

Розроблено аналітичний спосіб розрахунку хімічних потенціалів компонентів в системі газ-тверде, заснований на термодинамічних розрахунках вуглецевих потенціалів газової суміші C–O–H–N (продуктів згоряння метано-повітряної суміші) і твердої фази (легованої сталі). Отримано розрахункові залежності описують вплив основних параметрів нагріву складу середовища, швидкості обтікання, а також взаємодію на втрати металу, пов'язані з обзвуглецюванням.

Виконано термодинамічні розрахунки вуглецевих потенціалів легованої сталі і продуктів згоряння природного газу різного компонентного складу ($\alpha=0,2,1,2$), температур металу і продуктів згоряння 1100 1500 К.

На основі аналізу структури теплового і дифузійного приграничних шарів доведено, що зменшення температури шару продуктів згоряння, що омиває тверде виріб, і швидкості обтікання поверхні зменшує дифузійний потік вуглецю в приграничному шарі. Даний ефект сприяє зниженню зневуглецювання сталі.

Встановлено, що при обігріві теплоагрегату за принципом непрямого радіаційного обігріву (НРО) при роботі плоскопалум'яного пальника, основний газовий обсяг, локалізований у поверхні металу, має температуру істотно меншу, ніж шар, прилеглий до кладки. Це зменшує втрати металу з зневуглецюванням в порівнянні з печами традиційної системи обігріву

Спалювання газу в плоскопалум'яних пальниках при інтенсивній циркуляції продуктів згоряння всередині робочого простору теплоагрегату забезпечує оброблюваних виробів однорідний склад продуктів згоряння, що є відповідним практично до рівноважного. Це дозволяє рекомендувати плоскопалум'яні пальники до широкого застосування в сучасних енерготехнологічних апаратах в промисловості

Ключові слова: термопід, приграничний шар, зневуглецювання, плоскопалум'яний пальник, контроль температурного режиму

RESEARCH OF THE IMPACT OF THE METHOD OF HEATING OF HEAT UNITS ON THE QUALITATIVE CHARACTERISTICS OF TREATED MATERIALS

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1. Introduction

Each heating process (in chemical technology, metallurgy, mechanical engineering and other industries) flows in a gas-solid system. Such processes are carried out at a certain temperature, which is set on the basis of the thermodynamic and heating characteristics of starting materials and processes [1].

Any heating process is carried out under optimum temperature conditions, ensuring maximum performance with high quality of a target product [2]. The rate of reaction between the solid and gaseous phases increases with increasing

temperature, hence the maximum performance of the heat unit is achieved at the maximum possible temperature of the process. The set optimum temperature should also take into account the conditions of side effects or reactions of the heating process [3].

The basis of current trends in the development and construction of high-performance heat units is the modular-block principle [4]. It lies in the unity of hardware-design (HD) and process-flow (PF) methods. In practice, the use of the HD method in the development of design features of heat equipment is associated with the need for strict compliance with the technology requirement, i. e., the PF method [5].

It is considered that the factors determining the quality of treated products are: uniformity of the temperature field on the product surface, composition of the gas atmosphere and time of heat treatment. Therefore, the study of the influence of little-known factors: the temperature field formed on the phase interface and the rate of gas flow around the heat-treated surface on the quality indicators of heating processes in the gas-solid system is an urgent task.

2. Literature review and problem statement

The major technological parameters associated with heat treatment of solid material in the gas-solid system are its losses. Losses are caused by oxidation and decarburization of the surface layer in heat-treatment and heating furnaces [6], carryover loss of gradient in electric heat-treatment fluidized bed furnaces [7], etc.

In [8], the results of studies on the phase composition and defect substructure of steel are given. It is shown that the phase composition depends on the conditions of heat treatment of solid material in the gas-solid system, but the causes of losses of the treated material are not studied.

The authors of [9] showed that during heating at the surface of the treated material at the interface, a boundary layer (dynamic, related to the rate of gas flow around the material, heating, concentration) is formed. This layer, according to [10], forms the potentials of the elements exchanging with each other. For example, oxygen and carbon (in oxidation and decarburization), graphite (in graphite preparation), etc.

In [11], it is found that the fundamental concept of heat and mass transfer in the gas-solid system is the phase element potential. The specified potential determines the activity of the element in the treated material, which is in equilibrium with gas or gas mixture under given conditions [11]. Therefore, the stated information can be considered as a tool that allows the calculation of chemical potentials of phase elements.

