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# INVESTIGATION OF THE KINETICS OF CHROMIUM DIFFUSION COATING FORMATION ON STEEL.

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**Abstract**

This study addresses a critical challenge in modern mechanical engineering: protecting component surfaces from corrosion and wear by applying protective diffusion coatings. Unlike traditional electroplating, which suffers from limitations due to the mismatch between the properties of the galvanic layer and the base metal, the diffusion method enables the creation of composite layers with superior mechanical and chemical characteristics.

The paper presents a mass transfer mechanism that accounts for the counter-diffusion of chromium and carbon, resulting in the formation of a chromium carbide layer ($Cr_{23}C_6$) followed by a decarburized zone. The process is mathematically described within the framework of a multiphase "Stefan problem" featuring moving phase boundaries. To solve the system of partial differential equations numerically, the authors employed a proprietary "auxiliary grid" method based on an implicit difference scheme, ensuring calculation stability despite the changing phase geometry.

Simulations were conducted for the chromizing of steel using a low-melting transport melt at a temperature ofT = 1223K. It was established that the migration rate

of the ferrite-austenite boundary is more than six times higher than the growth rate of the carbide layer.

A comparison of the calculated results with experimental data demonstrated high convergence, with the discrepancy in phase thickness not exceeding 10%. The developed model allows for the effective prediction of protective layer parameters during high-temperature saturation.

Keywords: Stefan problem, numerical methods, moving interphase boundary, kinetics mass transfer, chromium carbide, decarburized zone, implicit difference scheme.

Introduction.

The most critical task in modern mechanical engineering is protecting the surfaces of machine parts and mechanisms from corrosion. One of the primary methods for preventing the development of corrosive processes is the application of protective coatings. Currently, metal surface chrome plating is a widely recognized technique. It provides a significant increase in the quality, reliability, and durability of components made from structural materials. Unfortunately, the simple and reliable method of electrolytic chromium deposition (electroplating) has several significant drawbacks due to the substantial difference in the physicochemical and mechanical properties of the electroplated layer and the base metal. During the operation of such coatings, considerable mechanical stresses arise at the "coating–base metal" interface.

The most effective way to create a chromium-containing protective surface layer is the formation of a protective diffusion coating.

As a rule, the phase composition of such a diffusion layer includes a chromium carbide phase ($Cr_{23}C_6$). The mechanical, strength, and chemical properties of this diffusion layer significantly exceed those of protective coatings obtained by electroplating. However, the technology for applying a protective diffusion coating to a metal surface is complex. It requires heating the metal surface to sufficiently high temperatures, prolonged high-temperature exposure to form a continuous diffusion layer, and precise control of the diffusion saturation process at all stages of coating creation.

As mentioned above, such a diffusion coating is a composite. It combines the properties of several chemical components. The physicochemical and mechanical properties of this composite material are determined by its structure and phase composition.

Diffusion growth or dissolution, and the emergence or disappearance of specific phase layers during the creation of a diffusion coating, are the limiting processes that determine the overall physicochemical properties and the durability of the material.

The high strength and corrosion resistance of surface diffusion layers, combined with a soft, ductile core (base metal), make it possible to achieve the desired operational properties. This is especially relevant when the material is used in complex physicochemical environments (high temperatures, aggressive media).

Mass transfer processes are generally diffusion-driven processes that occur at the external surface and moving phase boundaries; they dictate the durability of the coating and the retention of the structural material's performance properties. Studying the kinetics of the diffusion redistribution of components during the diffusion saturation of metal surfaces allows for a more precise understanding of the coating formation

mechanism, identification of processes affecting the properties of protective layers, and the outlining of ways to improve them.

Research Objectives and Scope.

In this work, we examine the characteristics of the diffusion saturation of steel with chromium from a low-melting transport solution onto the steel surface (base metal). During such saturation, the following are formed: a coating consisting of chromium carbide ($Cr_{23}C_6$) and a subsequent decarburized transition zone. This zone arises as a result of the counter-diffusion of carbon toward the sample surface and its subsequent involvement in a chemical reaction to form the chromium carbide phase. As our studies (Fig. 1) and data from [1] show, the dimensions of the decarburized transition zone are several times larger than the thickness of the diffusion coating layer and can vary widely. This is determined by both the carbon content in the steel (base metal) and the duration of the diffusion coating application. At the same time, the carbon concentration in the transition zone can vary from ferritic to pearlitic composition.

