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FORMATION OF TWO-PHASE ZONES DURING INTERNAL OXIDATION OF BINARY ALLOYS

In the paper the formation patterns of two-phase regions during the internal oxidation process in low-alloyed binary alloys is studied. The goal of the research is the creation of a mathematical model for the internal oxidation process, which is to describe the kinetics of formation and evolution of internal oxidation zones, the study of the patterns governing the two-phase zone formation during internal oxidation, the study of the space-time dynamics of the structural parameters of the two-phase area, namely the number of the oxide particles, their average radius and the phase volume, at different stages of the internal oxidation zone evolution.

The two-phase process of diffusion saturation with light components applied to binary alloys is analyzed theoretically. The conditions for formation of disperse oxide particles are formulated. A mathematical model for the formation of two-phase areas as well as the numerical solution for the system of equations describing the kinetics of formation and evolution of the two-phase area for different values of the process parameters is proposed.

The modeling and experiments demonstrate that the distribution of structural parameters of the two-phase area has complex, non-monotonous nature. The influence of the main parameters of the process on the kinetics of the formation of the two-phase area in a lightly-alloyed binary nickel-based alloy plate is also determined. All stages of the plate's oxidation process are studied – from the inception of the particles to the coalescence of second-stage particles.

The results of the work could be used for developing new technologies in thermal and chemical-thermal treatments for disperse strengthening of materials using internal oxidation, as a physical basis for seeking ways of providing certain distributions of the internal oxidation zone structural parameters, which are required to give the alloy a necessary set of physical and mechanical properties.

The comparison of the modeling and experimental results shows a good correlation, which allows them to be recommended for developing new technologies in disperse strengthening, new heat-resistant steels, disperse-strengthened magnetic materials and electrotechnical alloys.

Key words: internal oxidation, binary alloys, two-phase area, internal oxidation area, internal oxidation area parameters, mathematical modeling, kinetics of internal oxidation zone formation.

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ФОРМУВАННЯ ДВОФАЗНИХ ЗОН В ПРОЦЕСІ ВНУТРІШНЬОГО ОКИСЛЕННЯ БІНАРНИХ СПЛАВІВ

Розглянуто закономірності утворення двофазних зон в процесі внутрішнього окислення слабологованих бінарних сплавів. Створено математичну модель процесу внутрішнього окислення, що описує кінетику формування та еволюції зони внутрішнього окислення; досліджено закономірності, що керують формуванням двофазної області в процесі внутрішнього окислення; вивчено просторово-часові зміни параметрів структури двофазної області – кількість частин окислів, їх середній радіус і об'єм фази – на різних стадіях еволюції зон внутрішнього окислення. Проведено теоретичний аналіз процесу дифузійного насичення легкокорухомими компонентами бінарних сплавів. Сформульовані умови виникнення дисперсних частин окислів. Запропоновано математичну модель формування двофазної області та проведено чисельне рішення систем рівнянь, що описують кінетику формування та еволюцію двофазної області для різних значущих чинників процесу.

Моделюванням та експериментально показано, що розподіл параметрів структури двофазної області має складний немонотонний характер. Визначені основні параметри процесу, що впливають на кінетику утворення двофазної зони в пластині слабологованих бінарних сплавів на основі нікелю. Вивчені всі стадії процесу окислення пластини – від зародження до коалесценції частинок другої фази.

Результати роботи можуть бути використані для розробки нових технологій термічної та хіміко-термічної обробки для дисперсного зміцнення матеріалів методом внутрішнього окислення, як фізичної основи для пошуку шляхів забезпечення певних розподілів параметрів структури зон внутрішнього окислення, необхідних для надання даному сплаву конкретного комплексу фізико-механічних якостей.

Порівняння результатів моделювання та експериментальних результатів показали їх хорошу відповідність, що дозволяє рекомендувати їх використовувати при розробці нових технологій дисперсного зміцнення, нових жароміцних сплавів, дисперсно-зміцнених магнітних матеріалів та електротехнічних сплавів.

Ключові слова: внутрішнє окислення, бінарні сплави, двофазна область, зона внутрішнього окислення, параметри зони внутрішнього окислення, математичне моделювання, кінетика формування зони внутрішнього окислення.

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ФОРМИРОВАНИЕ ДВУХФАЗНЫХ ЗОН В ПРОЦЕССЕ ВНУТРЕННЕГО ОКИСЛЕНИЯ БИНАРНЫХ СПЛАВОВ

Изучены закономерности формирования двухфазных областей в процессе внутреннего окисления слабологированных бинарных сплавов. Целью исследования явилось создание математической модели процесса внутреннего окисления, описывающей кинетику формирования и эволюции зоны внутреннего окисления; исследование закономерностей, управляющих формированием двухфазной области в процессе внутреннего окисления; изучение пространственно-временного изменения параметров структуры двухфазной области – числа частиц окислов, их среднего радиуса и объёма фазы – на различных стадиях эволюции зоны внутреннего окисления. В работе выполнен теоретический анализ процесса диффузионного насыщения легкоподвижным компонентом бинарных сплавов. Сформулированы условия образования дисперсных частиц окислов. Предложена математическая модель формирования двухфазной области и проведено численное решение систем уравнений, описывающих кинетику формирования и эволюции двухфазной области для различных значений параметров процесса.

Моделированием и экспериментально показано, что распределения параметров структуры двухфазной области имеют сложный немонотонный характер. Определено влияние основных параметров процесса на кинетику формирования двухфазной области в пластине слабологированных бинарных сплавов на основе никеля. Исследованы все стадии процесса окисления пластины – от зарождения частиц до коалесценции частиц второй фазы.

Результаты работы могут быть использованы для разработки новых технологий термической и химико-термической обработок для дисперсного упрочнения материалов методом внутреннего окисления, как физическая основа для поиска путей обеспечения заданных распределений параметров структуры зоны внутреннего окисления, необходимых для придания данному сплаву требуемого комплекса физико-механических свойств.

Сравнение результатов моделирования и экспериментальных результатов показало их хорошее соответствие, что позволяет рекомендовать их для разработки новых технологий дисперсного упрочнения, новых жаропрочных сталей, дисперсно-упрочненных магнитных материалов

и электротехнических сплавов.

