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Creating a model of diffusion deposition of metal coatings from melts of low-melting metals

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Abstract. The object of the research is to apply a diffusion layer of nickel from a liquid lead melt, and the subject is the optimal interaction of factors that influence the creation and growth of a diffusion layer. In this paper, the main factors affecting the rate of formation of the nickel coating are analyzed, the effective diffusion coefficients of nickel coatings are calculated for the 1.0036 and 1.0503 steels, and the activation energy for diffusion is determined. Based on the data obtained, empirical formulas are obtained for determining the thickness of the diffusion layer as a function of temperature and saturation time of the process.

1. Introduction

The production of diffusion coatings from the liquid metal solution medium is based on the isothermal mass transfer of components in the solid phase (metal of the product and the coating element) through the liquid phase separating them (transport melt). The nature of the transfer is significantly dependent on the physicochemical processes that are determined by the saturating medium and the composition of the base metal [1,2].

The formation of a diffusion metal coating consists of four main stages.

1. Reaction in the transport melt (formation of active atoms in the transport medium).
2. Transfer of active atoms to the surface layer.
3. The reaction of interactions of atoms with the surface, proceeding in two stages: a) absorption and b) adsorption.
4. Diffusion - the movement of adsorbed atoms inside the metal [3].

The purpose of this work is to determine the theoretical and practical principles of the formation of a diffusion metal coating from a liquid metal melt.

2. Materials and methods

The subject of research was samples and products of the 1.0036 and 1.0503 steels. As a transport melt, granulated lead was used CH TU 6-09-02-557-95. Coatings were formed on the basis of nickel grade NP1.

The main data necessary for estimating the kinetics of the diffusion saturation process in obtaining coatings from liquid metal media are: diffusion coefficients, process activation energies, changes in the concentration or flux of diffusant on the surface and distribution of its concentration in the diffusion zone, etc.

The effective diffusion coefficient is found from the values of the graph of the concentration of the diffusant distribution in the diffusion layer.

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After finding the effective diffusion coefficient, to obtain empirical formulas that allow to determine the thickness of the coating depending on the temperature and time of diffusion saturation, it is necessary to convert the equation:

$$\delta = K\sqrt{D\tau} \quad (1)$$

Taking into account the equation of the temperature dependence of the diffusion coefficient, the formula takes the form:

$$\delta^2 = K^2 D_0 t e^{\left(-\frac{Q}{RT}\right)} \quad (2)$$

where: Q is the activation energy of the diffusant (heat of diffusion);
R is the gas constant [J / (mol·K)];
T – absolute temperature [K].
This relationship shows that at a constant temperature δ will be a function of the process time. Then, replacing the constant $K^2 D_0 t e^{(-Q/RT)}$ after 2p, we get:

$$\delta^2 = 2pt \quad (3)$$

To find 2pt, it is necessary to build a graphical dependence $\delta^2 = f(\tau)$ and calculate the tangent of the angle of the straight lines [4].
After logarithm (equation 2 and 3), we get:

$$\ln 2p = \ln K^2 D_0 - \frac{Q}{RT} \quad (4)$$

At T=∞; $\frac{1}{T} = 0$ the exponential term is 1 and the equation takes the form:

$$\ln 2p = \ln K^2 D_0 \quad (5)$$

By plotting graphically the dependence $\ln 2p = f(\frac{1}{T})$, we obtain the numerical value lnK^2D_0 for the studied materials, since the equation is a straight line equation that cuts the value of ln on the ordinate axis lnK^2D_0 [4-6]
The activation energy is determined by the graph from the equation:

$$\frac{Q}{RT} = \ln K^2 D_0 - \ln 2p \quad (6)$$

From the graph $\ln 2p = f(1/T)$ it follows that:

$$tg\alpha = \frac{Q}{R} \quad (7)$$

From here we find Q and substitute in (6); we get:

$$tg\alpha = \left(\ln K^2 D_0 - \ln 2p\right) / T \quad (8)$$

The found values of $\ln K^2 D_0$ and $\ln 2p$ are substituted into equation 8 for the corresponding temperatures and we find three values of the tangent of the angle of inclination of the straight lines. For calculation, the arithmetic average of these values is taken.
The calculated values of the diffusion activation energy Q allowed us to obtain an empirical formula for determining the thickness of the diffusion layer δ from the temperature T and the time of diffusion saturation τ:

$$\delta = K\sqrt{A}e^{\left(-\frac{Q}{RT}\right)}\sqrt{\tau} \quad (9)$$

Using this formula, one can calculate the depth of the layer at different temperatures and times of the diffusion saturation process. When determining the value of $K\sqrt{A}$, the formula replaces the value of the layer thickness obtained experimentally at a certain temperature and process time [5,7,8].

3. Research results

Based on the obtained graph of diffusant concentration distributions over the depth of the diffusion zone (Figure 1), effective diffusion coefficients were calculated (Table 1).