Given the above, the following mechanism of mass transfer during the formation of the coating layer and the transition zone can be proposed:

1. In the first stage, the process is controlled by the diffusion of chromium into γ- and α- iron, accompanied by the precipitation of the carbide phase in the near-surface layers in the form of dispersed inclusions. A decarburized transition zone begins to form near the chromium carbide layer.

2. After the formation of a continuous carbide layer, its growth (Phase I) is controlled by the diffusion of chromium through the carbide to the mobile interface $\Gamma_1$, where all carbon supplied to it is bound into chromium carbide.

This system is ternary: it includes a carbide-forming element (chromium), a saturation element (carbon), and a base metal element (iron).

On one hand, the carbide-forming element (chromium) diffuses into the base metal matrix, forming the chromium carbide phase. On the other hand, the saturation element (carbon) actively moves toward the boundary of the newly formed chromium carbide layer and reacts with the chromium, which, in turn, has diffused through the carbide layer from the sample surface. In this case, two phases - ferritic and pearlitic compositions - may be present in the transition region.

As studies [2] show, the carbon concentration in Phase 1 is constant, while in the 2nd and 3rd phases, it can vary, as noted above, from ferritic to pearlitic composition; i.e., another mobile interface $\Gamma_2$ may form between the ferrite and pearlite phases.

It should be noted that after the formation of a continuous carbide layer, a region of dispersed inclusions of this phase forms beneath it. However, its dimensions are negligible compared to the decarburized zone [1, 2]; therefore, here and below, we will assume that between the carbide and the decarburized zone (i.e., at the $\Gamma_1$ interface), the carbon concentration changes abruptly from the stoichiometric value in the carbide to the solubility limit in the ferrite.

