Modeling of phases and chemical compounds formation under the treatment conditions of the materials and alloys by particle beams

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Abstract

Some models of coating deposition are described. The features of the coupling model are shown. The examples of stresses and strains calculations in the system are presented. The connects with elements redistribution and composition change due to the reactions.

1 Introduction

Modern methods of material synthesis, surface treatment, coating deposition and materials cutting and welding connect with the transformation of various energy forms to the heat energy. There are many physical and chemical phenomena accompanying the technology stages and favoring to composition and properties change of materials. Surface layers structure and properties formation is effect of various irreversible physical and chemical processes which are not taken into consideration in traditional mathematical models. If the final state could be investigated experimentally, so, as a rule, the staging of the processes accompanying the treatment belongs to discussion questions. Practically, the processes going during the treatment in irreversible conditions represent the content of black box. It is very significant to understand, what level of blackness of black box? Is it possible to retrieve the information from mathematical modeling of technology processes stages?

In our works, using the information on initial reagents, specimen geometry, technology conditions, the dependencies of the properties on the temperature etc., we formulate the mathematical problems with initial and boundary conditions, write down kinetic equations, state equations and the relations for the fluxes, choose numerical methods, develop the algorithms, make the analytical estimations and then we carry out numerical experiment allowing to obtain the information on the physical and chemical processes during technology and for finally state. All models are coupling. As examples, the models of the coating growth on the specimen surface and the models of surface treatment using particle beams are discussed.

Let mark, that known application packages allow to calculate of one physical fields using information on another fields. But it is not relates to chemical reacting systems. Ours models are really coupling, but designed computer programs are not universal, though they are admitted the modification. That is, we calculate not only the result of the reaction, but take into account the result effect on the chemical conversion course.

2 Isothermal models

Mathematical model of coating growth on the plane substratum at the condition of deposition from electro arc plasma was suggested in [1]. It was assumed that the coating growth in isothermal conditions, and no isothermal stage is vary short. The rate of the coating growth is determined by technology conditions. In the simplest variant of the coating formation from titanium in nitrogen environment on the iron substratum includes the diffusion equations for nitrogen in the substratum and in the growing coating:

$$0 < x < h_1 : \qquad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left[D_1(C_1, C_2)\frac{\partial C_1}{\partial x}\right]; \tag{1}$$

$$h_1 < x < h_1 + h(t) : \qquad \frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x}\left[D_2(C_1, C_2)\frac{\partial C_2}{\partial x}\right]; \tag{2}$$

where h_1 is the thickness of the substratum, C_1, C_2 is the mass concentrations of nitrogen in the substratum and in the coating, D_1, D_2 are diffusion coefficients.

There is the functional dependence

$$D = \left(1 + \alpha C + \beta C^2\right) \cdot D_0$$

The boundary conditions could be presented in the form:

$$x = 0 : \qquad \frac{\partial C}{\partial x} = 0,$$

$$x = h_1 : \qquad D_1\frac{\partial C_1}{\partial x} = D_2\frac{\partial C_2}{\partial x} \quad \text{and} \quad C_1 = \gamma C_2,$$

$$x = h_1 + h(t) : \qquad C_2 = C_e,$$

where C_e is the nitrogen concentration in plasma; γ is distribution ratio.

More complex no isothermal model was described in [2] taking into consideration the multi component composition of the cathodes and plasma.

3 Coating growth in no isothermal conditions

Thermal diffusion model of the coating growth on the surface is similar to above but includes thermal conductivity equation additionally to diffusion ones. For multi component system we have in the coating and in the substratum the equations

$$\rho C_\sigma \frac{\partial T}{\partial t} = -\nabla \bullet \mathbf{J}_q, \tag{3}$$

$$\rho \frac{\partial C_k}{\partial t} = -\nabla \bullet \mathbf{J}_k, \tag{4}$$

where the heat and mass fluxes includes the cross effects. For example, if the coating forms from the high-melting metal Me and carbon we have

$$\mathbf{J}_1 = \rho D_{11}\nabla C_1 - \rho D_{12}\nabla C_2 - \rho D_{11}C_1 S_{T1}\nabla T$$

$$\mathbf{J}_1 = \rho D_{21}\nabla C_1 - \rho D_{22}\nabla C_2 - \rho D_{22}C_2 S_{T2}\nabla T$$

$$\mathbf{J}_q = -\lambda\nabla T - A_1\nabla C_1 - A_2\nabla C_2$$

where T is the temperature, C_σ is heat capacity at constant stresses; ρ– density; λ_T,D_{ik}, A_1, A_2– transfer coefficients; S_{Tk}– Soret coefficients.