Ключевые слова: внутреннее окисление, бинарные сплавы, двухфазная область, зона внутреннего окисления, параметры зоны внутреннего окисления, математическое моделирование, кинетика формирования зоны внутреннего окисления.

Introduction. In recent years, the number of materials which have their necessary service qualities formed in the process of disperse hardening of the hard mix using second stage particles, has increased considerably. The most widespread techniques for the manufacturing of such materials are thermal aging and powder-based metallurgy techniques. However, during the manufacture of high-strength and heat-resistant materials it is common for the requisite qualities to be achieved through the formation of disperse second-stage particles in the surface layers of the material only. As well, there is often the need to have various qualities both in the surface layer and throughout the volume of the material, which the aforementioned methods cannot provide. The most promising method for creating a disperse-hardened surface layer is the internal oxidation process (as well as internal nitration, borating, etc.).

However, both in theoretical and experimental aspects, the kinetics of two-phase area formation and its evolution throughout the internal oxidation process are not sufficiently studied, which somewhat holds back the wide practical use of the internal oxidation process.

Relevant research analysis. The theoretical analysis of the internal oxidation process is complex, as the task is concerned with a wide array of parameters, and the manifestations of internal oxidation take many forms and are hard to systemise. The analysis of literary data [1 – 10] shows that the existing models don't consider the process of two-phase area formation and don't always provide a satisfactory description of the *internal oxidation zone (IOZ)* growth kinetics. For a more comprehensive description of the internal oxidation process, the kinetics of the diffuse interaction of growing particles with the hard mix in the two-phase area need to be considered. For describing the change of the parameters of the two-phase area, such as the number of particles $N(x, t)$, their average radius $\bar{R}(x, t)$ and the volume of the phase $V_\phi(x, t)$, the particle size distribution functions in each IOZ section must be considered.

In turn, the lack of systematic and detailed experimental data makes it difficult to develop and specify the theory of the internal oxidation process.

The goal of the work is the creation of a quantitative model of binary alloy internal oxidation, which describes the IOZ formation and evolution kinetics, the study of patterns in the formation of two-phase area during internal oxidation and study of the space-time dynamics of the two-phase area structural parameters, namely the number of particles, $N(x, t)$, their average radius $\bar{R}(x, t)$ and phase volume $V_\phi(x, t)$, at different stages of the evolution stages of the internal oxidation zone.

In regards to that, the works [11 – 18] contain a theoretical analysis of the diffuse saturation process using light components applied to binary alloys. Based on that, the conditions for the formation of disperse nuclei of the second phase and the process of their growth is observed. A model is formed for the two-phase area formation process during internal oxidation, including the formation of the new phase particles and their diffuse growth (dissolution) during their interaction with the hard mix. Numerical solutions for the system of equations which describes the two-phase area formation kinetics for different values of the parameters of the internal oxidation process in a binary alloy plate are presented. All stages of the internal oxidation process in the plate are studied – from formation, to the coalescence of second stage particles. Experimentally studied is the kinetics of the internal oxidation of $Ni-Cr$, $Ni-Ti$ alloys, the experimental data are compared to the data obtained from the mathematical model.

Main results. We study the formation of the two-phase area during the internal oxidation process. Within this study, we shall look into the question regarding the use of constant diffusion coefficients in problems of diffuse saturation of binary alloys using light components, i.e. mostly the diffusion in $Fe-Me-O$ type systems, where the diagonal diffusion coefficient of the O element in the hard mix exceeds considerably the corresponding coefficient for the alloying element: $D_{11} \gg D_{22}$.

For that purpose, the following system of equations for diffusion in the hard mix of three-component systems was solved using a perturbation method:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} D_{ii} \frac{\partial C_i}{\partial x} + \frac{\partial}{\partial x} D_{ij} \frac{\partial C_i}{\partial x}, \quad (i, j = 1, 2; i \neq j) \quad (1)$$

with the following boundary conditions:

$$\begin{aligned} C_1(0) &= C_1^1; & C_1(\infty) &= C_1^0; \\ C_2(0) &= C_2^1; & C_2(\infty) &= C_2^0; \end{aligned} \quad (2)$$

where $C_i (i=1, 2)$ is the concentration of the i -th component. The index of 1 hereinafter corresponds to the O component, and 2 for the alloying element. $D_{ij} (i, j=1, 2)$ are the diffusion coefficients, which are normally used as component concentration functions. Here it is shown that under the condition of

$$\left| \frac{1}{2} \varepsilon_{12} (C_2^1 - C_2^0) \right| \ll 1 \quad (3)$$

one could use the solutions of diffusion equation (1) with constant diffusion coefficients D_{11} , D_{12} , D_{22} and $D_{21} = 0$:

$$C_1(\xi) = C_1^1 - \left[C_1^1 - C_1^0 + \frac{D_{12}}{D_{11}} (C_2^1 - C_2^0) \right] \operatorname{erf} \frac{\xi}{2\sqrt{D_{11}}} + \frac{D_{12}}{D_{11}} (C_2^1 - C_2^0) \operatorname{erf} \frac{\xi}{2\sqrt{D_{22}}}, \quad (4)$$

$$C_2(\xi) = C_2^1 - (C_2^1 - C_2^0) \operatorname{erf} \frac{\xi}{2\sqrt{D_{22}}}, \quad (5)$$

where $D_{12}/D_{11} = \varepsilon_{12}C_1^1$, $\xi = x/\sqrt{t}$ is the generalised coordinate, and ε_{12} is the interaction parameter.

The work provides a comparison of the numerical solution to equation (1) (with diffusion coefficients that depend on the concentration) with solution (4) for variable values of C_2^0 (and, accordingly, the parameter $A = \left| 1/2\varepsilon_{12} (C_2^1 - C_2^0) \right|$). A correlation is obtained for the maximum deviation of these solutions from the parameter A , which allows us to evaluate the error resulting from the use of constant diffusion coefficients. For values of the parameter A that don't exceed 0.19, the relative solution error in (4) does not exceed 5%.