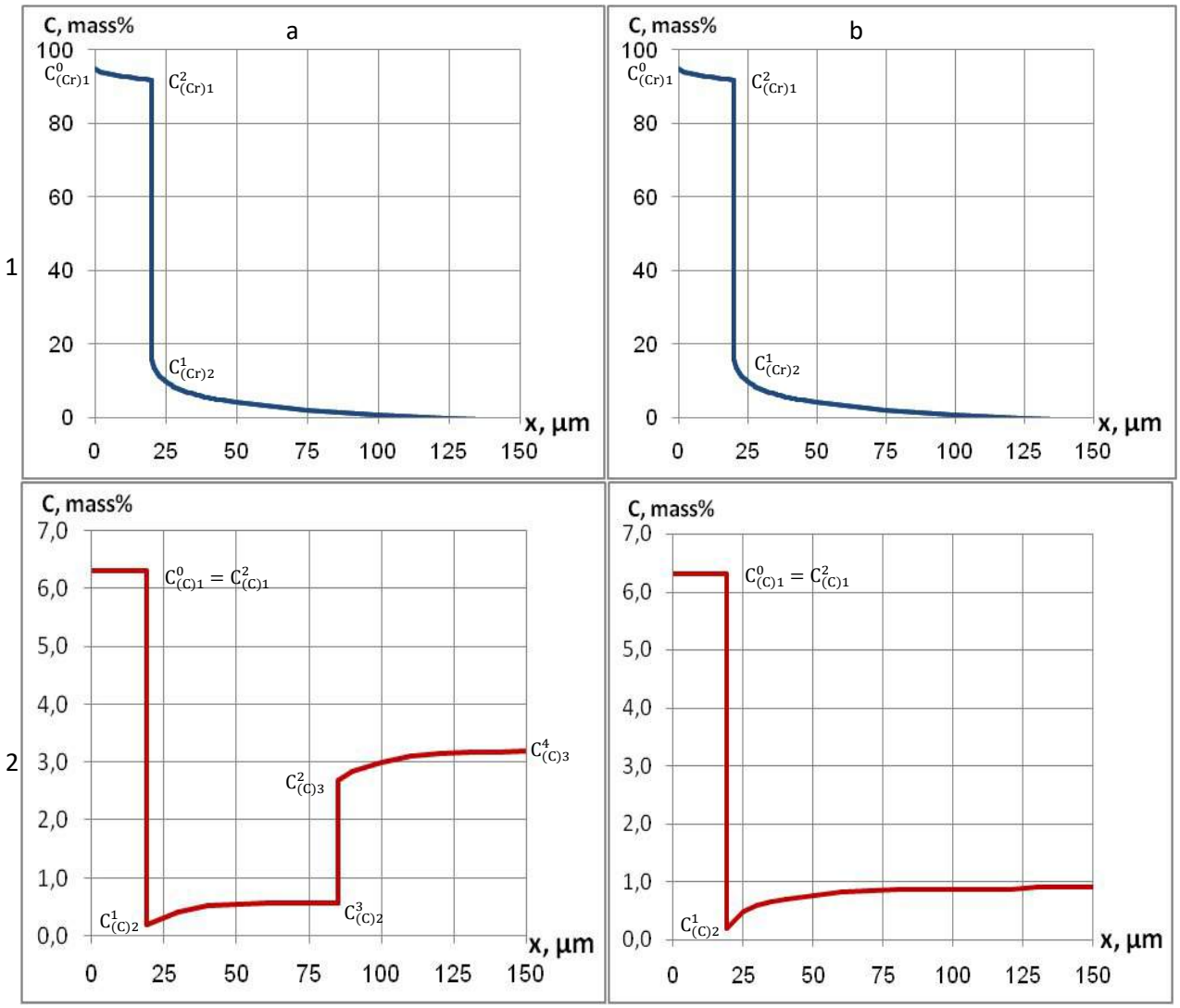


Fig. 1. Distribution of chromium (1) and carbon (2) concentration for:
a – carbon steel; b – low-carbon steel

The mathematical description of this case (Fig. 1a) is more general, since if the second mobile interface is absent (carbon concentration changes monotonically, $\Gamma_2=\infty$; Fig. 1b), the concentration distribution in the phases will be a particular solution to the general problem.

Thus, due to the reaction at the interface, a carbon flux is observed from the bulk of the steel toward the "coating element carbide – base metal" interface. In this case, the diffusion of the carbide-forming element (in our case, chromium, Cr) in the presence of several phases (q=1, 2, … Q) is described by a system of second-order partial differential equations.

Based on Fick's second law, we can write:

$$\frac{\partial C_{(Cr)q}(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_{(Cr)q}\left(T, C_{(Cr)q}\right)\frac{\partial C_{(Cr)q}(x,t)}{\partial x}\right) \quad (1)$$

where: q = 1, 2, … Q – phase number;
x,t – current coordinate and time;
$C_{(Cr)q}(x,t)$ – concentration profile (Cr) in the q-th phase;

$D_{(Cr)q}(T, C_{(Cr)q})$ – diffusion coefficient (Cr) in the q-th phase (generally depends on the diffusant concentration and temperature);

T – temperature of the diffusion zone.

As mentioned above, the diffusion of chromium occurs in two phases: chromium carbide and the decarburized zone (ferrite). Therefore, q, the phase number, can take the values q=1 or q=2 in our case.

Hereafter, the following notation will be used:

$C_{(Cr)q}$ and $D_{(Cr)q}$ — the concentration and diffusion coefficient of the protective layer element (chromium) in the q-th phase;

$C_{(C)q}$ and $D_{(C)q}$ — the concentration and diffusion coefficient of the interstitial impurity (in this case, carbon, C) in the q-th phase;

$\Gamma_q$ — the coordinate of the right-hand boundary of the q-th phase.

The formation of the protective layer (chromium carbide) was carried out from a liquid phase (chromium saturation from a sodium melt at a temperature of T = 1273K for 2 to 10 hours). This method ensures a constant concentration of the coating element on the surface of the protected metal. Since the thickness of the diffusion layer can reach several tens of microns, the dimensions of the base matrix can be considered semi-infinite compared to the diffusion layer for the diffusant.