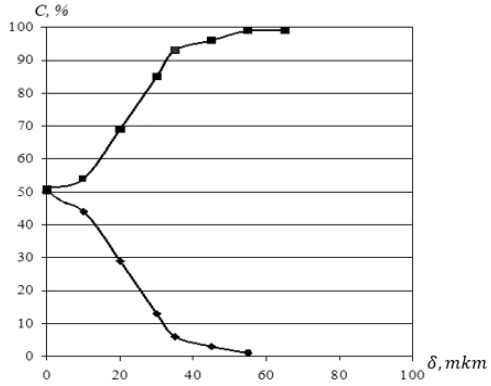

Figure 1. Distribution of Fe and Ni over the depth of the diffusion zone with an exposure τ = 10h ,t = 1100 ° C (● – Ni, ■ – Fe)

Table 1 Effective nickel diffusion coefficients.

Saturated material	Effective diffusion coefficient Ni D_{Fe}^{Ni} cm^2/s
1.0036	$3.6 \cdot 10^{-7}$
1.0503	$1.6 \cdot 10^{-6}$

Figures 2 and 3 show the dependences of the thickness of the layers on the steels used on the time and temperature of the process when it is saturated with nickel from a liquid metal lead melt.

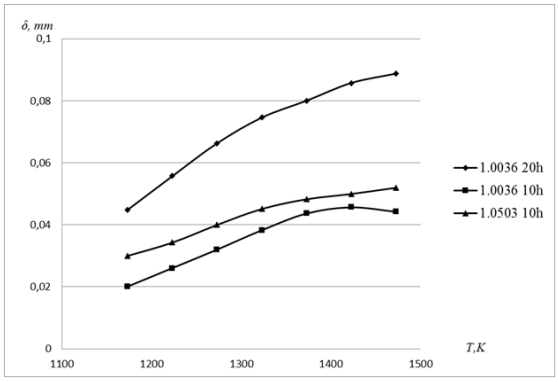

Figure 2. Dependence of nickel coating thickness on the process temperature

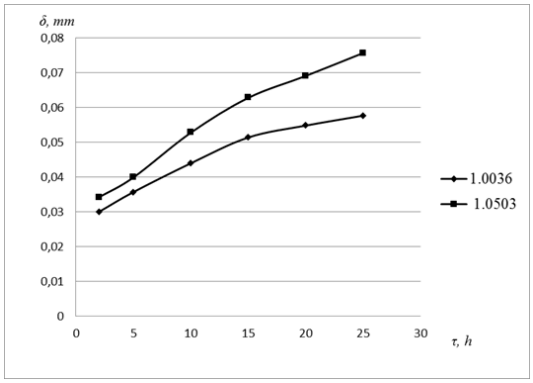

Figure 3. Dependence of nickel coating thickness on the process time, t = 1100 °C

The transformed equality (equation 1) taking into account the temperature diffusion coefficient (equation 2) shows that the thickness of the diffusion coating is a function of time. By building graphical dependencies $\delta^2 = f(\tau)$ (Figure 4) we find 2p, which is a substitute for a constant value $K^2 D_0 t\, e^{\left(-\frac{Q}{RT}\right)}$ as the slope of the straight line. For verification by the equation 3 the calculation was made. The obtained values are presented in table 2.

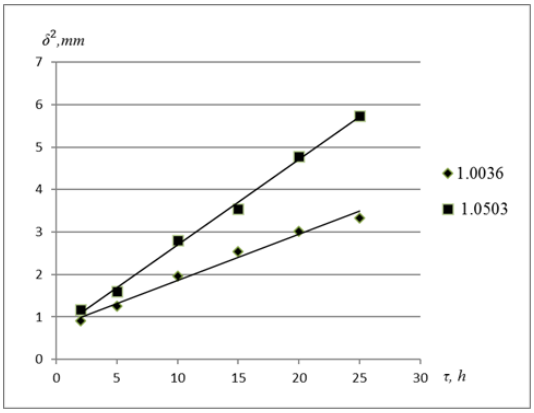

Figure 4. Dependence $\delta^2 = f(\tau)$ at t=1100 ºC

Table 2. Calculated values 2p.

Temperature		$\frac{1}{T}\cdot 10^{-3}$	1.0503		1.0036	
ºC	K		$2p\cdot 10^{-3}$	ln2p	$2p\cdot 10^{-3}$	ln2p
1000	1273	0.786	0.16	-8.74	0.108	-9.134
1100	1373	0.728	0.236	-8.351	0.196	-8.537
1200	1473	0.679	0.274	-8.204	0.201	-8.511

Taking into account equations 4 and 5, we build the dependence $\ln 2p = f(\frac{1}{T})$ (Figure 5) and find the value $\ln K^2 D_0$ as the point of intersection of lines with the axis of ordinates for the materials used. The values found are presented in Table 3.