Using the corresponding isometric sections of the triple balance diagram for $Fe-Me-O$ types, conditions for $Me_{\omega_2}O_{\omega_1}$ type disperse phase formation are studied in diffuse saturation of binary alloys. The condition for formation of new phase nuclei is the oversaturation of the hard mix. To analyse the saturation of the hard mix, the oversaturation function $L(\xi)$ is introduced:

$$L(\xi) = \Phi(\mu_1, \mu_2) - \Phi(\mu_1^\rho, \mu_2^\rho) = \frac{2\gamma V_m}{R_k}, \quad (6)$$

where R_k is the critical radius of new phase nuclei, γ is the surface tension coefficient, and V_m is the new phase molecule volume.

The function $\Phi(\mu_1^\rho, \mu_2^\rho)$ is an equation for solubility on an isometric slice of the triple diagram. For $Fe-Me-O$ type systems, which form a stoichiometric compound $Me_{\omega_2}O_{\omega_1}$, the solubility line equation is as follows:

$$\Phi(\mu_1^\rho, \mu_2^\rho) = \ln \left\{ (a_1^\rho)^{\omega_1} (a_2^\rho)^{\omega_2} \right\} = \frac{\Delta G}{kT}, \quad (7)$$

where a_i^ρ and ω_i ($i=1,2$) respectively are thermodynamic activities for components at the solubility lines and stoichiometric coefficients; ΔG is the free energy from $Me_{\omega_2}O_{\omega_1}$ formation.

Using Wagner's decomposition for thermodynamic activities

$$a_i = C_i \exp(\varepsilon_{ii}C_i + \varepsilon_{ij}C_j + \dots), \quad (i, j = 1, 2) \quad (8)$$

and considering the smallness of C_i and ε_{22} we get:

$$\Phi(\mu_1^\rho, \mu_2^\rho) = \ln \left\{ (C_1^\rho)^{\omega_1} e^{-|\varepsilon_{12}|C_2^\rho \omega_1} (C_2^\rho)^{\omega_2} \right\} = \frac{\Delta G}{kT}. \quad (9)$$

The function $\Phi(\mu_1, \mu_2)$ describes an arbitrary virtual diffusion path, which a figurative point follows through the condition diagram during changes in the alloy's composition in the diffusion zone (Fig. 1). If the diffusion path crosses a two-phase path, then $L(\xi) > 0$, and this corresponds to the presence of hard mix oversaturation.

If we consider the smallness of concentration changes in components within the diffusion zone, we can consider $C_1^\rho(\xi) = C_1^\rho(0) = C_1^1$ and $\frac{dC_1^\rho}{dC_2^\rho} = \text{const}$. Then, considering (4) and (5) the oversaturation function can be written as:

$$L(\xi) = \left\{ \omega_1 (C_2^0 - C_2^1) |\varepsilon_{12}| \left[1 - \frac{dC_1^\rho}{dC_2^\rho} \frac{1}{C_1^1 |\varepsilon_{12}|} \right] \operatorname{erf} \frac{\xi}{2\sqrt{D_{22}}} - \left[1 - \frac{C_1^0}{C_1^1} + |\varepsilon_{12}| (C_2^0 - C_2^1) \right] \operatorname{erf} \frac{\xi}{2\sqrt{D_{11}}} \right\}. \quad (10)$$

From (10) we see that the maximum of $L(\xi)$ is at the coordinate

$$\xi_m = 2 \sqrt{D_{22} \ln \left\{ \frac{(C_2^0 - C_2^1) |\varepsilon_{12}| \left[1 - \frac{dC_1^\rho}{dC_2^\rho} \frac{1}{C_1^1 |\varepsilon_{12}|} \right] \sqrt{\frac{D_{11}}{D_{22}}}}{1 - \frac{C_1^0}{C_1^1} + |\varepsilon_{12}| (C_2^0 - C_2^1)} \right\}}. \quad (11)$$

Under the conditions of

$$(C_2^0 - C_2^1) |\varepsilon_{12}| \left[1 - \frac{dC_1^\rho}{dC_2^\rho} \frac{1}{C_1^1 |\varepsilon_{12}|} \right] > 0; \quad (12)$$

$$C_1^1 - C_1^0 + C_1^1 |\varepsilon_{12}| (C_2^0 - C_2^1) > 0 \quad (13)$$

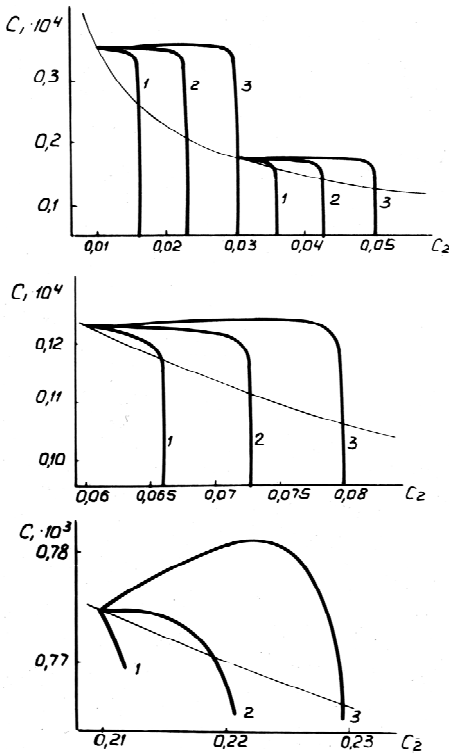


Fig. 1 – Virtual diffusion paths, calculated based on (4) and (5) for various sections of the

solubility line: $\frac{\Delta G}{RT} = -40$, $\varepsilon_{12} = -2,5$;

$D_{11} = 0,1 \cdot 10^{-5} \frac{cm^2}{s}$; $D_{22} = 0,1 \cdot 10^{-8} \frac{cm^2}{s}$;

$$1. |\varepsilon_{12}| (C_2^0 - C_2^1) < \sqrt{\frac{D_{22}}{D_{11}}};$$

$$2. |\varepsilon_{12}| (C_2^0 - C_2^1) = \sqrt{\frac{D_{22}}{D_{11}}};$$

$$3. |\varepsilon_{12}| (C_2^0 - C_2^1) > \sqrt{\frac{D_{22}}{D_{11}}}.$$

The kinetics of two-phase area formation in the process of internal oxidation is considered. A mathematical model was formulated for the internal oxidation process, as well as computer modeling of the two-phase area formation process in a plate of a binary alloy during diffuse oxygen saturation was carried out. The modeling results and the experimental results were compared. Below is the system of equations which was used to describe this process.