Consequently, the boundary conditions at the external and interphase boundaries can be written as follows:

$$C_{(Cr)1}(0, t) = C^0_{(Cr)1}; \quad C_{(Cr)1}(\Gamma_1, t) = C^2_{(Cr)1} \tag{2}$$

$$C_{(Cr)2}(\Gamma_1, t) = C^1_{(Cr)2}; \; C_{(Cr)2}(\infty, t) = 0 \tag{3}$$

In addition to these, the mass balance equation at the mobile interphase boundary is included:

$$-D_{(Cr)1}\frac{\partial C_{(Cr)1}}{\partial x}|_{x=\Gamma_1-0} = -D_{(Cr)2}\frac{\partial C_{(Cr)2}}{\partial x}|_{x=\Gamma_1+0} + \left(C^2_{(Cr)1} - C^1_{(Cr)2}\right)\frac{d\Gamma_1}{dt} \tag{4}$$

In the numerical solution algorithm, it was assumed that all considered phases already exist at the initial moment of diffusion saturation (even if their thickness is infinitesimally small). Based on the established kinetic mechanism for the formation of the carbide layer and the decarburized transition zone during chrome plating, it is assumed that carbon in Phase 1 is entirely bound within the carbide. Consequently, in this case, the analysis of the carbon diffusion redistribution kinetics can be limited to Phases 2 and 3, remaining within the framework of binary (two-component) diffusion, as these regions consist only of a carbon-iron compound. This approach significantly simplifies the solution to the problem. Considering binary diffusion allows for a solution to Fick's second law with constant diffusion coefficients.

For the binary 'carbon-iron' system, carbon diffusion is described by an equation similar to Equation (1) for the 'chromium-carbon' system:

$$\frac{\partial C_{(C)q}(x, t)}{\partial t} = \frac{\partial}{\partial x}\left(D_{(C)q}(T, C_{(C)q})\frac{\partial C_{(C)q}(x, t)}{\partial x}\right) \tag{5}$$

With the following boundary conditions for the three phases:

the 1st phase – chromium carbide (constant carbon concentration throughout the

entire thickness of the chromium carbide layer), the 2nd phase – the decarburized zone (ferrite zone), and the 3rd phase – the austenite zone:

$$\mathbf{C_{(C)1}}(x,\mathbf{t}) = C^{\mathbf{0}}_{\mathbf{(C)1}} = C^{\mathbf{2}}_{\mathbf{(C)1}};\ \mathbf{C_{(C)2}}(\Gamma_{\mathbf{1}},\mathbf{t}) = C^{\mathbf{1}}_{\mathbf{(C)2}};\quad \mathbf{C_{(C)2}}(\Gamma_{\mathbf{2}},\mathbf{t}) = C^{\mathbf{3}}_{\mathbf{(C)2}} \qquad (\mathbf{6})$$

$$\mathbf{C_{(C)3}}(\Gamma_{\mathbf{2}},\mathbf{t}) = C^{\mathbf{2}}_{\mathbf{(C)3}};\quad \mathbf{C_{(C)3}}(\infty,\mathbf{t}) = C^{\mathbf{4}}_{\mathbf{(C)3}} \qquad (\mathbf{7})$$

At the interfaces $\Gamma_1$ (between chromium carbide and ferrite) and $\Gamma_2$ (between ferrite and austenite), the carbon balance equations are written as follows:

$$-D_{(C)2}\frac{\partial C_{(C)1}}{\partial x}|_{x=\Gamma_1+0} + \left(C^{2}_{(C)1} - C^{1}_{(C)2}\right)\frac{d\Gamma_1}{dt} = 0 \qquad (8)$$

$$-D_{(C)2}\frac{\partial C_{(C)2}}{\partial x}|_{x=\Gamma_2-0} = -D_{(C)3}\frac{\partial C_{(C)3}}{\partial x}|_{x=\Gamma_2+0} + \left(C^{3}_{(C)2} - C^{2}_{(C)3}\right)\frac{d\Gamma_2}{dt} \qquad (9)$$

The system of equations (1)–(9) mathematically provides a complete description of phase evolution during high-temperature diffusion chrome plating.

