layer and small size of heated zone in substrate, the simplest thermal-physical model of controlled synthesis of the coating in Cartesian coordinate system includes two dimensional thermal conductivity equation

\[
C \frac{\partial T}{\partial t} + \frac{c_A \rho_A h_A(t)}{h_s + h_{A0}} [U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y}] = \left[ \frac{\partial}{\partial x} \left( \lambda_{\text{eff}} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda_{\text{eff}} \frac{\partial T}{\partial y} \right) \right] + W_h - H_{\text{loss}} + \Phi_{ch} \tag{1}
\]

where

\[
U = \frac{\lambda_A}{c_A \rho_A} \frac{h_A}{h_s} \quad \text{and} \quad V = \frac{\lambda_A}{c_A \rho_A} \frac{h_A}{h_s} \frac{\partial h_A}{\partial y} -
\]

convective velocities appearing due to powder layer shrinkage;

\[
C = \frac{[h_s c_A \rho_s + h_A(t) c_A \rho_A]}{h_s + h_{A0}} -
\]
effective heat capacity, J/(kg·K);

\[
\lambda_{\text{eff}} = \lambda_s \frac{h_s}{h_s + h_{A0}} + \lambda_A \frac{h_A(t)}{h_s + h_{A0}} -
\]
effective thermal conductivity, J/(cm·s·K).

External heating term \( W_h \) corresponds to electron beam moving along the treated surface and absorbed in powder volume; heat losses are provided with heat thermal radiation; summary chemical heat release is determined by the kinetics of chemical reactions:

\[
\Phi_{ch} = -\sum_{k=1}^{n} h_k \frac{dy_k}{dt}.
\]

Here \( h_k \) – are partial molar enthalpies of species participating in reactions, J/mole; \( y_k \) – are their molar concentrations, mole/cm³. The system of kinetical equation is written as

\[
\frac{dy_k}{dt} = \sigma_k, \quad k = 1, 2, ..., n,
\]

where

\[
\sigma_k = \sum_{i=1}^{r} \nu_{ik}\phi_i, \quad k = 1, 2, ..., n,
\]

\( \nu_{ik} \) – is the stoichiometric coefficient of \( k \)-species in the \( i \)-reaction; \( \phi_i \) – is the rate of chemical reaction with number \( i \), \( r \) – 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 poorly permeable layer of the forming product.

If treated layer contains the inert particles with volume fraction \( \eta \), this can be taken into account in the heat capacity, that is

\[
c_A \rho_A = c_M \rho_M (1 - \eta) + c_P \rho_P \eta.
\]

When the porosity \( \theta \) leads to properties change and powder layer thickness evolution, the model is modified [19]. For example, formula for heat capacity (3) turns to
If the coupling between strain, temperature and concentration fields are taken into account, the model becomes a more complex [18]. In this case all effective properties will include some mechanical properties of substrate and synthesized coating. Additional term with coupling coefficient appear in the right part of thermal conductivity equation [20]. The relations between stresses and strains are written down in differential form

\[ d\sigma_{ij} = 2\mu d\varepsilon_{ij} + \delta_{ij} \left\{ \lambda \varepsilon_{kk} - 3K \left[ \theta dp + \alpha_T dT + \sum_{k=1}^{n} \alpha_k dC_k \right] \right\}. \]  

(4)

where \( \lambda, \mu \) – Lame coefficients, \( K=\lambda+2\mu/3 \) is bulk module, \( \alpha_T \) – is thermal expansion coefficient; \( \alpha_k \) – are concentration expansion coefficients; \( C_k \) – are mass concentrations of species (connected with molar concentrations by usual reactions). The motion equation has usual form.

If mass exchange between solid and liquid phases happens due to the melting and chemical reactions, the additional terms have been included in balance equations (2).

Boundary and initial conditions are formulated for each case under study in a specially manner.

The simple particular variants of this model are interested for qualitative analysis.