In three-component systems, which consist of a hard mix and new phase particles $Me_{\omega_2} O_{\omega_1}$, diffusion equations in the hard mix are as follows:

the maximum lies within the interval of $(0, \xi_{\text{bound}})$ and $L(\xi_m) \geq 0$. Conditions (12) and (13) hold for $C_2^0 > C_2^1$. Thus, with $C_1^\rho(0) = C_1^1$ and $C_2^\rho(0) = C_2^1$, i.e. even without oversaturation on the outer surface ($L(0) = 0$), nuclei of the new phase can form within the diffusion zone, if the initial concentration of the alloying element exceeds its balance concentration, which is established during the saturation process. Analysis shows that the conditions for formation of the two-phase zone are more permitting as the difference of $(C_2^0 - C_2^1)$ increases, as the concentration C_2^0 of the alloying element in the initial binary alloy decreases (at a constant value of $(C_2^0 - C_2^1)$), as the absolute interaction parameter value $|\varepsilon_{12}|$ increases, and as the ratio of the diffusion coefficients D_{11}/D_{22} increases (Fig. 1).

The work considers the possibility of two-phase area formation within an undersaturated hard mix on the surface ($L(0) < 0$). It is demonstrated that due to the presence of a maximum on the $L(\xi)$ curve, an event could occur where at some distance from the surface a part of the oversaturation function around the maximum coordinate will be in the positive area. With this, the two-phase area should be preceded by an area that starts from the surface, free of second phase emissions (Fig. 2).

The existence of the near-surface area that is free of second-stage particles is verified experimentally, under surface conditions that correspond to an undersaturated hard mix.

The two-phase area's boundary blurring, which depends on the gradient of the oversaturation function in the intersection point of $L(\xi)$ with the zero ordinate (Fig. 2), is theoretically analysed. An expression is obtained for correlating the boundary blurring values in two-phase areas, which correspond to the rising and falling branches of the oversaturation function. Based on this analysis, a method is proposed for evaluating the diffusion coefficient of the alloying element D_{22} according to the data on two-phase area boundary blurring from an experiment on the internal oxidation in surface undersaturation conditions.

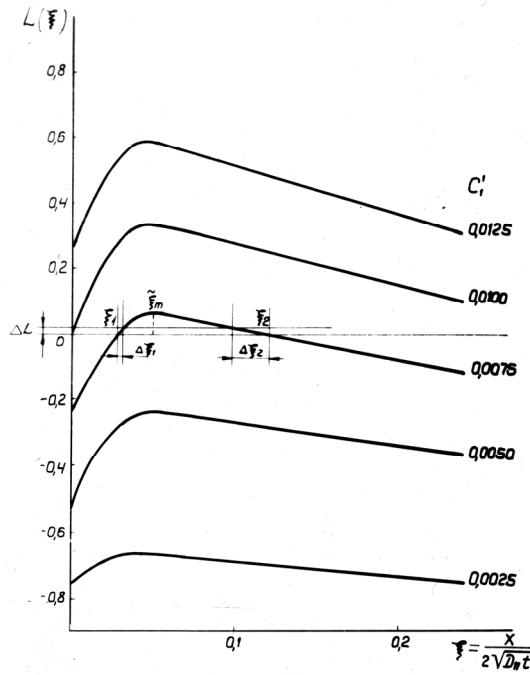


Fig. 2 – Distribution of oversaturation function $L(\xi)$ in accordance to the oxygen concentration at the surface of the sample C_1^1 .

$$C_2^0 = 0,12; C_2^1 = 0,10; C_2^2 = 0,10;$$

$$C_1^0 = 0,0; C_1^1 = 0,01; \varepsilon_{12} = -2,5;$$

$$D_{11} = 0,1 \cdot 10^{-5} \frac{cm^2}{s}; D_{22} = 0,1 \cdot 10^{-8} \frac{cm^2}{s}.$$

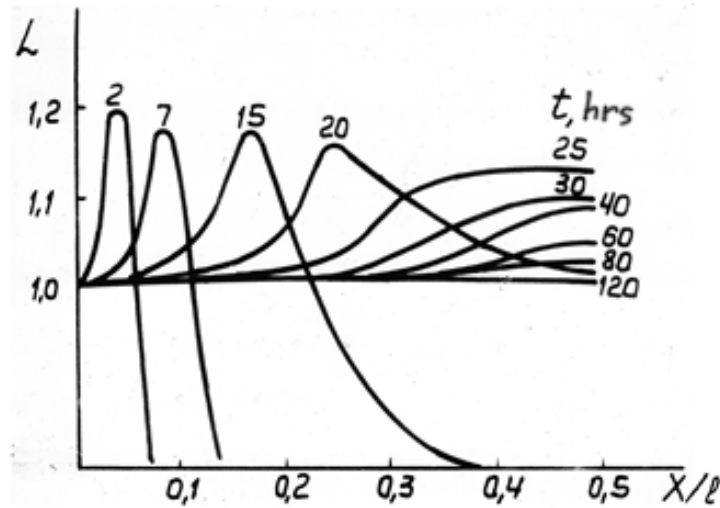


Fig. 3 – Distribution of the oversaturation function throughout the plate's depth $C_1^0 = 0,0; C_1^1 = 0,01; C_2^0 = 0,12; C_2^1 = 0,10;$

$$D_{11} = 0,1 \cdot 10^{-7} \frac{cm^2}{s}; D_{12} = -0,5 \cdot 10^{-9} \frac{cm^2}{s}; D_{22} = 0,1 \cdot 10^{-11} \frac{cm^2}{s};$$

$$\alpha = 0,1 \cdot 10^{-17} \frac{cm^3}{s}; \mu_0 = 0,1 \cdot 10^{16} s^{-1}; \chi = 0,35 \cdot 10^{14} cm^{-2};$$