The method of determining the chemical potentials of a gas mixture as atomic partial Gibbs functions allows a sequential analysis in the gas-solid system during heat treatment [12]. The analytical method for calculating the chemical potentials of the gas-solid system components is not given in the work, which can be explained by a different research direction.

Thus, the method of determining the chemical potentials of the treated solid-phase material (carbon, hydrogen and others) can be considered as a tool that will allow solving the urgent problem of minimizing the loss of the treated material in modern heat-power units. The calculation of the gas phase potentials, based on the analysis of the structure of the thermal and diffusion boundary layers taking into account the requirements of technologies (PF method), will allow influencing the hardware and structural design of the heating process (HD method) [13].

Therefore, these studies represent a promising aspect of introduction of modern heat-power units in the industry.

3. The aim and objectives of the study

The aim of the work is to develop an analytical method for calculating the chemical potentials of the gas-solid system components based on partial Gibbs functions.

To achieve this aim, the following objectives were accomplished:

- to perform thermodynamic calculations of carbon potentials of the C–O–H–N gas mixture (for example, combustion products of the methane-air mixture) and the solid phase (alloyed steel) in a wide range and changes in velocity and flow parameters;

- to analytically and experimentally determine the effect of temperature T_∞ and rate of gas flow around the metal u_∞ with various compositions α on metal loss with oxidation and decarburization.

4. Thermodynamics of heat and mass transfer of gas-solid systems

The fundamental concept in the analysis of heat transfer in the gas-solid (metal) system (oxidation – reduction, carburization – decarburization) is the phase element potential (oxygen, carbon, etc.). The definition of the potential of the gas mixture element as the activity of the element in the alloy, which is in equilibrium with the gas mixture under given conditions is known [12].

The method of determining the chemical potentials of the gas mixture as atomic partial Gibbs functions is the most common and allows for a complete and consistent analysis in the gas-metal system [12]. According to [12], the chemical potential of the k -th element of the phase, consisting of i components, can be determined as Gibbs partial atomic energy.

$$\Pi_k \equiv \left. \frac{\partial G_i}{\partial N_k} \right|_{T,P,N_i \neq K} \quad (1)$$

The relationship of the chemical potential of the k -th element with the chemical potentials i of the components μ_i is determined by the equation:

$$\Pi_k = \sum_{i=1}^I \mu_i \frac{\partial n_i}{\partial N_k},$$

where N_i is the number of gram-atoms of the k -th chemical element in the system.

On the example of combustion products of the methane-air mixture consisting of 51 components (gas phase) and alloyed steel (solid phase), thermodynamic calculations of carbon potentials of the gas and solid phases in the gas-metal system are performed. Thermodynamic data for each component of the gas mixture were selected from [14].

Gibbs energy for the specified set of components can be expressed as follows:

$$G = \mu_{CO} n_{CO} + \mu_{CO_2} n_{CO_2} + \mu_{H_2} n_{H_2} + \mu_{O_2} n_{O_2} + \mu_{N_2} n_{N_2} + \mu_{H_2O} n_{H_2O} + \mu_{CH_4} n_{CH_4}. \quad (2)$$

Chemical potentials of the components μ_i , included in (2), assuming an ideal gas mixture, were determined using the equation:

$$\mu_i = G_i^0(T) + RT \ln x_i + RT \ln P = G_i^0(T) + RT \ln P_i, \quad (3)$$

where G_i^0 is the Gibbs energy corresponding to the standard state of the i -th component, x_i is the mole fraction of the component; $x_i = n_i/n$, where n is the total number of moles of the

mixture components; R is the gas constant; P_i is the partial pressure of the i -th component; P is the total pressure of the gas mixture; T is the gas phase temperature.

The equilibrium composition of the gas mixture was found by minimizing (2). Taking into account (3) using the Lagrange multiplier method, we obtain a system of $k+1$ equations with the same number of unknowns, composition and potentials of the elements. The numerical solution of the system was carried out by the Newton-Raphson method.