3. The simplest stationary model

The solution in the form of travelling wave can be found at the following approximation: strains are small; all reactions can be described by summary scheme “reagent → product”; the summary reaction proceeds without melting, porosity and properties are calculated or found experimentally for some temperature typical for the process; mechanical properties of substrate and coating are identical. The external source helped for the reaction initiation and for the plane front formation and leaved the specimen. Because the specimen “substrate-coating” is thin, the generalized plane stressed state takes a place and stress tensor component perpendicular to the specimen plane equals to zero \( \sigma_{33}=0 \). Plane reaction front is characterized by temperature and composition gradients only in the direction of reaction front propagation, hence \( \varepsilon_{22}=0 \) and we have

\[ \varepsilon_{11} = \varepsilon_{11}(t,x); \quad \varepsilon_{33} = \varepsilon_{33}(t,x); \quad \sigma_{11} = \sigma_{11}(t,x); \quad \sigma_{22} = \sigma_{22}(t,x). \]

In this case, one-dimensional thermal conductivity equation coupled with deformations, kinetic equation for conversion level and one motion equation written for strain component in the front direction are necessary.

Using assumed simplifications and (4) we come to the equation system

\[ c_\sigma \rho \frac{\partial T}{\partial t} - V_n \frac{\partial T}{\partial x} = \lambda_T \frac{\partial^2 T}{\partial x^2} + Q(y,T) - 3K\alpha_T T \frac{2\mu}{\lambda + 2\mu} \left[ \frac{\partial \varepsilon_{11}}{\partial t} - V_n \frac{\partial \varepsilon_{11}}{\partial x} \right], \]

\[ \frac{\partial y}{\partial t} - V_n \frac{\partial y}{\partial x} = W(y,T), \]

\[ \rho \left[ \frac{\partial^2 \varepsilon_{11}}{\partial t^2} - 2V_n \frac{\partial^2 \varepsilon_{11}}{\partial t \partial x} + V_n^2 \frac{\partial^2 \varepsilon_{11}}{\partial x^2} \right] = 4\mu(\lambda + \mu) \frac{\partial^2 \varepsilon_{11}}{\partial x^2} - \frac{2\mu}{\lambda + 2\mu} 3K\alpha_T \frac{\partial^2 T}{\partial x^2}. \]

In the coordinate system connecting with reaction front moving to the right with the velocity \( V_n \) in initial substance we have the conditions

\[ x \rightarrow +\infty: \quad y = 0, T = T_0, \varepsilon_{11} = 0. \]

In the reaction product, all perturbations attenuate.

It is demanded to find the solution in the form of travelling wave.

In suitable dimensionless variables, the mathematical model for stationary wave takes the form
\[-V \frac{d\theta}{d\xi} = \frac{d^2 \theta}{d\xi^2} + \omega(\theta + \sigma)V \frac{de}{d\xi} - V \frac{dy}{d\xi}, \quad (5)\]

\[-V \frac{dy}{d\xi} = \varphi_1(y)\varphi_2(\theta), \quad \varphi_2(\theta) = \exp \left[ -\frac{(1 - \theta)(1 + \sigma)}{\gamma(\theta + \sigma)} \right]; \quad (6)\]

\[\alpha^2 V^2 \frac{d^2 e}{d\xi^2} = \frac{d^2 e}{d\xi^2} \frac{d^2 \theta}{d\xi^2} - S = \kappa(e - \theta). \quad (7)\]

\[\xi \rightarrow +\infty: \theta = 0, \quad y = 0. \quad (8)\]

Here

\[\theta = \frac{T - T_0}{T_s - T_0}, \quad \xi = \frac{x}{[(\kappa_T/k)\exp(E/RT_s)]^{\frac{1}{2}}}, \quad e = \frac{\varepsilon_{11}}{\varepsilon_s}, \quad s = \frac{\sigma_{11}}{\sigma_s}, \]

dimensionless variables,

\[T_s = T_{b0} = T_0 + \frac{Q}{c_0\rho} - \]

combustion temperature for classical solid phase combustion model,

\[V = V_n \left[ \frac{\exp(E/RT_s)}{k\kappa_T} \right]^{\frac{1}{2}} - \]

velocity of stationary front that should be found during problem solution;

\[\sigma = \frac{T_0}{T_{b0} - T_0}; \quad \kappa = \frac{2\mu}{\lambda + 2\mu}, \quad \alpha^2 = \frac{\rho}{2(\lambda + \mu)} \frac{\lambda + 2\mu}{2\mu} \frac{\kappa_T k}{\exp(E/RT_{b0})}, \]

\[\omega = \frac{(3\kappa_T)^2 (T_{b0} - T_0)}{2(\lambda + \mu)k_{\sigma}\rho} \frac{2\mu}{\lambda + 2\mu}, \quad \gamma = \frac{RT_{b0}^2}{E(T_{b0} - T_0)} << 1 - \]

parameters of the model.

