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COMPUTATIONAL-EXPERIMENTAL APPROACH TO PREDICTION OF MASS-TRANSFER PROCESSES IN METALLIC COATINGS OF GAS-TURBINE BLADES AND THEIR SERVICE LIFE

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A computational-experimental approach to analysis of long-time processes of mass transfer of aluminum in metallic MCrAlY coatings of gas-turbine blades and to prediction of their service life is proposed. The approach is based on the mathematical model describing the oxidation and diffusion processes in the coating and in the alloy of a blade, the parameters of which are identified by the data of short-time experiments. The results of theoretical and experimental determination of the aluminum-concentration distributions in the coating and in the basic alloy of a gas-turbine blade and the results of prediction of the service life of the coating are presented. It is shown that this approach allows one to perform analysis of long-time processes of mass-transfer in metallic coatings of gas-turbine blades and predict their service life with a high degree of accuracy.

The blades of modern, stationary gas-turbine plants are protected from high-temperature oxidation by metallic coatings of the type MCrAlY. The main element that prevents oxidation of the coating of a blade and the blade itself is aluminum (Al), whose content in the coating can vary from 6 to 12%. The service life of the coatings of stationary-gas-turbine blades should be tens of thousands of hours at working temperatures of 900–1000^{o}C; therefore, it is very expensive and, every so often, impossible to determine this parameter experimentally. Calculation analysis (simulation) of long-time processes of mass transfer of the main oxide-forming elements (Al in our case) in the coating and in the basic alloy of gas-turbine blades is a practicable and cheap method of estimating their service life. The mass-transfer processes determining the service life of the coating of a gas-turbine blade at its working temperatures are oxidation (formation of an Al_2O_3 oxide film on the outer surface of the coating) and diffusion of Al to the oxide-film boundary and to the basic alloy of the blade.

The available models describing the processes of high-temperature oxidation and diffusion in MCrAlY coatings can be divided into two types:

1) simple, approximating empirical dependences of the type of power or other laws [1–4] describing the change in the mass and thickness of the oxide film with time;

2) models comprising dependences of the first type and differential equations describing the diffusion of oxide-forming elements in the system oxide–coating–basic alloy [5, 6].

The form of the first type of dependences and the values of their parameters (multipliers, exponents, etc.) may change in a wide range depending on the type and composition of the alloy and the temperature and time intervals within which an experiment was conducted (a short-time experiment is usually conducted for 2000–3000 h). Such dependences are true, as a rule, for those temperature and time conditions for which they have been obtained. They cannot be used for analysis of the diffusion processes occurring inside coatings; therefore, long-time processes of oxidation and diffusion can be analyzed only with the use of mathematical models describing these physicochemical processes qualitatively and quantitatively, i.e., with models of the second type.

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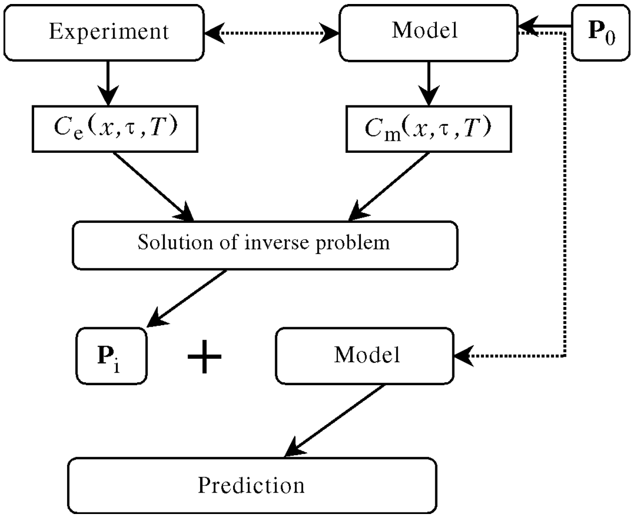

Fig. 1. Scheme of the computational-experimental approach to prediction of mass-transfer processes in coatings of gas-turbine blades and their service life.

