KINETICS OF PHASE TRANSFORMATIONS IN THIN FOILS WITH COATINGS PRODUCED BY THE METHODS OF ION-PLASMA DEPOSITION

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Utilization of foils as samples for investigation of thermally induced processes of phase transformations demonstrates some advantages over massive samples:

1) relaxation times of nonequilibrium processes are for orders of magnitude less

2) possibility to use non-destructive methods of analysis such as Mossbauer spectroscopy, Roentgenphase analysis and Rutherford back scattering for obtaining reliable information

3) obtaining quantitative information about formed phases on surface and in the bulk of a sample.

We believe that magnetron deposition is the most suitable for modification of foil properties due to its advantages for making thin coatings. In the Institute there were designed and manufactured ion-plasma installments for making coatings of different function [1].

Objects for investigation were two- and three-layer foils Fe-Be subjected to various thermal treatments (annealings). Thermal annealing was performed in a muffle furnace at pressure $6 \cdot 10^{-6}$ mm.Hg. at temperature 720°C. This temperature was achieved for 30 min, cooling of the samples was performed after the vacuum system finished its work and was characterized by the time interval compared to the heating time.

Mossbauer spectra were taken using two methods – registration of γ-quanta in the geometry for absorption (MS) and registration of conversion electrons in the backscattering geometry (CEMS) from both sides of samples. In the first case there was determined the averaged phase state of the whole sample; in the second – of near-surface layers of the thickness ~0.1-1 μm depending on concentration of Be atoms. The method of reconstruction for distribution functions of partial spectra ultrafine parameters was used for processing and analyzing the spectra. The method was realized in a computer code DISTRI that is a part of a software package MSTools [2]. Roentgenphase analysis of the samples was performed at a diffractometer DRON-2 with β-filter and radiation from Cu-Kα. The measurements were performed in the geometry Bragg-Brentano from both sides of the samples. The Rutherford backscattering experiments were performed at a recharging accelerator UKP-2-1 of Institute of Nuclear Physics NNC RK. More detailed information on obtained results is available in [3, 4].

As an example, fig.1 presents curves of relative content of the phases formed at isothermal annealing for the systems Be(1.2 μm)-Fe(11μm) (fig. 1a) and Be(1μm)-Fe(11μm)-Be(1.2μm) (fig. 1b) obtained in processing of CEMS-spectra. One can see that in the first case there is complete dissolution of berylliun with formation of beryllium alloy in iron (α-Fe(Be)), and in the second case there is observed stabilization of $FeBe_2$ phase on the surface. If the first case can be explained (described) within the conventional models, one needs entirely new approach for description of the stabilization.

Below we comment on the main ideas of the developed physical model. Let concentration of component B in A does not exceed solubility limit C_B independently on the method of introduction of B into A. In this case the system tends to the minimum of Gibbs free energy. Schematically this is represented by an arrow from the point P at fig. 2a. Approximation to equilibrium via diffusion mechanism can be described by Fick's classical law. Let us consider a case of two-phase region (α+β) in equilibrium (schematically represented by the point K, fig. 2 and fig. 3a). Let in the region of the material denoted by a step at fig. 3a the α-phase is

supersaturated. The system will tend to equilibrium through diffusion by α-matrix and, when meet inclusions of β-phase, will merge them (fig. 3b). For substitution alloys the diffusion undergoes vacancy mechanism, i.e. it is required the presence of thermally equilibrium vacancies, but they are not required for merging process. Therefore, the rate of diffusion is much less than the rate of phase transformations. Let us transform a system at fig. 3a to create a non-uniform in depth distribution of β-phase (see fig. 3c). If surface effects are not taken in consideration, there will remain the equilibrium between the phases α and β. Let there was formed a layer with supersaturated β-phase (schematically denoted as β* at fig. 3c); then atoms will diffuse by β-matrix and absorb inclusions of α-phase. At that the β-phase propagates into the bulk and the rate of its growth would decrease gradually. Similar mechanism is also characteristic for supersaturation of α-phase. It follows from the above stated that the governing parameter in the model of phase-formation mechanisms in layered systems is the size of formed inclusions of new phase λ.