In accordance with (1), the carbon potential of the gas mixture was calculated by differentiation of Gibbs energy (2) by the amount of carbon N_C :

$$\Pi_C = \partial(\mu_{CO}n_{CO} + \mu_{CO_2}n_{CO_2} + \mu_{H_2O}n_{H_2O} + \mu_{H_2}n_{H_2} + \mu_{O_2}n_{O_2} + \mu_{N_2}n_{N_2} + \mu_{CH_4}n_{CH_4}) / \partial N_C.$$

To determine the carbon potential μ_C of the solid phase, which is the steel containing Ni, Cr, Mn, Si as alloying materials whose chemical composition is close to SHKH15SG steel, it is necessary to know a_C^{al} – carbon activity in austenite in the presence of alloying elements [15]:

$$\mu_C = a_C^{al} = (f_C^{al} a)_{N_C = \text{const}},$$

where f_C^{al} is the activity coefficient taking into account the effect of alloying elements on carbon activity in austenite; a_C is the carbon activity in unalloyed austenite:

$$\lg a_C = \frac{2105}{T} - 0,6735 + \frac{317}{T} \frac{N_C}{1 - N_C} + \lg \frac{N_C}{1 - 5N_C}.$$

From [11], it follows that:

$$f_C^{al} = \Pi f_C^j,$$

where f_C^j is the activity coefficient taking into account the influence of the j -th alloying element on the carbon activity in austenite. The influence of Ni, Cr, Mn, Si is determined from the empirical dependencies proposed in [11].

$$\begin{aligned} f_C^{Ni} &= \frac{4950}{T} N'_{Ni}, \\ f_C^{Si} &= 10,35 N'_{Si}, \\ f_C^{Cr} &= -\frac{1710}{T} N'_{Cr}, \\ f_C^{Mn} &= -4,15 N'_{Mn}, \end{aligned} \quad (4)$$

In (4), N'_j is the atomic fraction of the alloying element in the alloy:

$$N'_j = [m_i] / \left([m_i] + \frac{A_j}{A_C} [C] + \frac{A_j}{A_{Fe}} [Fe] \right),$$

where A_j is the atomic weight of the j -th element; $[m_j]$ is the element content in the alloy.

Carbon potential of the solid phase [15]:

$$\mu_C = \mu_{gr}^0(T) + RT \ln a_C^{al}, \quad (5)$$

where μ_{gr}^0 is the carbon potential of graphite in the standard state.

If near the interphase surface, the difference in chemical potentials of the elements is small, then the interfacial carbon flow can be represented as a linear function [11]

$$J_C = \beta'_C(T)(\mu_C - \Pi_C) = \beta'_C \Delta \mu_C.$$

On the other hand, the diffusion flow $J_C = \beta_C \Delta C_C$, where

$$\Delta C_C = \frac{\beta'_C}{\beta_C} \Delta \mu_C,$$

where $\beta'_C(T)$ is the phenomenological mass transfer coefficient; β_C is the carbon mass transfer coefficient from the wall to the flow, referred to the difference in carbon concentration ΔC_C across the boundary layer.

When heated, the gas-dynamic boundary layer is formed at the metal surface, which practically determines the decarburization process [14].

Oxygen-containing gases diffuse from the gas boundary layer into the metal, interacting with the metal carbon and the metal itself, oxygen forms carbon oxide and the process of scale formation occurs. At the same time, carbon is transported in the opposite direction (decarburization process) [15]. Both processes cause a decrease in the oxygen content in the boundary layer with respect to the main gas flow.

In [16], it is shown that under the diffusion regime of carbon particle burning in the oxygen-containing atmosphere, near the particle surface there is practically no pure oxygen in the molecular or atomic form. At the same time, the maximum content of carbon-containing components due to the reaction of CO_2 coal conversion at the surface: $CO_2 + C(T) = 2 CO$. Oxidation of CO_2 and CO occurs in the layer at some distance from the particle, and with further removal, the share of oxygen-containing components increases. Thus, in the gas layer, as the particle approaches the latter, the oxidizer-to-fuel ratio α decreases and a decrease in the share of oxygen-containing components $\Delta C_O(Y)$ corresponds to an increase in the share of carbon-containing substances $\Delta C_C(Y)$. Assume that:

$$\Delta C_C(Y) = -\Omega(Y) \Delta C_O(Y),$$

where $\Omega(Y)$ is the proportionality coefficient.