$$\omega_1 = 3; \omega_2 = 2; l = 600 \mu m.$$

$$\frac{\partial C_i}{\partial t} = D_{ii} \frac{\partial^2 C_i}{\partial x^2} + D_{ij} \frac{\partial^2 C_j}{\partial x^2} + D_{ii} \frac{\partial Q}{\partial x} \frac{\partial C_i}{\partial x} + D_{ij} \frac{\partial Q}{\partial x} \frac{\partial C_j}{\partial x} + C_{io} \frac{\partial Q}{\partial t},$$

$$(i, j = 1, 2; i \neq j);$$

$$\frac{\partial C_i}{\partial t} = D_{ii} \frac{\partial^2 C_i}{\partial x^2} + D_{ij} \frac{\partial^2 C_j}{\partial x^2} + D_{ii} \frac{\partial Q}{\partial x} \frac{\partial C_i}{\partial x} + D_{ij} \frac{\partial Q}{\partial x} \frac{\partial C_j}{\partial x} + C_{io} \frac{\partial Q}{\partial t},$$

$$(i, j = 1, 2; i \neq j), \quad (14)$$

where $Q = \ln(1 - V_\phi)$; $V_\phi = \frac{4}{3} \pi \int_0^\infty R^3 f(R) dR$ is the new phase particle volume; C_{io} is the concentration of the i -th component in the phase.

The distribution function for second stage particles in sizes $f(R, t)$ for each section of x (x is the coordinate in the direction that is perpendicular to the diffusion front) is determined from the continuity equation:

$$\frac{\partial f}{\partial t'} + \frac{\partial v_R f}{\partial R} = \mu(R, t'), \quad (15)$$

where R is the particle radius, t' is the relative time, counting from the t_1 moment of first nucleus formation in the current section, $\mu(R, t')$ is the rate of second stage nuclei formation in the current

section. The nuclei growth rate $v_R = \frac{dR}{dt}$ is determined from the substance mass balance at the nucleus boundary and in a quasi-stationary approximation (considering the weak dependence of the critical nuclei radius on the time for the times which slightly exceed t_1) already looks as follows:

$$v_R = \frac{a}{R^2} \left(\frac{R}{R_k} - 1 \right), \quad a = const. \quad (16)$$

The inception function $\mu(R, t')$ shall be defined as follows:

$$\mu(R, t') = \mu_0 \exp(-\chi R_k^2) \delta[R - R_k(t)], \quad (17)$$

where $\chi = \frac{8\pi}{3kT} \gamma^2 V_m$, δ is the delta-function.

Equations (14) – (17) form a closed system, solving which allows finding the value of $f(R, t)$ in each section, and accordingly determine the number of particles N , the average radius \bar{R} and the sum volume of the second phase V_ϕ .

The numerical solution was done with the sample plate using a grid built in the space of $\mathbf{R}, \mathbf{x}, \mathbf{t}$. An implicit difference scheme was used. For each new time step, an iterative process between equations (14) and (15) was done until a high-precision correlation was reached.

The modeling results show that hard mix oversaturation reaches a maximum point on the surface, which moves towards the middle of the plate over time (Fig. 3). With large times, the middle of the plate forms a slowly relaxing area with the maximum oversaturation of the hard mix. The

relaxation speed of the oversaturation in each of the deeper sections of the plate decreases. The kinetics of oversaturation in each section of the plate (Fig. 4) has the following stages: growth of the oversaturation until some maximum value, the stage of a rapid decrease in oversaturation, and a long stage of an asymptotic tendency towards a balanced state.

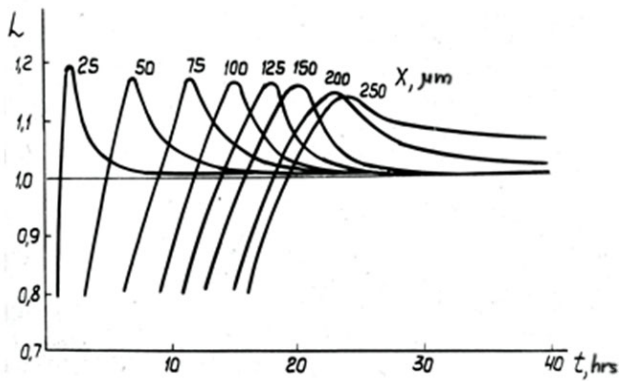


Fig. 4 – Kinetics of the oversaturation function in various sections of the plate. Here the oversaturation functions is normalised according to its value at the balance: $L/L_p(x, t)$;

$$L = a_1^{\omega_1} a_2^{\omega_2} = C_1^{\omega_1} e^{-|\epsilon_{12}| C_2^{\omega_2}} C_2^{\omega_2};$$

$$L_p = a_{1p}^{\omega_1} a_{2p}^{\omega_2} = (C_1^p)^{\omega_1} e^{-|\epsilon_{12}| C_2^p \omega_1} (C_2^p)^{\omega_2}.$$

ly increases, which is due to the influence of diffusion tensions from the opposite surfaces of the plate. The time until

Correspondingly, we can distinguish the stages of two-phase area formation: the turbulent formation and growth of particle, the intense growth of particles as formation of new particles fades, formation is absent at the asymptotic stage (oversaturation tends towards zero), and the growth of new stage particles with the hard mix material gradually gives way to coalescence growth.

The distribution of particle number N , average radius \bar{R} and sum value of the second phase V_ϕ across the plate's thickness is non-monotonous (Fig. 5, 6). The curves $N(x)$, $\bar{R}(x)$ and $V_\phi(x)$ reach a maximum, which tends towards the centre of the plate over time. It is shown that the dependence $N(x)$ cannot be described with an $N \sim x^n$ type expression, as the n parameter also depends on the coordinate x and the duration of the process t.