The boundary conditions for plane surface are similar to previous. So, on the growing surface we write

$$-J_q = q_0 \frac{d\xi}{dt} - \sigma\varepsilon\left(T^4 - T_W^4\right), -J_k = m_k y_k \frac{d\xi}{dt},$$

where $y_k$is mol concentration of the particles near the specimen, mol/m3, q_0 is the heat source due to energy loss by ions at the collision with surface:

$$q_0 = k\left(\frac{V_1^2}{2} m_1 y_1 + \frac{V_2^2}{2} m_2 y_2\right),$$

T_W is the vacuum camber walls temperature, V_1, V_2 are the particles velocities. The law of the coating growth follows from momentum conservation law:

$$\frac{d\xi}{dt} = \frac{y_1 V_1 + y_2 V_2}{y_1 + y_2}$$

At the initial time moment the temperature equals to T_0, the coating absents.

When the coating growths on the cylindrical surface, the problem would be consider as two dimensional in cylindrical coordinate system (Fig.1). But taking into account the experimental conditions, we can assume that the atoms and ions are distributed along the cylindrical specimen uniformly. Than, the problem turns in one-dimensional [3] and

$$\nabla \bullet ... = \frac{1}{r}\frac{\partial}{\partial r} r...$$

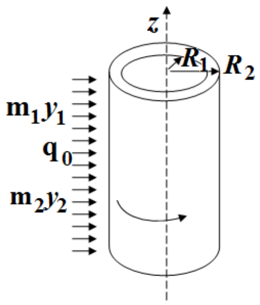

Figure 1: Illustration to problem formulation

Besides the diffusion and thermal process there are other processes are observed at the conditions of coating growth. For example, the new phases form in the coating and in the substratum near the interface. To describe the chemical conversions we add to the right part of the equations (1),(2) or (3),(4) corresponding summands.

For example for Me and carbon deposited from plasma, we can include in the model the formation of chromium carbide Cr_3C_2 and ferric carbide FeC. In the case of coating deposition using a cathode of Ti, the system will proceed the reaction of two chemical compounds:

$$Ti + C \to TiC; \qquad Fe + C \to FeC.$$

When using a cathode based on Zr:

$$Zr + C \to ZrC; \qquad Fe + C \to FeC.$$

Than we write instead (3), (4):

$$\rho C_\sigma \frac{\partial T}{\partial t} = -\nabla \bullet J_q + \sum_{i=1}^{r} Q_i^\sigma \varphi_i,$$

$$\rho \frac{\partial C_k}{\partial t} = -\nabla \bullet J_k + r_k, k = 1, 2,$$

$$\rho \frac{\partial C_k}{\partial t} = r_k, k = 4, 5,$$

where C_k are mass concentrations of species ($C_1 - Cr$; $C_2 - C$; $C_3 - Fe$; C_4- FeC; C_5 - refractory metal carbide); r_k species sources in the reactions; φ_i are the reaction rates; r is the reaction number ; Q_i^σ is the heat release in the reaction with number i. In this case we have

$$\sum_{k=1}^{5} C_k = 1.$$

This model was investigated in [4].

4 Coupling model

The mechanical stresses and strains could be appearing due to the difference in the materials and new phase difference and temperature gradient. It was shown in [1, 2] that the diffusion stresses can be large quite in isothermal models.

To evaluate the mechanical stresses in the first approximation we can use known quasi static problems of thermal elasticity theory, because the temperature in these technologies is more less then the melting temperature

In this work the temperature and concentration stresses are taken into account. Than the relations between stresses σ_{ij} and strains ε_{ij} take the form:

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - K\omega\right], \tag{5}$$

where

$$\omega = 3\left[\alpha_T\left(T - T_0\right) + \sum_{k=1}^{n_D}\alpha_k^c\left(C_k - C_{k0}\right) + \sum_{l=1}^{n_{ch}}\alpha_k^{ch}\left(C_l - C_{l0}\right)\right],$$

the first sum corresponds to concentration changes for moving components, the second give the deformation connecting with new phases formation. Thermal and concentration expansion coefficients could be found from additional considerations. It is not possible to separate the tresses and strains of different nature experimentally. But we can evaluate the role each of them numerically.