However, obtaining an analytical solution for such a problem is possible only for a very limited class of problems with simplified boundary conditions.

In a general sense, the class of problems describing a phase transition with mobile phase boundaries is known as the 'Stefan problem.' In its classical formulation, this problem was originally defined for soil freezing. To solve similar types of problems for multiphase systems with complex boundary condition formulations, several numerical calculation schemes have been proposed in recent years to track both the kinetics of interphase boundary movement and the change in concentration distribution within phases over time.

The most suitable numerical schemes have proven to be those based on the implicit difference scheme. This difference scheme is absolutely stable for any temporal and spatial step sizes and allows the use of kinetic coefficients without any restrictions. It is also applicable for solving problems where the grid function may undergo discontinuities of both the first kind (as in the soil freezing problem) and the second kind (diffusion problems with a concentration jump) at the phase interface.

The main difficulty in applying the implicit difference scheme is related to the changing geometry of the phases. It lies in the fact that, as the interphase boundary moves, a spatial grid node previously belonging to one neighboring phase disappears in that phase and emerges in the other. This causes the grid function at this node to become undefined, as it has no history within this particular phase at the previous time layer.

A finite-difference approximation of derivatives involving this spatial grid node cannot be written without additional assumptions. The methods for overcoming this difficulty constitute the specific features of various solution techniques based on the implicit difference scheme.

To calculate this specific problem of steel chrome plating, the 'auxiliary grid' method developed by the authors [3] was used. This method allows for the resolution of the aforementioned issues and can be applied not only to multiphase diffusion systems under non-isothermal saturation conditions [4] but also to multidimensional problems. However, the introduction of an 'auxiliary grid' significantly complicates the calculation algorithm.

Results and Discussion.

The resulting numerical solution was used to predict the thickness of the carbide layer and the decarburized zone during the chrome plating of Grade 45 steel (at a chrome plating temperature of T = 1223K). The following chromium concentration values at the boundaries were used in the calculations:

$C^0_{(Cr)1} = 95$ масс %; $C^2_{(Cr)1} = 94{,}67$ масс %; $C^1_{(Cr)2} = 16$ масс %

The diffusion coefficients of chromium in carbide and ferrite were taken at the saturation temperature T=1223K:

$D_{(Cr)1} = 1{,}7\ 10^{-15}$ м$^2$/с; $D_{(Cr)2} = 5{,}66\ 10^{-14}$ м$^2$/с

Carbon concentrations at the boundaries [5]:

$C^0_{(C)1} = C^2_{(C)1} = 5{,}33$ масс %; $C^3_{(C)2} = 0{,}08$ масс %;

$C^2_{(C)3} = 0{,}16$ масс %; $C^4_{(C)3} = 0{,}45$ масс %

And the diffusion coefficients at the saturation temperature T=1223K:

$D_{(C)2} = 1{,}94\ 10^{-11}$м$^2$/с; $D_{(C)3} = 2{,}36\ 10^{-10}$м$^2$/с

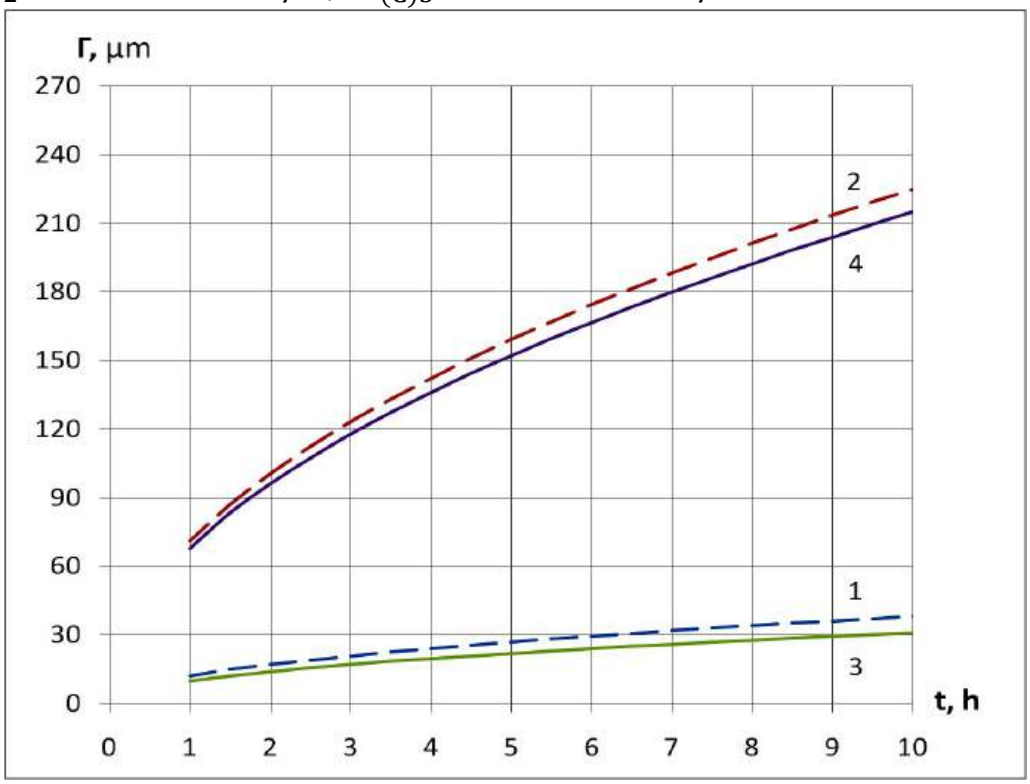


Fig. 2. Change in the thickness of the carbide layer (curves 1, 3) and the carbon-depleted ferritic zone (curves 2, 4) on steel 45 during chromium plating. 1, 2 – experimental data [6]; 3, 4 – numerical calculation.

The calculation yielded the following results (Fig. 2).

As seen from the figure, the migration rate of interface $\Gamma_2$ is more than six times higher than that of interface $\Gamma_1$. This indicates that a significant decarburized zone will form during the chrome plating process (Fig. 2, curve 4). To verify the obtained calculated dependencies, comparisons were made with studies on the chrome plating of Grade 45 steel samples at a temperature of 1273K from a sodium melt [6] for various holding times (from 2 to 10 hours). According to the data in [6], measurements of

microhardness and thermoelectric power (TEP) of the carbide phase and the decarburized zone samples made it possible to determine their dimensions for the corresponding time intervals (2, 4, 6, 8, and 10 hours).

The values of microhardness and TEP in the coating do not depend on the saturation time. However, in the decarburized zone, these characteristics vary. For instance, with a saturation time of 2–6 hours, the microhardness in the decarburized zone changes from $2{,}5 \cdot 10^7$ N/m$^2$ at the coating interface to $1.8\ 10^7$ N/m$^2$ in the base metal. With longer holding times, the microhardness ranges between $(1 \div 1{,}4)\ 10^7$ N/m$^2$ and varies insignificantly across the thickness of the decarburized zone. All this evidence suggests that the carbon concentration beneath the coating can vary from a ferritic to a pearlitic composition.

Based on the microhardness measurements, curves showing the time-dependent changes in the dimensions of the carbide (curve 1) and decarburized (curve 2) zones were plotted (Fig. 2). The calculation results for the corresponding zones (3 — for the carbide, 4 — for the decarburized zone) are also presented here. As shown in the figure, the results are in satisfactory agreement with the experimental data. The discrepancy between the calculated data and the experiment does not exceed 10%.

Conclusion.

Based on the above, the following conclusions can be drawn:

1. A mechanism of diffusion kinetics for the application of carbide-forming elements to steel has been established, allowing the redistribution of elements in the system to be analyzed from the perspective of binary diffusion.

2. A mathematical model has been constructed, and the problem of carbon redistribution during chrome plating has been solved.

3. The agreement between the calculated data and experimental results is satisfactory.

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