The kinetics of the internal oxidation front in the plate has the following quality: as it tends towards the centre of the plate, the speed of internal oxidation zone quick-

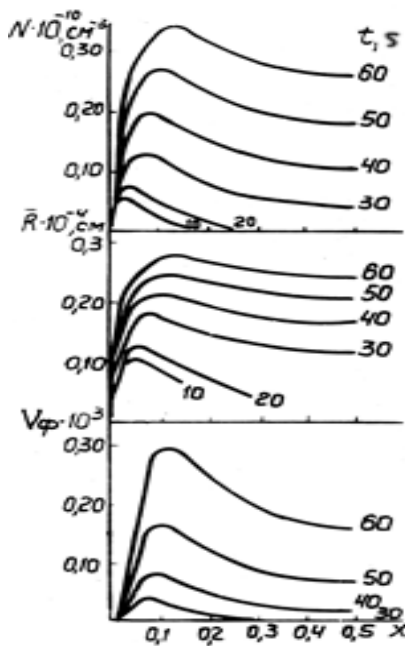


Fig. 5 – Distribution of N , \bar{R} and V_ϕ in plate sections for different times in the process of internal oxidation.

$$C_1^0 = 0,0; C_1^1 = 0,01; C_2^0 = 0,12; C_2^1 = 0,10;$$

$$D_{11} = 0,1 \cdot 10^{-5} \frac{cm^2}{s}; D_{12} = -0,5 \cdot 10^{-7} \frac{cm^2}{s};$$

$$D_{12} = -0,5 \cdot 10^{-7} \frac{cm^2}{s};$$

$$\mu_0 = 0,1 \cdot 10^{16} s^{-1}; \chi = 0,35 \cdot 10^{14} cm^{-2};$$

$$\omega_1 = 3; \omega_2 = 2; l = 100 \mu m.$$

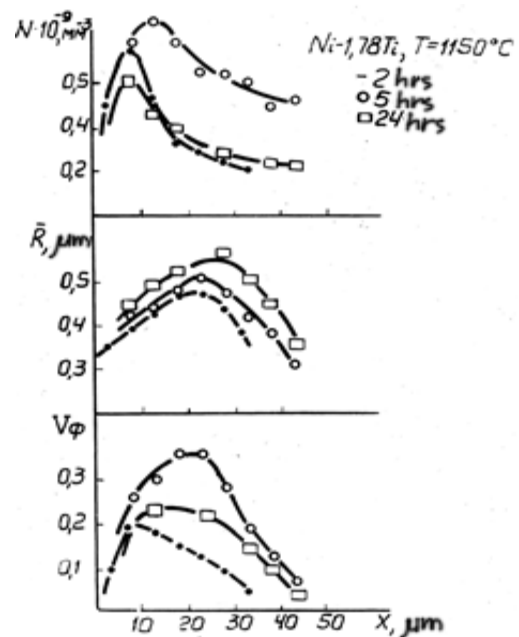


Fig 6 – Distribution of particle number N , their average radius \bar{R} and phase volume V_ϕ across the thickness of alloy $Ni - 1,78\% Ti$ $l = 100 \mu m, T = 1150^\circ C$.

From a numerical experiment with different initial values of C_2^0 for alloying elements we can determine that the number of particles N , their average radius \bar{R} and phase volume V_ϕ in the plate increases as the content of the alloying element increases, since with the increase in the initial concentration of C_2^0 with a constant level of C_2^1 the oversaturation level of the hard mix increases.

complete internal oxidation is sped up several times. Under the negligible influence of runoffs (the phase volume is small) on the diffusion of the components in the hard mix, the times for full internal oxidation t_1 , and t_2 for the plates of varying thickness l_1 , и l_2 correspond as the square of their thickness ratios: $t_2 / t_1 = (l_2 / l_1)^2$.

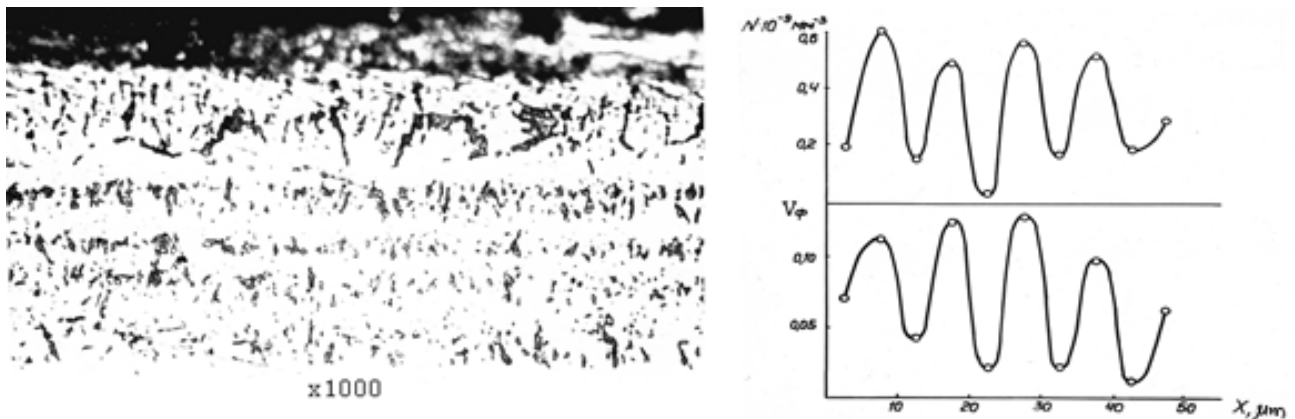


Fig. 7 – Distribution of particle number N and phase volume V_ϕ in a sample section of $Ni - 2,5\%Al - 1,5\%Hf$, internally oxidized using thermal cycling.