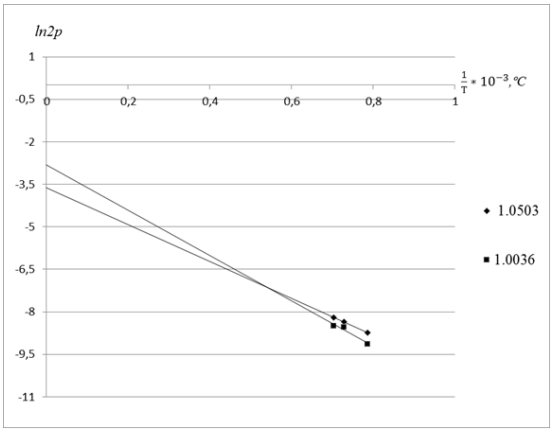

Figure 5. Dependency $\ln 2p = f(\frac{1}{T})$, τ =10 h

Table 3. Numerical values $\ln K^2 D_0$.

Saturated material	$\ln K^2 D_0$
1.0036	–2.818
1.0503	–3.627

The activation energy is determined from equation 6 according to the schedule $\ln 2p = f(\frac{1}{T})$ as tangent divided by gas constant. Using equation 8 and the values found $\ln K^2 D_0$ and $\ln 2p$, we calculate the tangent of the angle of slope of the line at the respective temperatures. The found value is substituted into the equation 7, from which we find the value of the heat of diffusion of nickel for the materials studied, the calculated data are given in table 4.

Table 4. Calculated values of the diffusion activation energy.

Saturated material	tgα	The activation energy Q, J/mol
1.0036	80945.34	67272.28
1.0503	5713.35	47477.94

The obtained values of the diffusion activation energy make it possible to obtain a general empirical formula for determining the thickness of the diffusion coating (equation 9).

Using formula 9, we find the value $K\sqrt{A}$ substituting the experimentally obtained value of layer thickness for certain values of temperature and time (table 5).

Table 5. Calculated values $K\sqrt{A}$.

Saturated material	$K\sqrt{A}$
1.0036	0.27
1.0503	0.134

Using the calculations, we were able to obtain formulas for determining the depth of the diffusion layer of nickel as a function of the temperature and time of diffusion saturation from lead melts.

$$1.0503:\ \delta = 0.134 * e^{\left(-\frac{2856,68}{T}\right)}\sqrt{\tau}$$

$$1.0036:.\ \delta = 0.27 * e^{\left(-\frac{4047,67}{T}\right)}\sqrt{\tau}$$

To compare the calculated and experimental data of the diffusion nickel coating, graphical dependences of δ on tº and τ saturation were built (Figure 6).

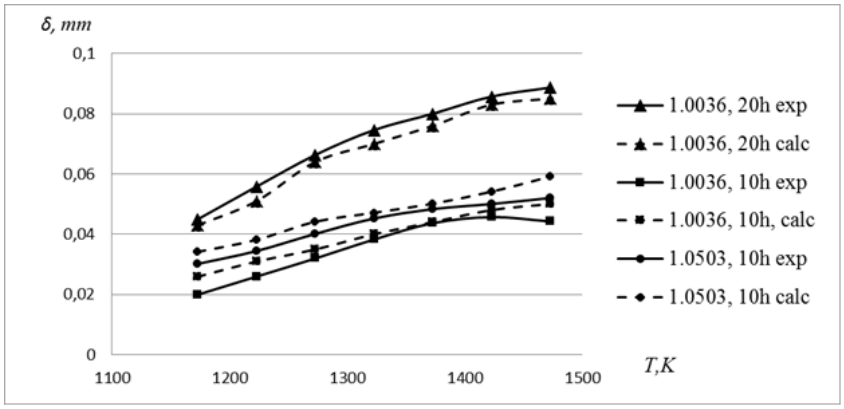

Figure 6. The calculated dependence of the thickness of the nickel coating 1.0036 at τ=20h, 1.0036 at τ=10h, 1.0503 at τ=10h.

Graphical dependencies show that the closest values of the calculated data with respect to the experimental ones are in the temperature range of 1100–1200 ºC (1273–1273 K). A small scatter of the

calculated thickness data in relation to the experimental data indicates the adequacy of the preparation and use of a mathematical calculation of the thickness of diffusion coatings.

4. Conclusion

After the study, the effective diffusion coefficients of nickel for steels were calculated:

1.0036 $D_{Fe}^{Ni} = 3.6*10^{-7}$ cm^2/s;

1.0503 $D_{Fe}^{Ni} = 1.6*10^{-6}$ cm^2/s.

The diffusion activation energy for steels is determined:

1.0036 – 47478 J/mol;

1.0503 – 67272 J/mol.

Empirical formulas for determining the thickness of the diffusion layer from the temperature and time of process saturation were obtained:

$$1.0503:\ \delta = 0.134 * e^{\left(-\frac{2856,68}{T}\right)}\sqrt{\tau}$$

$$1.0036:.\ \delta = 0.27 * e^{\left(-\frac{4047,67}{T}\right)}\sqrt{\tau}$$

The use of the obtained results may allow one in practice to ensure the effective use of the application of diffusion coatings from liquid metal melts.

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