However, it is often difficult or impossible to use the second type of models for analysis of the above-indicated long-time processes because of the absence of reliable values of their input parameters, such as the diffusion coefficient of the oxide-forming element. In the literature, there are only data on the diffusion coefficients of alloys having simple compositions (binary or ternary), whereas alloys used in practice have more complex compositions. We will consider a coating alloy containing five elements — nickel, cobalt, chromium, aluminum, and yttrium. In the literature, there are no data on the diffusivity of aluminum in this alloy. In [7], the data on the diffusivity of aluminum in a ternary NiCrAl alloy, which is very close in composition of basic elements to the above-indicated alloy, are presented.

The computational-experimental approach proposed in the present work makes it possible to find the effective diffusion coefficient of aluminum and other unknown parameters of the model on the basis of solution of the inverse diffusion problem. This approach was used in [8] for analysis of the mass transfer of chromium with the formation of chromium oxide in a coating and the diffusion of chromium into the basic alloy; however, the service life of the coating was not estimated in this work.

The aim of the present work is analysis of the mass transfer of aluminum in MCrAlY coatings of gas-turbine blades and prediction of their service life with the use of the computational-experimental approach based on the mathematical model describing the diffusion and oxidation process in the coating and in the alloy of a blade, the parameters of which are identified by the data of short-time experiments.

As will be shown below, this approach makes it possible to analyze long-time processes of mass transfer in metallic coatings of gas-turbine blades and predict their service life with a high degree of accuracy.

Computational-Experimental Approach. The approach, in essence, is as follows: one selects a model of mass transfer and a set of experimental data, which, in combination, would make it possible to obtain, on the basis of solution of the inverse diffusion problem, a more adequate model for analysis of long-time mass-transfer processes in metallic coatings and prediction of their service life with the use of a definite service-life criterion.

The scheme of the approach (Fig. 1) for prediction of mass-transfer processes is as follows:

1. Construction (selection) of a mathematical model that would adequately describe the main physical processes occurring in the system under study that determine the service life of the coating. In our case, only models of the second type can be used in this approach. Such a model makes it possible to calculate the distribution (profile) of the aluminum concentration C_m.

2. Fulfillment of short-time experimental investigations for the purpose of determining the laws of formation of an oxide film and aluminum-concentration distributions in the coating and in the basic alloy (C_e) at different temperatures and exposure times (times of treatment of coating samples in furnaces).

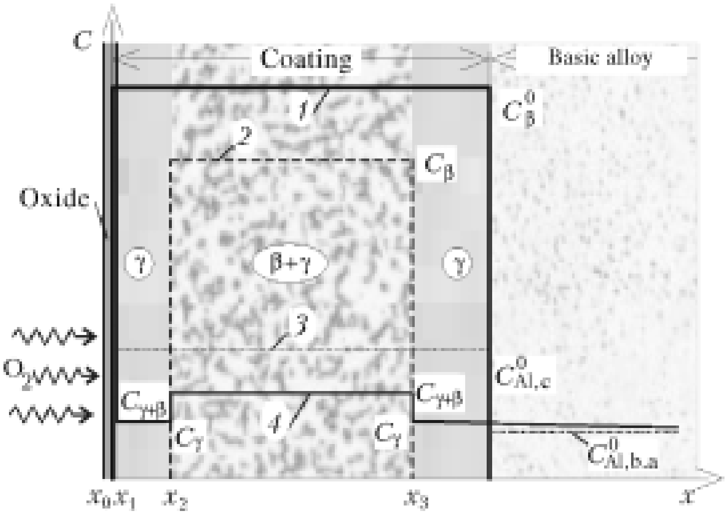

Fig. 2. Typical aluminum-concentration distribution in the oxide, the coating, and the basic alloy of a gas-turbine blade: 1, 3) concentration distribution of the β phase and aluminum at $\tau = 0$; 2, 4) the same distribution at $\tau > 0$.