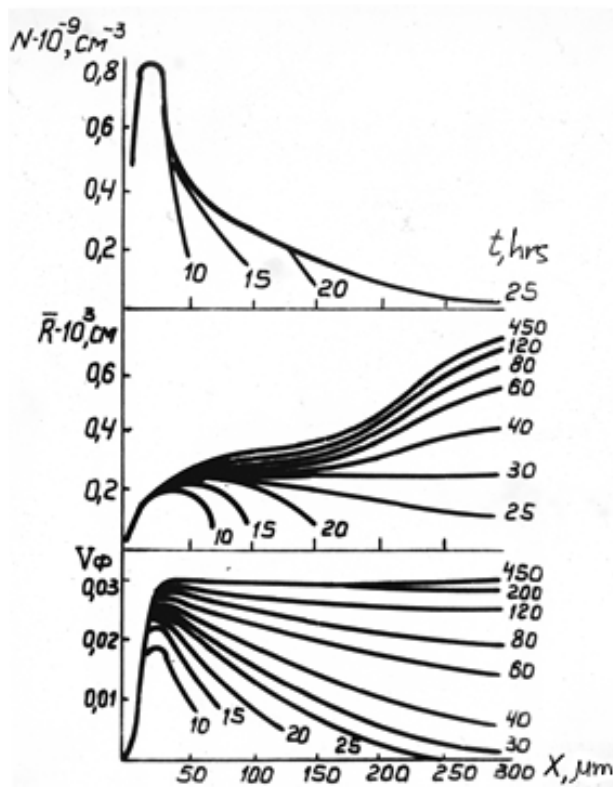


Fig. 8 – Distributions of N , \bar{R} , and V_ϕ across the thickness of the plate for various times of the internal oxidation process. $C_1^0 = 0,0$; $C_1^1 = 0,01$; $C_2^0 = 0,12$;

$$C_2^1 = 0,10; D_{11} = 0,1 \cdot 10^{-7} \frac{cm^2}{s}; D_{12} = -0,5 \cdot 10^{-9} \frac{cm^2}{s};$$

$$D_{22} = 0,1 \cdot 10^{-11} \frac{cm^2}{s}; \frac{2\gamma V_m}{kT} = 0,7 \cdot 10^{-7} cm;$$

$$\alpha = 0,1 \cdot 10^{-17} \frac{cm^3}{s}; \mu_0 = 0,1 \cdot 10^{16} s^{-1};$$

$$\chi = 0,35 \cdot 10^{14} cm^{-2}; \omega_1 = 3; \omega_2 = 2; l = 600 \mu m.$$

The comparison of internal oxidation processes at different thicknesses of plates under equal values of relative time t/l^2 shows that the number of particles N , the average radius \bar{R} and sum volume of the phase V_ϕ in each section of the plate increase with increasing the plate thickness.

Based on the modeling results for internal oxidation processes under a constant temperatures, the possibility to get a "striped" internal oxidized zone structure using thermal cycling is demonstrated, where the two-phase area stripes alternate with second-phase emission free stripes. The width of two-phase stripes, their number and intervals in between can be regulated by the thermal cycling parameters.

Experiments with the $Ni - 2,5\%Al - 1,5\%Hf$ alloy, as well as $Ni - Ti$ alloys have resulted in the striped internal oxidation zone pattern (Fig. 7).

A material with such a striped structure in the internal oxidation zone is in essence a composite, and thus the programmed oxidation of diluted alloys can be considered a promising method of manufacturing such composites.

The asymptotic of the internal oxidation processes in binary alloys was studied. For a sample binary alloy plate the theoretical aspect of the asymptotic stage of the internal oxidation is considered, the internal oxidation process in the plate is modeled up to and including the asymptotic stage, and the late stage of the internal oxidation in an $Ni - 1\%Cr$ alloy is experimentally proven.

It is shown theoretically and using modeling that at the asymptotic stage of the internal oxidation process the number of particles N and phase volume V_ϕ across the thickness of the plate vary only slight over time (Fig. 8, 9); the distribution of the average particle radius \bar{R} throughout the section of the plate is leveled out, and over long process times \bar{R} doesn't depend on the coordinate.

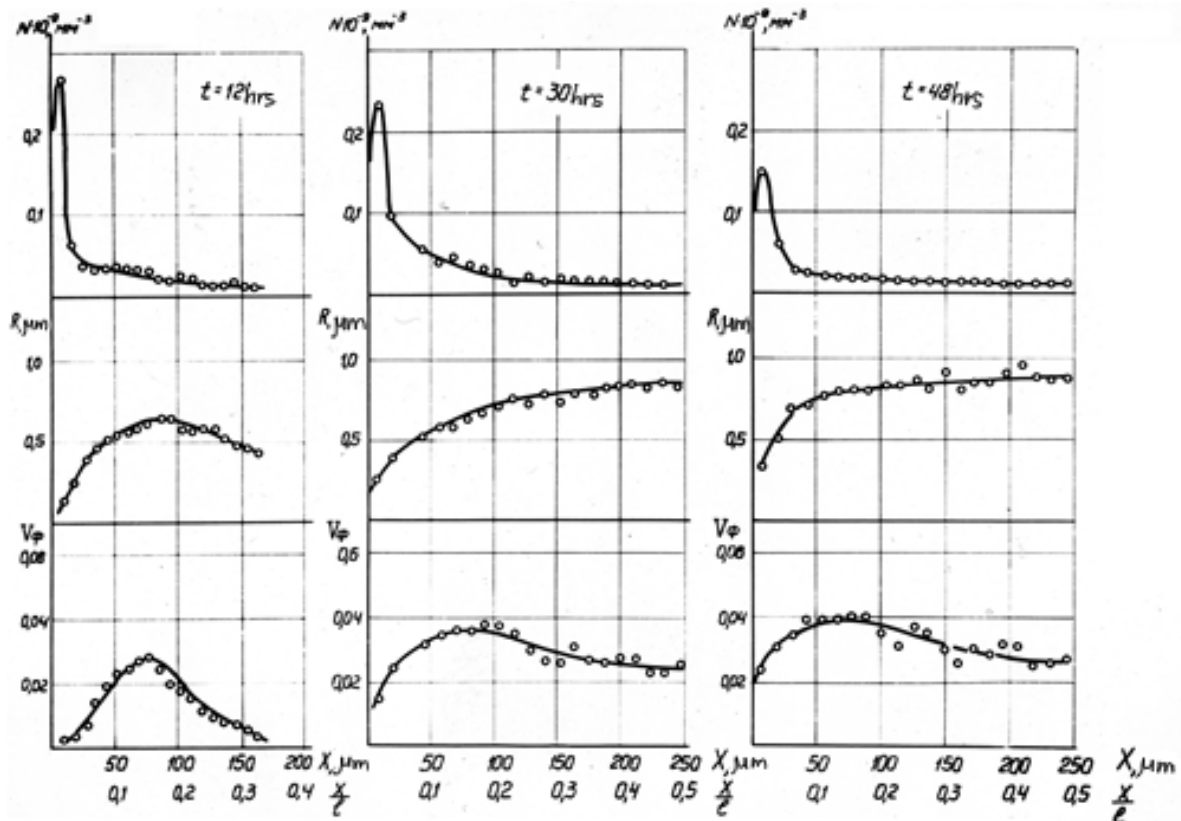


Fig. 9 – Distributions of N , \bar{R} , and V_ϕ across sections of an $Ni-1\%Cr$ alloy plate depending on internal oxidation times.
 $l = 500 \mu m$; $T = 1150^\circ C$.