The model (5)-(8) is integrated exactly only partially and then it is solved by method of joint asymptotic expansion. The solution can be presented in the form

\[\left(1 + \frac{\omega\sigma}{1 - \alpha^2 m_0\gamma}\right)\theta_b + \frac{1}{2} \frac{\omega}{1 - \alpha^2 m_0\gamma}\theta_b^2 - 1 = 0, \quad (9)\]

\[m_0 = \exp \left( -\frac{1 - \theta_b}{\gamma} \right), \quad (10)\]

Similarly to [20], equations (9),(10) give two different mode for reaction front propagation – slow and quick. Equation (9) has two type of positive solutions \(\theta_b < 1\) for \(\alpha << 1\) and \(\theta_b > \theta_{b1} > 1\) for \(\alpha > 1\), depending on parameters \(\omega, \sigma, \alpha\). Equation (10) gives for this solutions the front velocities \(m_0 < 1\) and \(m_0 > 1\) correspondingly. In contrast to [20], parameters \(\omega\) and \(\alpha\) include other complexes from physical properties, that diminishes the area of stationary mode existence.
4. The controllable mode for coating synthesis

Chemical reactions in composite powders can continue during electron beam coating deposition because they contain some fraction of active components [21, 22]; inert inclusions in reacting mixture lead to chemical heat release increase, however they promote heat accumulation; there are large heat losses to substrate, however the heat accumulation in substrate assists to reaction maintenance and reaction front propagation. The synthesis conditions of composite powders give the finally composition far from equilibrium one, and electron beam can help controlling the velocity of coating synthesis or detail formation from composite powders. This process can be described on the base of the model presented above. For example, for the system Ti-Al-C, in reacting mixture the phases TiAl, TiAl₃, Ti₃Al, TiC, Ti₂C, Ti₃C₂, TiC₂, Al₃C₄, AlC, Ti₅AlC, Ti₅AlC₂ [23-25] can present additionally to pure elements. Thermodynamic analysis had shown that more than 20 reactions are possible in this system. In the system Ti-Al-Si the phases TiSi, TiSi₂, Ti₅Si, Ti₅Si₃ and Ti₅Si₄ additionally to intermetallic phases can appear [26]. For each species we have the equations (2). The reactions retardation by solid products is taken into account in kinetic functions. Formal kinetic parameters are calculated based on thermodynamics. However, activation energies should be proved, because diffusion through product layer is limiting stage for the reactions with participation of solid substances. The examples of models of coating formation for simple systems were discussed in [14-17]. Figure 1 illustrates the stationary mode formation initiated by moving electron beam for the composite powders. The substrate is made from iron. External source was put out, when quasi stationary maximal temperature was established. Depending on beam and detail parameters, the stationary mode can be various. For beam radius \( r = 0.5\text{cm} \) and capacity density in the beam \( q_0 = 6 \times 10^5 \text{W/cm}^2 \) maximal temperature after the beam forms very quickly; then reactions start that leads to maximal temperature increase. After dotted line, the external heating absents. The temperature slowly decreases, and new stationary mode forms.

![Figure 1](image1.png)

**Figure 1.** Temperature dynamics during stationary mode establishment. a) maximal temperature in time; b) temperature distribution along the direction of electron beam for different time moments: 1. – 0.05, 2. – 0.15, 3. – 0.45, 4. – 0.95, 5. – 1.45, 6. – 1.95, 7. – 2.2, 8. – 2.7, 9. – 4.95 second.

5. Conclusion

So, the generalized model of reaction front propagation on the substrate is suggested. It was shown that stationary mode is possible when coupling effects are taken into account for these conditions. Stationary mode can establish when reactions are initiated by electron beam. Note that the models for self-similar mode of reaction propagation in the layer placed on substrate are interested not only for electron-beam melting. It is possible to initiate the self-sustaining process on the substrate using laser beam [27, 28]. However in numerous papers, for example [26, 29-31], where exothermal powder compositions have...
been used, this question does not discuss. The inert particles presence, the difference in the properties of reagents and products, and etc. can be taken into account in the model.

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