3. Identification of the unknown parameters $\mathbf{P}_i$ of the model by the experimental data on the basis of solution of the inverse diffusion problem to obtain minimum values of F and close profiles of C_m and C_e.

4. Long-range prediction of the mass-transfer processes in a coating and of its service life on the basis of the model constructed (item 1) with the mass-transfer parameters determined (item 3).

It is common to use a simpler prediction scheme (Fig. 1): model + model parameters taken from the literature $\mathbf{P}_0$ = prediction. This scheme can be used for alloys having simple compositions, such as the ternary alloy investigated in [5, 6]; however, its predictions for complex compositions can be insufficiently exact because of the inexactly known parameter of the model $\mathbf{P}_0$. Therefore, the use of the complete scheme of the computational-experimental approach based on the model with identified parameter $\mathbf{P}_i$ makes it possible to do much more exact predictions.

The computational-experimental approach proposed involves identification of the model parameters (item 3) by the data of short-time experiments on the basis of solution of the inverse diffusion problem (identification problem). The solution of the inverse diffusion problem reduces to the search for such values of the parameters $\mathbf{P}_i$ for which the quantity

$$F = \left\{ \sum_{j=1}^{m} [C_{j\mathrm{m}}(\mathbf{P}) - C_{j\mathrm{e}}]^2 / m \right\}^{0.5} \to \min . \tag{1}$$

The method of solving the inverse diffusion problem is described in more detail in [8, 9].

We estimated the service life of protective MCrAlY coatings, assuming that the model parameters identified are independent of time, the aluminum diffusivity is effective, and the oxide film is free of spallings.

Let us now analyze the process of oxidation and diffusion of aluminum in a coating of thickness 100 μm containing 35% nickel, 30% cobalt, 24% chromium, and 8.4% aluminum (here and below, the concentration is given in mass percents, unless otherwise specified) with the use of the computational-experimental approach proposed.

Physical and Mathematical Models. Below is a description of the physical model of the diffusion redistribution of aluminum in the oxide–coating–basic alloy system that was obtained on the basis of analysis of the results of experimental investigations of the oxidation and diffusion processes in NiCoCrAlY coatings [5, 6] (Fig. 2).

An oxide is formed as a result of the combination of aluminum with oxygen that absorbs from the gas medium and, due to diffusion through the x_1–x_0 oxide layer, arrives at the oxide–coating interface x_1. Aluminum diffuses from the coating in two directions:

1) to the oxide–coating interface x_1, where it reacts with oxygen;

2) to the coating–basic alloy interface.

As a result of the diffusion of aluminum, a one-phase zone with a decreased aluminum content (γ phase) is formed in the coating on both the oxide side and the basic-alloy side (Fig. 2). The aluminum-concentration profile for the $(\gamma+\beta)$-phase NiCoCrAlY coating has a step shape. Four main zones can be separated: the oxide region $x_0 < x < x_1$; the region $x_1 < x < x_2$ depleted of aluminum, where only the γ phase exists; the region $x_2 < x < x_3$, where the γ phase and the β phase exist simultaneously; the region $x > x_3$ depleted of aluminum with the γ phase in the coating and in the basic alloy. All the boundaries in this model are mobile. The boundaries x_2 and x_3 move to meet each other because of the decrease in the content of the β phase in the $(\gamma+\beta)$-phase zone $x_2 < x < x_3$ of the coating, from which aluminum diffuses into the basic alloy (substrate) and to the oxide boundary x_1. The total content of aluminum C and its content in the β phase in the $(\gamma+\beta)$-phase zone $x_2 < x < x_3$ decreases with time, and the relation between them is determined by a given mass ratio.

A mathematical model of the above-considered processes is described in [6] and is given below in the version of the authors.