It is necessary to find the stresses and strains in hollow cylinder of finite size due to the heating and composition change. Similar problem from thermal stresses theory is contained in [5]. To solve this problem we assume that the temperature and concentration distributions are known for any time moments. External loading absent, gravity force are not taken into account. The cross-sections of cylinder, perpendicular to it axis, remain plane. In this case we have one dimensional problem and

$$\varepsilon_{rr} = \frac{du}{dr}, \varepsilon_{\varphi\varphi} = \frac{u}{r}, \varepsilon_{r\varphi} = \varepsilon_{rz} = \varepsilon_{\varphi z} = 0,$$

$$\sigma_{r\varphi} = \sigma_{rz} = \sigma_{\varphi z} = 0$$

$$\varepsilon_{zz} = const.$$

The single equilibrium equation remains in our conditions:

$$\frac{d\sigma_{rr}}{dr} + \frac{\sigma_{rr} - \sigma_{\varphi\varphi}}{r} = 0.$$

This equation will be correct in each layer of cylinder. The boundary condition

$$r = R_1 : \sigma_1 = 0;$$

speak that internal surface is free from the loading. Second condition

$$r = R_2: \quad u_1 = u_2, \sigma_1 = \sigma_2;$$

reflects the condition of ideal contact. External surface is free from the loading also:

$$r = R: \quad \sigma_2 = 0.$$

Here σ_1 is radial component of stress tensor in the substratum, σ_2 - is radial component of stress tensor in the growing coating; u_1 and u_2 are corresponding radial displacements.

The additional condition (integral equilibrium condition)

$$\int_{R_1}^{R(t)} \sigma_{zz}(r)\, rdr = 0 = \int_{R_1}^{R_2} \sigma_{zz,1}(r)\, rdr + \int_{R_2}^{R(t)} \sigma_{zz,2}(r)\, rdr \tag{6}$$

serve to find the value ε_{zz}. Using (5) and accepting the properties as constant, we shall find the solution in the form

$$u_k = \frac{1}{3}\frac{1+\nu_k}{1-\nu_k}\frac{1}{r}\int_{R_k}^{r} \omega_k(r)\, rdr + \frac{A_k}{2}r + \frac{B_k}{r},$$

$$\varepsilon_{rr,i} \equiv \varepsilon_i = \frac{1}{3}\frac{1+\nu_i}{1-\nu_i}\left[\omega_i(r) - \frac{1}{r^2}\int_{R_i}^{r} \omega_i(r)\, rdr\right] + \frac{A_i}{2} - \frac{B_i}{r^2},$$

$$\varepsilon_{\varphi\varphi,i} = \frac{1}{3}\frac{1+\nu_i}{1-\nu_i}\frac{1}{r^2}\int_{R_i}^{r} \omega_i(r)\, rdr + \frac{A_i}{2} + \frac{B_i}{r^2}, i = 1,2$$

$$\sigma_k = -\frac{E_k}{3(1-\nu_k)}\frac{1}{r^2}\int_{R_k}^{r} \omega_k(r)\, rdr + \frac{E_k}{(1-2\nu_k)(1+\nu_k)}\left[\frac{A_k}{2} + \nu_k\varepsilon_{zz}\right] - \frac{1}{r^2}\frac{B_k E_k}{1+\nu_k},$$

where A_1, B_1, A_2, B_2 are integration constants, E_k, ν_k - elastic modules and Poison's coefficients.

To calculate the stresses and strains the temperature and concentration field could be known. But the stresses can effect on the transfer processes. Based on irreversible thermodynamics, we can obtain the equations for the heat and mass fluxes. This leads to the transmission coefficients change that is represented in[7]

As a result, we come to coupling problem, for the solution of which a special algorithms is used.

The parameters, used in this model, could be calculated on the base of known theories. The algorithms of the calculation in corpore is described in [8]. Some parameters used for stresses and strains calculations are presented in the Table.

Mechanical properties of substances

	Ti	C	Fe	Zr	ZrC	TiC	FeC	
E	96	76	190	95	475	494	200	GPa
ν	0,3	0,27	0,28	0,27	0,3	0,32	0,29	
α_T	8,2	2	4	5,6	7	8	4,7	$\cdot 10^{-6}, K^{-1}$

The examples of stress and strains distribution in the system substratum – growing coating" are presented on the figures 2 and 3. The radial stresses and displacements are continuous, that correspond problem formulation. The break in σ_{zz} and $\sigma_{\varphi\varphi}$ connects with the difference between the properties of materials. Because the growing coating more uniform than transient zone, the stress and strain distribution change weak with time.