The rate of change of carbon concentrations in the boundary layer will be bound by [11]:

$$\frac{dC_C}{dY} = -\Delta C_O(Y) \frac{\partial \Omega(Y)}{\partial Y} - \Omega(Y) \frac{dC_O}{dY}. \quad (6)$$

Based on the assumption of triple analogy (heat, mass, momentum transfer), for the boundary layer of the heated product under the assumption of equal thickness of the thermal and diffusion layers, $Le = Le_T = Sc = Sc_T$ can be written:

$$\frac{\Delta C_O}{\Delta C_{Om}} = \frac{\Delta T}{\Delta T_m}, \quad (7)$$

where ΔC_O and ΔC_{Om} are the current and maximum changes of oxygen concentration in the boundary layer, respectively; ΔT , ΔT_m are the current and maximum temperature changes in the boundary layer, respectively; $Le = Le_T = Sc = Sc_T$ are the Lewis and Schmidt numbers, respectively.

We differentiate (6) by the thickness of the boundary layer:

$$\frac{dC_o}{dY} = \frac{\Delta C_{O_m}}{\Delta T_m} = \frac{dT}{dY},$$

$$\frac{dC_o}{dY} = -\Omega \frac{\Delta C_{O_m}}{\Delta T_m} \frac{dT}{dY} = \text{const} \frac{dT}{dY}. \quad (8)$$

The temperature distribution in the boundary layer is determined by [17]:

$$T_l - T_0 = 5 \left(\frac{q_0''}{\rho c} \right) \frac{Pr}{\sqrt{\tau_0 / \rho}},$$

$$T_b - T_0 = 5 \left(-\frac{q_0''}{\rho c} \right) \frac{\ln(5Pr+1)}{\sqrt{\tau_0 / \rho}},$$

$$T_\infty - T_b = \left(-\frac{q_0''}{\rho c} \right) \frac{1}{\sqrt{\tau_0 / \rho}} \left(\frac{U_\infty}{\sqrt{\tau_0 / \rho}} - 14 \right), \quad (9)$$

where T_0, T_l, T_b, T_∞ are the temperatures of the surface of the metal treated in the environment of combustion products and laminar sublayer boundaries, the intermediate layer and the main flow outside the boundary layer, respectively; q_0'' is the heat flow density; τ_0 is the wall shear stress; ρ is the gas (combustion products) density; c is the gas heat capacity; U_∞ is the gas phase velocity outside the boundary layer (flow rate); $Pr = \nu/a$ is the Prandtl number; ν is the coefficient of kinematic viscosity; a is the coefficient of thermal diffusivity.

In (8), the density ρ and the heat capacity of the gas c were calculated at an average temperature of $0.5 (T_0 + T_l)$. Considering that

$$\frac{\tau_0}{\rho} = f_x \frac{U_\infty^2}{2},$$

where $f_x = 0.059 \text{ Re}^{-0.2}$ is the local coefficient of friction; $\text{Re} = U_\infty L / \nu$ is the Reynolds number; L is the length of the flow area.

When using average integral f_x on the length L , we get:

$$\frac{\tau_0}{\rho} = \frac{0,059}{1,6} \left(\frac{L}{\nu} \right)^{-0,2} U_\infty^{1,8}.$$

Taking into account the adopted two-layer (diffusion and thermal) model of the boundary layer, it is possible to calculate the value of the carbon concentration gradient at the treated surface:

$$\frac{dC_c}{dY} \Big|_{\text{surf}} = -\Omega \frac{\Delta C_{O_m}}{T_\infty - T_0} \frac{T_l - T_0}{y_l} =$$

$$= -\Omega \frac{\Delta C_{O_m}}{T_\infty - T_0} \left(\frac{T_l - T_0}{5\nu} \right) U^*, \quad (10)$$

where $y_l = 5\nu/U$ is the laminar sublayer thickness; $U^* = \sqrt{\tau_0 / \rho}$ is the dynamic speed;

$$\Delta C_{O_m} = -\frac{\Delta C_c}{\Omega} = \Omega^{-1} (\Pi_c - \mu_c).$$

From (10), it follows that the gradient of carbon concentrations in the gas phase at the metal surface and, therefore, the carbon flow are also determined by the gas phase temperature and structure of the boundary layers (dynamic, thermal).

Taking into account the sign of the gradient $\frac{dC_c}{dY} \Big|_{\text{surf}}$, it is obvious that at $\Pi_c > \mu_c$, there is the process of decarburization of the steel surface.