The processes of diffusion and oxidation of aluminum in the region $x_1 < x < x_\infty$ are described by the basic diffusion equation:

$$\frac{\partial C}{\partial \tau} = \frac{\partial}{\partial x}\left[D_{\mathrm{ef}} \frac{\partial C}{\partial x}\right], \tag{2}$$

$$\tau > 0\,, \quad x_1 < x < x_\infty\,, \quad C = C\,(x, \tau)\,, \quad x_1 = x_1\,(\tau)\,, \quad x_2 = x_2\,(\tau)\,, \quad x_3 = x_3\,(\tau)$$

with initial conditions

$$C\,(x, 0) = C\,(x) = \begin{cases} C_{\mathrm{c}}^0\,, & 0 < x < x_{\mathrm{c}}\,; \\ C_{\mathrm{b.a}}^0\,, & x \geq x_{\mathrm{c}}\,, \end{cases} \tag{3}$$

and conditions at the boundary x_∞

$$\frac{\partial C\,(x_\infty, \tau)}{\partial x} = 0 \tag{4}$$

and the condition at the boundary x_1, describing the flow of aluminum going into the formation of the oxide due to the aluminum-concentration gradient

$$J = -D_{\mathrm{ef}} \frac{\partial C\,(x_1, \tau)}{\partial x}\,. \tag{5}$$

On the other hand, this flow is equal to

$$J = J_{\mathrm{Al_2O_3}} - J_{dx_1}\,,$$

where $J_{\mathrm{Al_2O_3}} = 100 \cdot \frac{dx_1}{d\tau}$ is the total flow of aluminum absorbed in the process of oxide formation; $J_{dx_1} = C(x_1, \tau) \frac{dx_1}{d\tau}$ is the flow formed due to the movement of the boundary x_1. In this case, the quantity J in (5) has the form

$$J = [100 - C\,(x_1, \tau)]\,\frac{dx_1}{d\tau}\,, \tag{6}$$

where the movement of the boundary x_1 is described by the equation

$$\frac{dx_1}{d\tau} = 0.5\,\frac{k}{\left(1+\frac{1}{s}\right)}\,\frac{\rho_{\mathrm{Al_2O_3}}}{\rho_c}\,\frac{1}{\sqrt{\tau}}\,, \tag{7}$$

obtained on the basis of the stoichiometric ratio between the aluminum and oxygen masses going into the formation of the aluminum oxide and the parabolic law of growth of the oxide film used in the model [5, 6]

$$\Delta x = x_1 - x_0 = k\sqrt{\tau}\;. \tag{8}$$

The coefficient k in (8) is determined by the experimental data on the growth of the thickness of the oxide film with time. Dependence (8) allows one to calculate the position of the outer boundary x_0 of the oxide film.

It is assumed that concentrations at the boundaries x_2 and x_3 are as follows:

$$C\,(x_{2-},\tau) = C_\gamma\,,\quad C\,(x_{2+},\tau) = C_{\gamma+\beta}\,.$$

$$C\,(x_{3-},\tau) = C_{\gamma+\beta}\,,\quad C\,(x_{3+},\tau) = C_\gamma\,,$$

and the movement of the boundaries and the decrease in the aluminum concentration are described by the equation of mass balance between the diffusion flows of aluminum at these boundaries and the flows caused by the difference between the aluminum concentrations in the $(\gamma+\beta)$- and γ phases

$$J_\Sigma = J_\gamma\,(x_{2-},\tau) + J_\gamma\,(x_{3+},\tau) = (C_{\gamma+\beta} - C_\gamma)\,\frac{dx_2}{d\tau} + (C_{\gamma+\beta} - C_\gamma)\,\frac{dx_3}{d\tau} + (x_3 - x_2)\,\frac{dC_{\gamma+\beta}}{d\tau}\,, \tag{9}$$