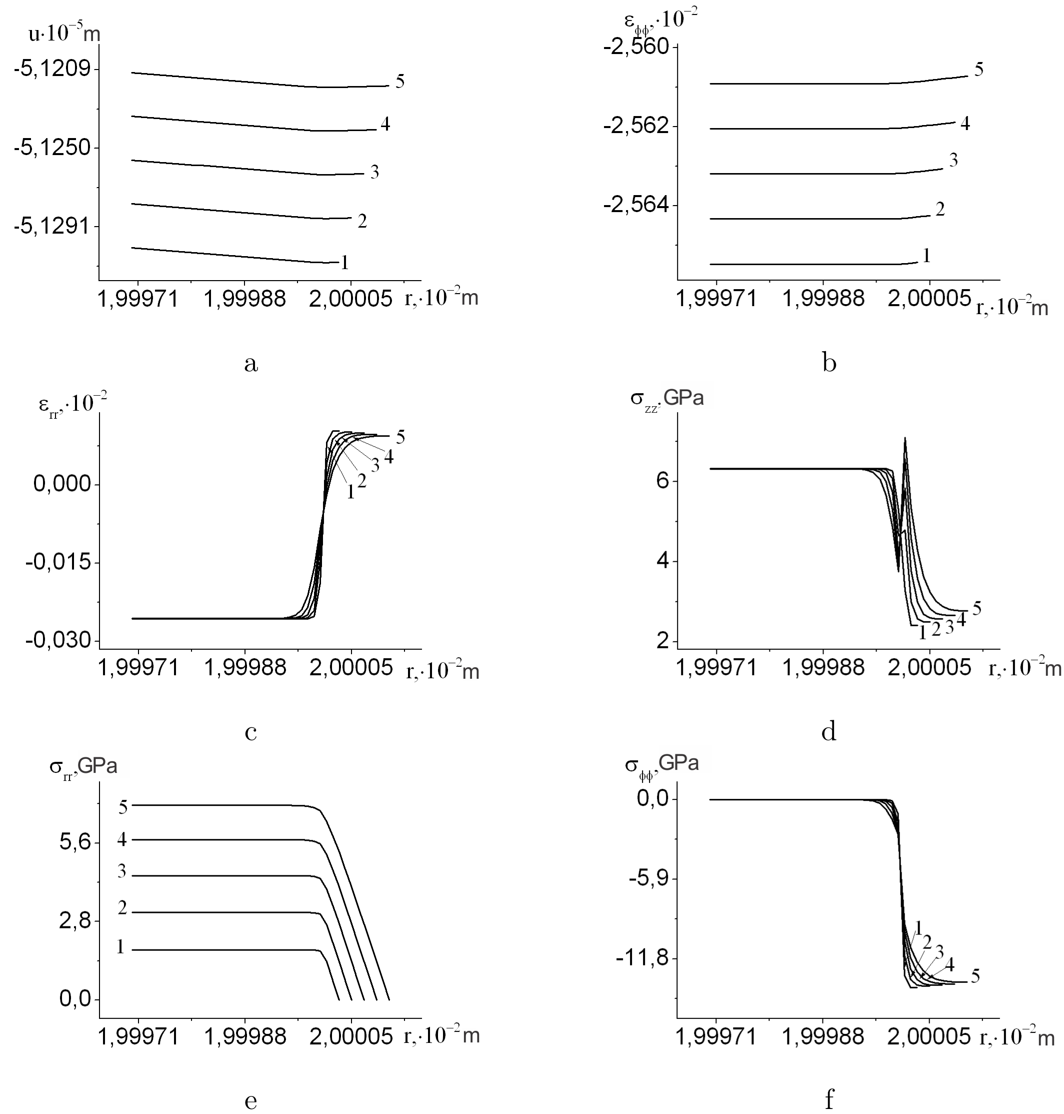

Figure 2: Displacements (a), angle strains (b), radial strains (c), axis stresses (d), radial stresses (e), angle stresses (f) along the radial coordinate at the Ti deposition for different time moments. 1.-t=400c; 2.-t=800c; 3.-t=1200c; 4.-t=1600c; 5.-t=2000c;

It is shown that the stresses at the Ti deposition are higher than at the Zr deposition. The strains stay very small in any case.