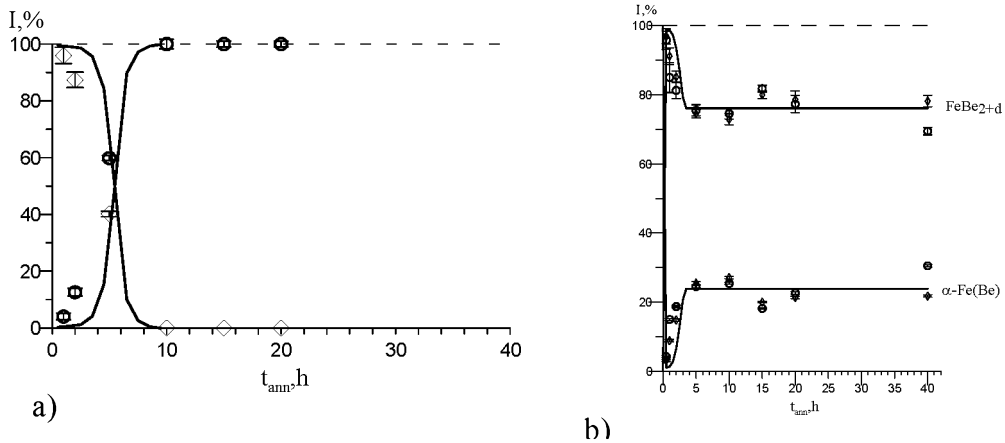

Fig.1. Relative intensities of I partial CEMS-spectra taken from the beryllium coating side for layered system Be-Fe depending on duration of the consequent isothermal annealing at T_{ann}=720°C: a) complete dissolution of beryllium (Be(1.2μ)-Fe(11μ)),, b) thermal stabilization (Be(1μ)-Fe(11μ)-Be(1.2μ)). o, ◊ -experiment, solid line - numerical calculations.

Below we present the algorithm for calculations. For one-phase region the time dependence for concentration of the components C_i is determined by the equation:

$$\frac{\partial C_i}{\partial t} = -div\vec{J}_i, \qquad (1)$$

where $\vec{J}_i$ – flow of atoms:

$$\vec{J}_i = D_{12}(C(x))\frac{\partial C_i(x)}{\partial x}. \qquad (2)$$

For binary system the coefficient of mutual diffusion is as follows:

$$D_{12}(C(x)) = C_1(x)D_2 + C_2(x)D_1, \qquad (3)$$

where D_1 and D_2 – diffusion coefficients of the component A into B and B into A (in our case those are Be into Fe and Fe into Be); C_1 and C_2 – atomic concentrations of the components A and B. For a binary solution $C_1+C_2=1$.

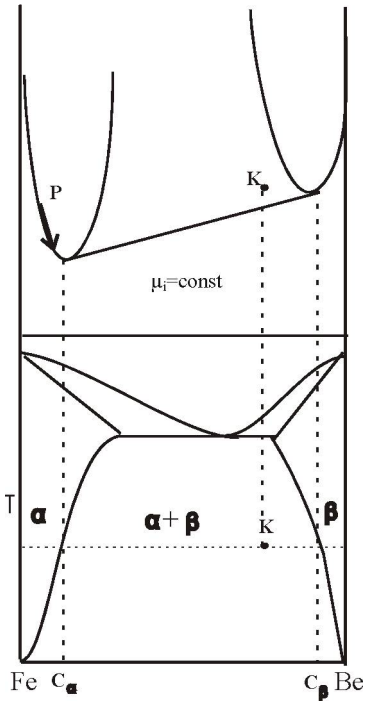

Fig.2.

a) Gibbs free energy μ_i-chemical potential of constant in two-phase region I-component (i=1,2),

b) Phase diagram

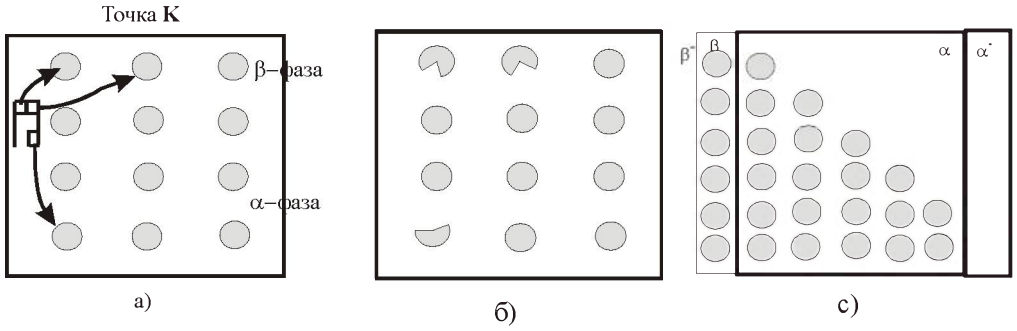

Fig.3. Schematic representation of physical model

Temperature dependence of diffusion coefficients D_1 and D_2 in one-phase regions is determined by Arrhenius law:

$$D_i = D_{0i}\, exp\left(-\frac{Q_{0i}}{RT}\right) \qquad (4)$$

where D_{0i} – frequency factor, Q_{0i} – activation energy for a corresponding atom, R – gas constant.