5. Analysis of the results of thermodynamic calculations

In accordance with the described method of determining the chemical potentials of the gas and solid phases of the gas-metal system, we consider the influence of previously little studied factors: the temperature of combustion products T_∞ and the rate of gas flow around the metal U_∞ with various a . The calculation was carried out using computer technologies [11].

The following factors were varied in the calculation: $q_0'' = 5-10 \text{ kW/m}^2$ (step -1 kW/m^2); $U_\infty = 6 \cdot 10 \text{ m/s}$ (step -2 m/s); $L = 0.3-1 \text{ m}$ (step -0.1 m); $T_0 = 1073-1673 \text{ K}$ (step -100 K).

The processing of the calculation data array was carried out with the use of the linfit regression function built in the MathCad mathematical package.

As a result of computer processing, the following dependencies were obtained:

- carbon potential of the gas phase Π_c on the gas phase temperature T_∞ and composition, determined by the oxidizer-to-fuel ratio α :

$$\Pi_c(T_\infty, \alpha) =$$

$$= \left[-7,719 \cdot 10^5 \cdot \tan(0,35\alpha) + 1,189 \cdot 10^5 \cdot \alpha^{20,7} \right] \cdot T_\infty^{-0,95} +$$

$$+ \left[13,24 \tan(0,35\alpha) - 46,53 \cdot \alpha^{20,7} \right]; \quad (11)$$

- carbon concentration gradient $\frac{dC_c}{dY}$ in the boundary layer with different compositions of combustion products α and surface flow rates (base metal temperature $T_0 = 1073 \text{ K}$):

$$\frac{dC_c}{dY}(U_\infty, \alpha) = \left[1,178 \cdot \cosh(1,4\alpha) + 1,567\alpha^{8,7} \right] \cdot U_\infty^{1,3}. \quad (12)$$

3D graphs constructed from (11), (12) are shown in Fig. 1, 2 respectively.

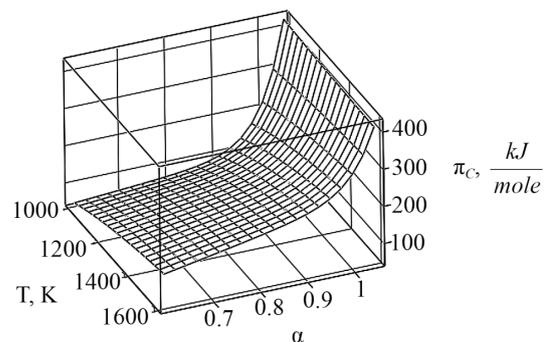


Fig. 1. 3D graph for π_c depending on the gas mixture temperature T and the oxidizer-to-fuel ratio α

With $\alpha \in \{0.6; 0.95\}$, the carbon potential of the gas phase decreases both with increasing temperature T and with increasing α .

In this case, temperature increase has no effect on chemical transformations within the set α . Consequently, the carbon potential of the gas phase will change slightly.

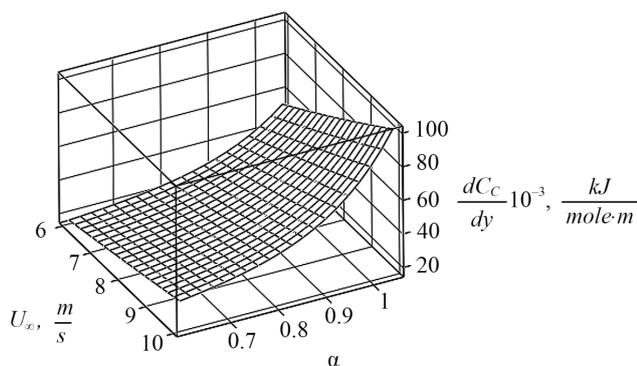


Fig. 2. 3D graph for $\frac{dC_C}{dy}$, depending on the compositions of combustion products α and surface flow rate U_∞ .

The calculation of the carbon concentration gradient in the boundary layer dC_C/dY depending on the oxidizer-to-fuel ratio (α) shows that steel decarburization is influenced by two factors: gas phase temperature of the metal T_∞ and flow rate (U_∞). The higher the gas phase temperature and surface flow rate, the higher the carbon concentration gradient in the boundary layer (dC_C/dY), therefore, the more the metal will be decarburized.