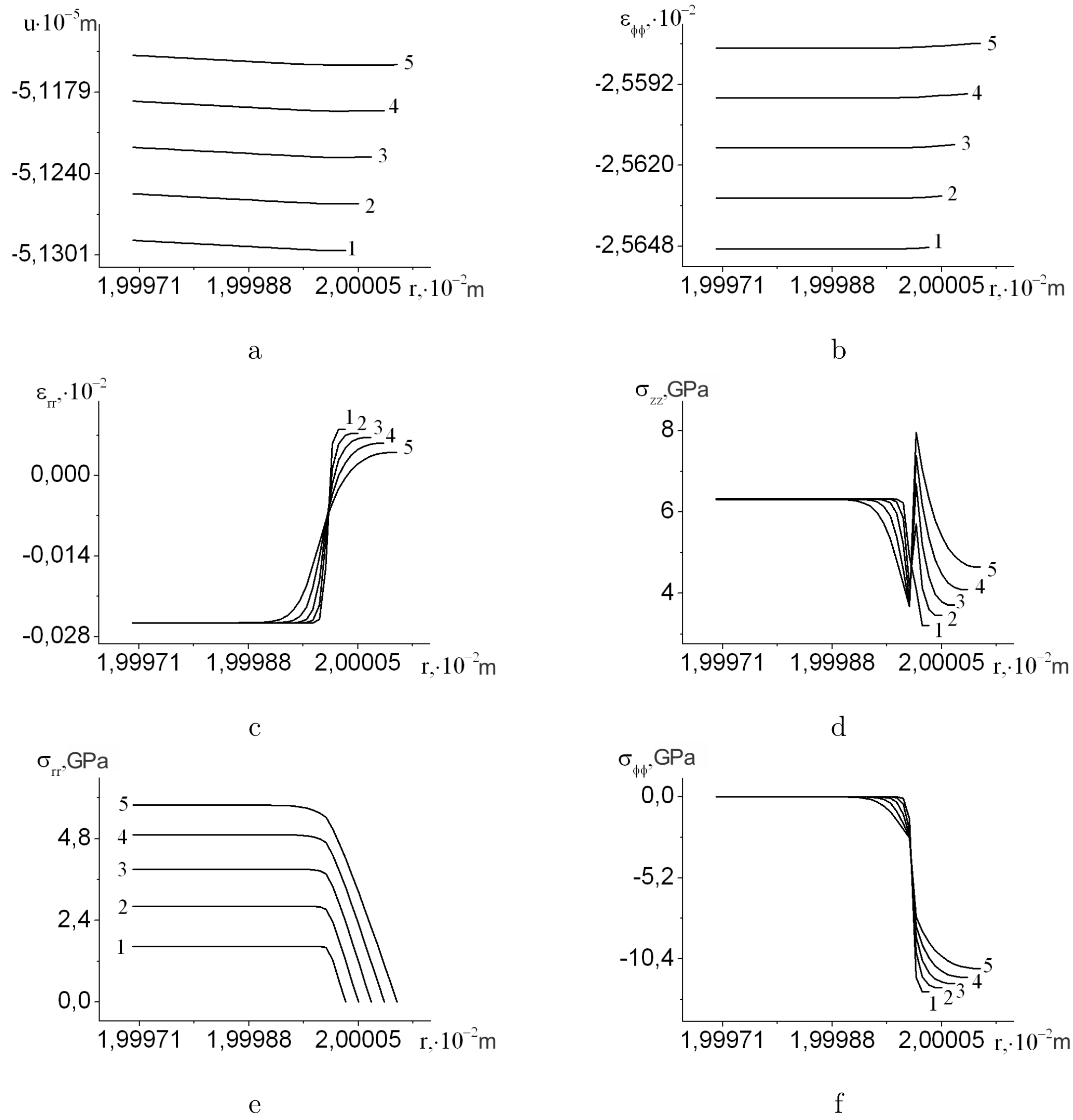

Figure 3: Displacements (a), angle strains (b), radial strains (c), axis stresses (d), radial stresses (e), angle stresses (f) along the radial coordinate at the Zr deposition for different time moments. 1.-t=400c; 2.-t=800c; 3.-t=1200c; 4.-t=1600c; 5.-t=2000c;

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