where $J_\gamma(x_{2-},\tau) = -D_{\mathrm{ef}}\,\frac{dC(x_{2-},\tau)}{dx}$ and $J_\gamma(x_{3+},\tau) = -D_{\mathrm{ef}}\,\frac{dC(x_{3+},\tau)}{dx}$ are the diffusion flows to the oxide and to the basic alloy, caused by the difference between the aluminum concentrations to the left and to the right of the boundaries x_2 and x_3 respectively. The right side of Eq. (9) describes the mass transfer of aluminum from the $(\gamma+\beta)$-phase zone $x_2 < x < x_3$ of the coating due to the movement of the boundary x_2 to the right and the boundary x_3 to the left and the decrease in the total concentration of aluminum in the $(\gamma+\beta)$-phase zone for the time $d\tau$. Expression (9), upon division of its terms by J_Σ, takes the form

$$1 = (C_{\gamma+\beta} - C_\gamma)\,\frac{dx_2}{d\tau}/J_\Sigma + (C_{\gamma+\beta} - C_\gamma)\,\frac{dx_3}{d\tau}/J_\Sigma + (x_3 - x_2)\,\frac{dC_{\gamma+\beta}}{d\tau}/J_\Sigma = g_2 + g_3 + g_{2,3}\,, \tag{10}$$

where g_2 and g_3 are fractions (weights) of the total aluminum mass removed from the coating due to the movement of the boundaries x_2 and x_3 respectively and $g_{2,3} = (1 - g_2 - g_3)$ is the fraction of the total aluminum mass removed from the coating due to the decrease in the content of aluminum in the β phase in the zone $x_2 < x < x_3$.

The relation between the total content of aluminum $C_{\gamma+\beta}$ and its content in the β phase $C_\beta(\tau)$ in the coating is described by the relation

$$C_{\gamma+\beta}\,(\tau) = C_\beta\,(\tau)\,C_\beta^{\mathrm{Al}} + [1 - C_\beta\,(\tau)]\,C_\gamma\,, \tag{11}$$

where C_β^{Al} = const is the aluminum content in the β phase.

Unlike the model described in [6], the model proposed involves ratio (10), in which the weights g_2 and g_3, in fact, determine the velocity of movement of the boundaries x_2 and x_3. This makes it possible to use expressions (2)–(11) for a wider range of coating compositions for which the velocity of movement of these boundaries is not determined completely by the concentration gradients $\frac{dC(x_{2-},\tau)}{dx}$ and $\frac{dC(x_{3+},\tau)}{dx}$. In the thermodynamic diffusion theory, the boundaries x_2 and x_3 can be determined by the complex processes of formation/dissolution of the β- and γ phases in solid solutions; however, the practical use of this theory for the complex systems considered presents a problem.