The conclusion about the influence of the gas phase temperature on the diffusion flow in the boundary layer with a constant composition of the gas phase qualitatively confirms the results of [18] in the field of chemical-heat treatment in special atmospheres. Experimental studies of decarburization of steel blanks in heating and heat-treatment furnaces confirm the obtained dependences [19].

Verification of the results of analytical studies on steel decarburization was carried out on the experimental stand (Fig. 3).

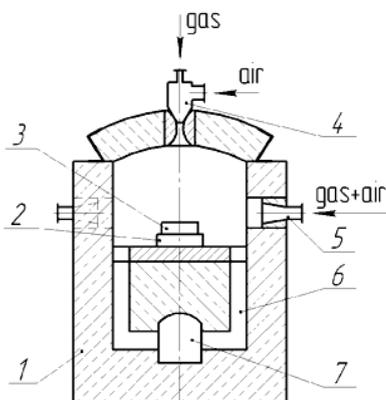


Fig. 3. Scheme of the experimental stand for conducting research on the effect of the heating method on steel decarburization: 1 – furnace lining; 2 – base for the test samples; 3 – test sample; 4 – flat-flame burner; 5 – GAP burner; 6 – smoke exhaust channels; 7 – central smoke exhaust flue

Two different heating systems were implemented on the stand:

- heating based on the principle of indirect radiant heating (IRH) using the flat-flame burner located in the roof (Fig. 3, pos. 4);

- traditional heating system (TH) with a short-flame burner GAP with side arrangement (Fig. 3, pos. 5).

Fuel – natural gas, oxidizer – air. Witness samples were specially prepared plates with a polished surface of SHH15SG steel. In total, 48 experiments – 24 experiments with each heating method on 96 samples were conducted.

In each of the experiments, heat studies were conducted (composition of combustible gas, metal heating temperature, furnace temperature, temperature of the layer of combustion products at the heated metal surface, composition of the gaseous medium, etc.). Metallographic studies on the depth of the decarburized layer, structure, scale layer thickness, scale grain-size indices were conducted. The chemical composition of the scale was also determined [13].

6. Discussion of the results of the study of the fire stand

As a result of the study, it was found that during heating the heat unit based on the principle of indirect radiant burning (IRH) during the operation of the flat-flame burner, the main gas volume has a temperature significantly lower than the layer adjacent to the lining. This is due to the fact that the operation of the flat-flame burner is based on the continuous flow of combustion products around the forming surfaces of the working space in which it is installed (Coanda effect). In this case, the maximum temperatures are concentrated in the lining and the radiation component of the heating process is prevalent.

The temperature difference $T_{in}-T_\infty$ (the main gas layer T_0 and the layer of witness samples T_∞ in the compared heating systems) is even higher $+(35\div 120)$ K with the heating system based on the IRH principle and $-(25\div 65)$ K – with the traditional heating system (TH). This is explained by the fact that in the implementation of the heating system with a short-flame burner GAP, the main gas volume in the working space has a temperature significantly higher than during the operation of a flat-flame burner, which is determined by the principle of the short-flame burner GAP. This makes it possible to assert that T_∞ with the IRH system is 100 or more K less than during heating with the TH system.

Thus, heating and heat treatment of various grades of steels in IRH furnaces equipped with flat-flame burners reduces the loss of metal with decarburization. This is due to:

- high degree of uniformity of metal heating in the absence of local overheating, which is a consequence of the high rate of circulation of natural gas combustion products in the working space of the furnace, due to the principle of flat-flame burners;

- practical uniformity of combustion products at the surface of heat-treated products and the absence of metal contact with products of incomplete combustion of natural gas, including atomic oxygen and radicals;

- lower average mass temperature of the layer of combustion products and gases that are in direct contact with heat-treated products.

Assessment of reliability of the studies and corresponding scientific findings is confirmed by the practice of introducing IRH furnaces with flat-flame burners for heat treatment and heating of products in the temperature range of 800–1,600 K in various industries, including mechanical engineering, metallurgy, etc. [20, 21].

7. Conclusions

1. The analytical method for calculating the chemical potentials of components in the gas-solid system based on thermodynamic calculations of carbon potentials of the C–O–H–N gas mixture (combustion products of the methane-air mixture) and the solid phase (alloyed steel) is developed. Its distinctive feature is the calculation of the rate of change of carbon concentrations in the boundary layer based on the assumption of triple analogy (heat, mass, momentum transfer) for the boundary layer of the heated product. The value of the carbon concentration gradient at the treated surface was determined taking into account a two-layer (diffusion and thermal) boundary layer model. Thermodynamic calculations of carbon potentials of alloyed steel and combustion products of natural gas of different composition ($\alpha=0.2\div 1.2$), metal and combustion products temperatures of 1,100–1,500 K are performed.