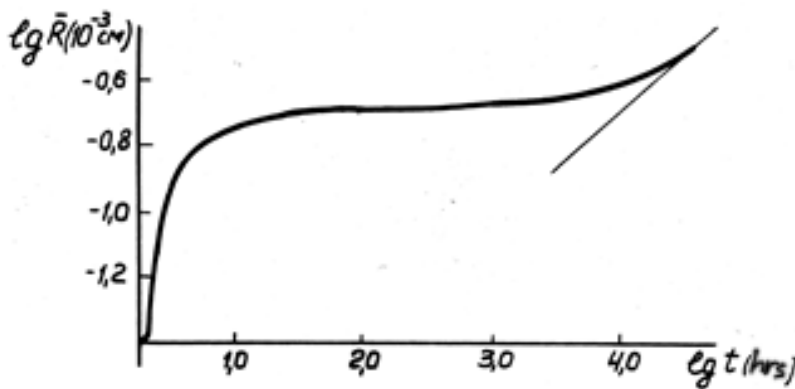


Fig. 10 – Kinetics of \bar{R} at the asymptotic stage of the internal oxidation process in the plate. $l = 600 \mu m$; $x = 25 \mu m$;

$$C_1^0 = 0,0; C_1^1 = 0,01; C_2^0 = 0,12; C_2^1 = 0,10;$$

$$D_{11} = 0,1 \cdot 10^{-7} \frac{cm^2}{s}; D_{12} = -0,5 \cdot 10^{-9} \frac{cm^2}{s}; D_{22} = 0,1 \cdot 10^{-11} \frac{cm^2}{s};$$

$$\alpha = 0,1 \cdot 10^{-17} \frac{cm^3}{s}; \mu_0 = 0,1 \cdot 10^{16} s^{-1};$$

$$\chi = 0,35 \cdot 10^{14} cm^{-2}; \omega_1 = 3; \omega_2 = 2.$$

presence of a diffuse substance flow towards the free surfaces of the plate (due to the system not being closed): the substance of diluting small particles doesn't completely contribute to the growth of larger ones.

As the oversaturation gradient for the hard mix in the plate decreases, the role of the diffuse streams towards free surfaces recedes, the system becomes progressively more closed and the asymptotic stage of the process comes to fruition as the Livshitz – Slezov coalescence with a kinetic law of $\bar{R}^3 \sim t$. The results explain the deviations from a cubical growth of \bar{R} towards $n > 3$ at later stages of disperse two-phase system evolutions, which have been frequently ob-

Modeling shows that with the increase of the average size of second stage particles over long times the variation in particle sizes in the given section also increases – the function of particle distribution across sizes is blurred. In each section of the internal oxidation zone there is over time an asymptotic tendency of the critical particle radius R_k towards \bar{R} . The right end of the distribution function tends towards the point with the abscissa $R/R_k = 3/2$, however a small "tail" of the distribution function remains at the ordinate of $R/R_k = 3/2$.

The growth of the average radius of particles $\bar{R}^n \sim t$ was studied using modeling and experiments. It was found (Fig. 10) that after the stage of rapid particle growth with the kinetic law characterised as $n \leq 2$, there is a stage of slow growth with $n \gg 3$, which can be established by the

served by numerous authors.

The coalescence processes in an internally-oxidized plate is unique for each section of the plate; at the same time, different sections of the internal oxidation zone could be in different stages of the two-phase zone's evolution – inception, growth, unstable and static coalescence. Plate sections, depending on the oversaturation gradient between them, interact diffusely as well. The oversaturation maximum at the asymptotic stage appears once again next to the plate's surface, however its value is small and is defined by (according to the Gibbs-Thompson law) a difference in \bar{R} for various sections of the plate. Diffusion processes linked to the oversaturation gradient which emerges across the thickness of the plate, define the process of evening out of \bar{R} across the plate's section.

The asymptotic tendency towards a constant phase volume happens from above, on the side of large value, which makes evident the existence of some comprehensive "sub-dilution" of second-phase particles during the transition into a stable coalescence. This process is also associated with the diffuse flow of substance into the surrounding environment.

The results of the theoretical study and modeling of the asymptotic stage of the internal oxidation process correspond well to the experimental data from the internal oxidation in a sample of $Ni-1\%Cr$ alloy.

Conclusions and prospects of future study. A physical model for the process of internal oxidation is considered, which is described by a system of equations for diffusion in three-component system of hard mixes containing second-phase particles and a continuity equation for the particle size distribution function. Numerical modeling was carried out for the internal oxidation process in a binary alloy plate for various values of kinetic and thermodynamic parameters.

It is shown that the oversaturation maximum tends towards the centre of the plate over time, where a slowly relaxing area is formed with maximum oversaturation. The kinetics of oversaturation in each section has the following stages: growth towards a certain maximum value, a rapid decrease in oversaturation and a lengthy asymptotic tendency towards balance. Correspondingly, we could define the stages of two-phase stage formation: emergence, particle growth, which gives way slowly to coalescence growth due to the oversaturation of the hard mix at the asymptotic stage.

The internal oxidation model developed in the paper allows looking into the patterns of two-phase area formation and expanding our understanding of the process' physics. This provides an opportunity to effectively control the internal oxidation process by changing the space-time parameters and the composition of the environment. The results of the work could be used to develop new industrial technologies in industrial hardening of materials via internal oxidation, in creation of new heat-resistant alloys, disperse-hardened magnetic materials and electrotechnical alloys. In particular, technologies in programmed internal oxidation are the most interesting, as they could allow for the manufacture of disperse-hardened materials with a layered composite structure.

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