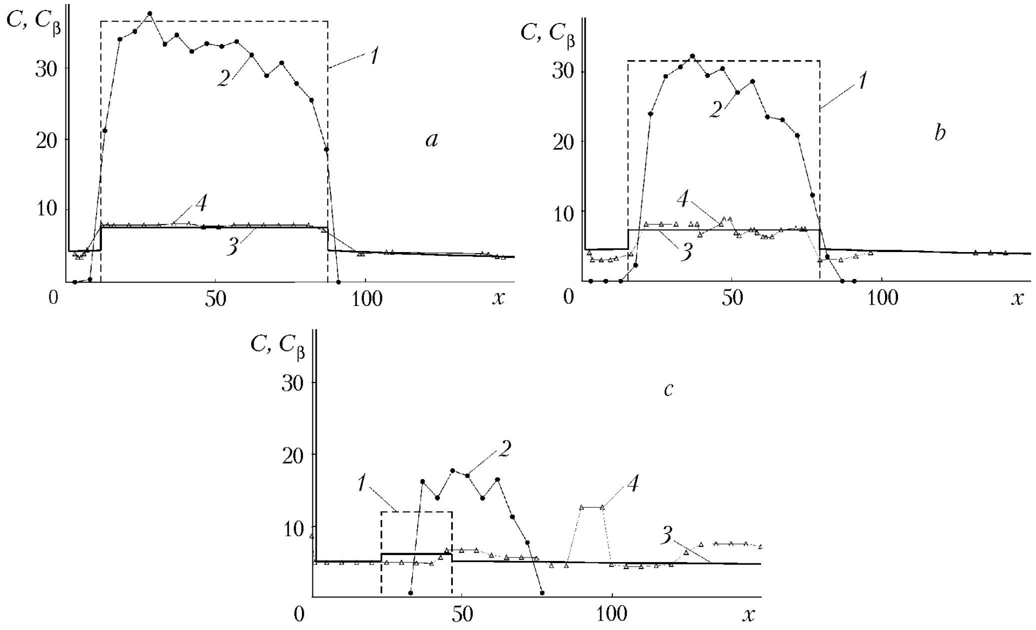

Fig. 3. Calculated and experimental concentration distributions of aluminum (%) and the β phase (vol.%) at a temperature of 950^{o}C and an exposure time of 300 (a), 1000 (b), and 5000 h (c): 1, 2) distribution of the β phase [1) calculation, 2) experiment]; 3, 4) distribution of aluminum [3) calculation, 4) experiment]. x, μm.

The above-described model has been formulated with the following assumptions:

a) the character of the main physicochemical processes occurring in the coating–substrate system does not change with time;

b) only one element (aluminum) participates in the formation of the oxide; this assumption for the coating considered is supported by 20,000-h experiments;

c) the oxide is formed only at the boundary x_1;

d) the diffusion coefficient D_{ef} determined on the basis of solution of the inverse diffusion problem is an effective characteristic independent of time;

e) spallings are absent on the oxide film;

f) new phases formed at the coating–basic alloy are ignored.

The above mathematical model of diffusion and oxidation processes is integrated with the use of the numerical finite-difference method by the implicit scheme.

Experimental. The initial aluminum content in the coating material considered was 8.4%. A coating of thickness 100 μm has been applied on a substrate made from an IM 738 LC alloy. The samples were held in air in electric furnaces at temperatures of 900, 950, and 1000^{o}C. As the experimental data, we used the results of the x-ray spectroscopic microanalysis for different exposure times giving the distributions of the aluminum weight concentration over the thickness of the coating and the basic alloy and the results of the micrographical analysis, giving the distribution of the volume concentration of the β phase in the coating (Fig. 3).

Results of Calculations. Calculations were done with the use of expressions (2)–(11). The above-described computational-experimental approach was used for the experimental conditions where the temperature of thermal treatment of samples was 950^{o}C and the exposure time was 300, 1000, and 5000 h. The parameters of the model were identified for exposure times of 300 and 1000 h (Fig. 3a and b). The calculated distributions of the total concentration of aluminum and its concentration in the β phase were compared with the experimental data obtained at an exposure time of 5000 h (Fig. 3c).

The main input parameters of model (2)–(11) are the diffusion coefficient D_{ef}, the weights g_2 and g_3, and the coefficient k (oxidation constant) in the parabolic law (7). The value of k was found by approximation of the experi-

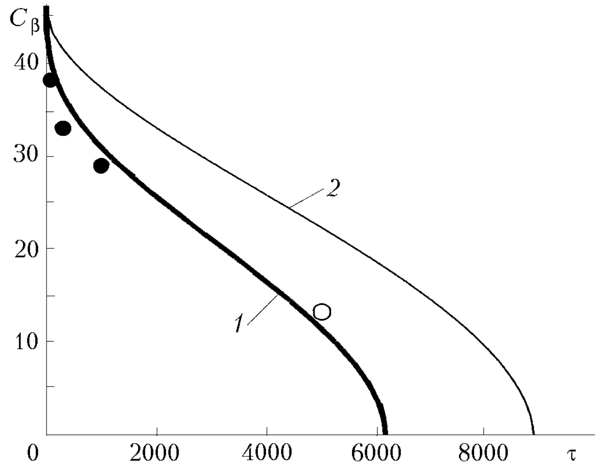

Fig. 4. Dependence of the β-phase concentration C_β (vol.%) in the coating on the time τ (h): 1) calculation at $D_{ef} = 2.4 \cdot 10^{-15}$ m^2/sec determined on the basis of solution of the inverse diffusion problem; 2) the same calculation at $D = 3.4 \cdot 10^{-16}$ m^2/sec [7]; the points denote experimental data (the dark points are used for identification of the model coefficients).