Combining (1) and (2) we have:

$$\frac{\partial C_i}{\partial t} = \frac{\partial D_i(x)}{\partial x}\frac{\partial C_i}{\partial x} + D_i(x)\frac{\partial^2 C_i}{\partial x^2}. \qquad (5)$$

For each time step there was calculated change in profile of the components' concentration. If the concentration lies in two-phase region, then the probability of inclusions of a phase in a two-phase region at depth x was determined as:

$$P_i = P(x) = \frac{C_\alpha - C(x)}{(C_\beta - C_\alpha)}. \qquad (6)$$

Here C_α =13% (α-Fe(Be)) and C_β =67% ($FeBe_2$) at temperature 720°C.

Coefficient of mutual diffusion $D_i(x,\lambda)$ in two-phase region depends both on depth x and size of inclusions λ

$$D_i(x,\lambda) = D_{zp} W_i, \qquad (7)$$

where D_{zp} corresponds to coefficient of mutual diffusion D_{12} at interface of one- and two-phase regions; the probability W_i of formation of diffusion channels at depth x_i:

$$W_i = \sum_{j=i}^{M} \Omega_j = \Omega_i + \Omega_{i+1} + \Omega_{i+2} + \ldots + \Omega_M . \qquad (8)$$

M – number of layers in two-phase zone, determined by the relation of thickness of a two-phase zone to the size of inclusion of a new phase. Probability of formation of diffusion channels at the depth x_i for enrichment component A (attack to phase enrichment component B):

$$\Omega_i = (P_1 \cdot P_2 \cdot \ldots \cdot P_i \cdot (1 - P_{i+1}) = \left(\prod_{j=1}^{i} P_j \right) (1 - P_{i+1}). \qquad (9)$$

It was supposed that all inclusions are of the same size λ. From the above presented one can see that wider two-phase region, stronger the attenuation of diffusion coefficients and the rate of phase formation decreases.

Initial condition was taken in the form:

$$C_{Âå} = \begin{cases} 1 & \text{at } 0 < õ < d_{Âå} \\ 0 & \text{at } d_{Âå} < õ < d \end{cases},$$

where d_{Be} – thickness of the produced coating, d – thickness of the whole sample. Boundary conditions corresponded to absence of flows at the sample surface:

$$\left. \frac{\partial C}{\partial x} \right|_{x=0;d} = 0 .$$

The system of equations (5) can be numerically solved using a standard software package IVPAG/DIVPAG of the library DIGITAL.

The main parameter of the computational model is coefficient of mutual diffusion. An additional parameter in the proposed model is size of inclusions λ of formed phases in two-phase regions.

Parameters of diffusion coefficient for iron in beryllium were taken from literature: - D_{Fe} =1cm^2/s, Q_{Be} = 220 kJ/mole. Because of absence of experimental data for diffusion

coefficient for beryllium in iron in the considered temperature range, it was considered as an adjusting parameter for fitting the experimental data.

Fig. 1 (a, b) presents the results of numerical calculations. As one can see in a layered system Fe-Be, good correspondence of numerical results with the experimental data is at $D_{Be} = 1{,}23 \cdot 10^{-3} \mu m^2/s$. There should be noted some characteristic peculiarities of developed physical model we propose.

At fig. 4 one can see that variations of sizes of phase inclusions within reasonable limits influence only slightly the kinetics of phase formation.

It is also of interest to represent the depth dependence of diffusion coefficient for beryllium at various instants of time in case of thermal stabilization (fig.5). One can see that in this system the diffusion coefficients decrease with time and gradually tend to zero. It is possible to make a conclusion that the main reason for thermal stabilization is formation of well-formed two-phase region.

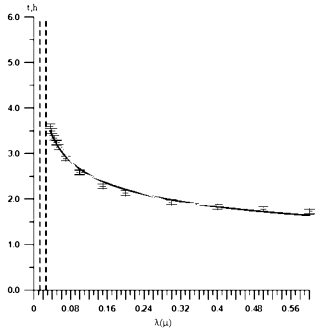

Fig.4. Time till the system becomes stable versus size of inclusions λ

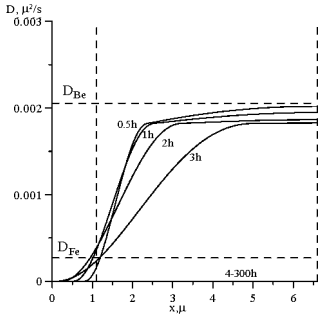

Fig.5. Diffusion coefficient versus sample depth at various instants of time for λ=0.05μ

Based on the obtained results along with the results of previous experimental investigations of the system Fe-Be [4, 5] one can make the following conclusions:

1. The authors have performed experimental investigations of thermally induced diffusion and phase transformations in the layered systems Fe-Be.
2. There was experimentally verified the condition of creation of thermally stable surface layers with given phase.
3. There was developed a physical model that enables to describe diffusion processes in a layered system with formation of thermally stable phases on surface of metallic samples.
4. There were performed numerical calculations that describe the obtained experimental data.

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