2. Based on the analysis of the structure of the thermal and diffusion boundary layers, it is proved that a decrease in

the temperature of the layer of combustion products flowing around the solid product and the surface flow rate reduces the diffusion flow of carbon in the boundary layer. This contributes to reducing the decarburization of steel. The influence of the heating system of the heat unit on the metal losses associated with decarburization is investigated. It is found that the method of heating of the heat unit based on indirect radiant heating using flat-flame burners reduces metal loss with decarburization compared to furnaces of the traditional heating system. This effect is achieved by providing uniform temperature fields in the working space of the heat unit and over the heat-treated surface. As well as practical uniformity of the composition of combustion products and exception of the contact of the treated surface (metal) with products of incomplete combustion, directly flowing around the metal, with a reduced flow rate of combustion products around the metal. Dependences describing the effect of the main parameters of heating the medium composition, flow rate, and their interaction on metal losses associated with decarburization are obtained.

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Розроблено технологію виготовлення склозв'язок-активаторів для інтенсифікації спікання керамічних матеріалів, зокрема – ангобних покриттів. Проведено порівняльний аналіз склозв'язок, отриманих за допомогою традиційної варки скла та шляхом золь-гель синтезу. Встановлено значну ефективність останнього, оскільки зменшуються енерговитрати на термообробку композиції (замість варки скла при 1300–1400 °С потрібна термообробка гелю до 600 °С) та підвищується однорідність склозв'язки (хімічний склад композиції усереднюється на молекулярному рівні).

Досліджено також різні золь-гель способи одержання склозв'язок-активаторів: порошковий золь-гель спосіб без прожарювання; золь-гель спосіб приготування розчинів солей; порошковий золь-гель спосіб з плавленням композиції. Зазначені способи відрізняються послідовністю та методом змішування вихідних компонентів, але обов'язковою є диспергація в гелеутворюючому агенті – етилсілікаті ЕТС-40. В якості основних складових активатора обрано розчинні солі $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2$ та $NaNO_3$. Вивчено особливості зміни фазового складу склозв'язок під час їх нагріву до 600 °С та встановлено, що отримані композиції наближуються до аморфного стану при температурах ~600 °С. При подальшому нагріванні дослідних склозв'язок до 1000 °С відбувається їх інтенсивне плавлення, при чому у перших двох способах в'язкість та поверхневий натяг розплавів є меншим, у порівнянні зі звичайним склорозплавом, тому змочувальна здатність склозв'язок-активаторів є вищою.

При введенні даних активаторів спікання до складів керамічних покриттів встановлено, що найбільш ефективним є активатор, отриманий способом приготування розчинів солей. Саме він після випалу при 1170 °С забезпечує формування найбільш щільної структури спеченого покриття зі зниженим водопоглинанням (не більше 0,05 %) та високою білизною поверхні (87–88 %). Розроблені активатори можуть стати альтернативою традиційним склозв'язкам, для варки яких потребуються значні енергоресурси.

Ключові слова: золь-гель спосіб, активатор спікання, ангоб, випал, водопоглинання

UDC 666.112.8

DOI: 10.15587/1729-4061.2018.150606

DEVELOPMENT OF A SOL-GEL TECHNIQUE FOR OBTAINING SINTERING ACTIVATORS FOR ENGOBE COATINGS

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1. Introduction

Under conditions of constant growth of energy costs and the deficit of energy resources, a pressing issue in the ceramic industry where products are annealed at high temperatures is energy efficiency. In order to ensure the intensive sintering process of ceramic products and coatings, it is required to achieve a high degree of activity of all components in the ceramic charge [1]. However, the activity of starting components under actual industrial conditions is often quite

low, which leads to the necessity to sinter materials at high temperatures. Otherwise, one observes a deterioration in the physical-mechanical characteristics of the fabricated products.

One of the possible solutions to the specified task is the application as part of the charge of specialized sintering activators [2], which would make it possible to significantly improve products quality, without introducing radical changes to the technological process, and to considerably reduce the temperature of their annealing.