mental data $\Delta x_e = f(\tau)$ for exposure times of 300 and 1000 h. In our case, $k = 7.5 \cdot 10^{-9}$ m/sec^2 for the temperature 950^{o}C. The diffusion coefficient D_{ef} and the weights g_2 and g_3 were determined based on solution of the inverse diffusion problem by the iteration method [9]; their initial values were taken to be $D_{ef} = 1.0 \cdot 10^{-15}$ m^2/sec, $g_2 = 0.33$, and $g_3 = 0.33$. The determined values of these parameters were $D_{ef} = 2.4 \cdot 10^{-15}$ m^2/sec, $g_2 = 0.24$, and $g_3 = 0.16$. The value of C_γ was taken to be 3.82%.

It is taken that the service life of an NiCoCrAlY coating is the time after which the β phase disappears in the coating. This is explained by the fact that, after this time, the aluminum content in the coating becomes insufficient for the formation of a protective oxide film. A blade, in the coating of which the β phase disappeared, cannot be further used; otherwise its coating and the basic alloy will rapidly oxidize, which is inadmissible. The results of calculation of the time of disappearance of the β phase in the coating at a temperature of 950^{o}C are presented in Fig. 4. Thus, it may be suggested that the service life of the NiCoCrAlY coating with an initial aluminum content of 8.4% and a thickness of 100 μm is 6200 h at a temperature of 950^{o}C. As the results of the investigations show, the service life of this type of coating increases almost fourfold with an approximately twofold increase in its thickness [6].

The exactness of estimation of the service life of a coating depends critically on the reliability of determination of the aluminum-diffusion coefficient. For example, for the system NiCrAl, which is most close to the alloy studied, the diffusion coefficient of aluminum determined by extrapolation and interpolation of the literature data [7] is equal to $D = 3.4 \cdot 10^{-16}$ m^2/sec. Figure 4 shows the curve of disappearance of the β phase, constructed with this diffusion coefficient (curve 2). When curve 1 is compared with curve 2, it is apparent that the estimation of the service life of the coating depends strongly on the exactness of determination of D. Therefore, the above-described computational-experimental approach can be considered as an exact method of estimating the service life of complex-composition metallic coatings of gas-turbine blades.

Thus, it has been demonstrated that the computational-experimental approach proposed can be used for modeling of long-time processes of mass transfer in protective coatings of gas-turbine blades. It has made it possible to obtain a good agreement between experimental and calculated profiles of the aluminum concentration and the β-phase content in the coating considered as well as to estimate the input parameters of the model used, in particular to determine the diffusion coefficient of aluminum, and predict the service life of the coating.

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NOTATION

C, weight concentration, %; D, diffusion coefficient, m^2/sec; MCrAlY, type of coating, where M (nickel and/or cobalt), Cr (chromium), Al (aluminum), and Y (yttrium) are basic elements; F, functional of discrepancy between the experimental and calculated values; J, concentration-flux density, m/sec; $\mathbf{P}$, vector of the model parameters; m, total number of space-time points of concentration measurement; k, constant of oxide-film growth, $m/sec^{1/2}$; s, stoichiometry coefficient; T, temperature, K; x, coordinate, m; ρ, density, kg/m^3; τ, time, sec. Subscripts: m, model; b.a, basic alloy; c, coating; e, experimental; i, determined based on solution of the inverse diffusion problem (identification); ef, effective; j, number of a concentration-measurement point; 0, initial, known from the literature; ∞, infinity; $-$, to the left of a boundary; $+$, to the right of a boundary.

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