Technological basis for the process of application of diffusion coatings in liquid metal melts with use of electric furnaces with air atmosphere

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Diffusion saturation of the components surfaces in the melts of low-melting metals is the most efficient among known technologies for application of coatings from a liquid phase. However, as soon as this technology is realized at present time with use of special units with protective media, it restricts principally its wide practice. This work presents the results of examination of application processes for diffusion coatings in the melts of low-melting metals using electric furnaces with air atmosphere. Use of this process in shaft or muffle furnaces, which are widely applied at the modern machine-building production facilities, means introduction of the important innovations in the existing technology due to the effect of electric furnace oxidizing medium on quality of obtained coatings. Thereby two following aims of the conducted investigations were formulated: comprehensive study of coatings forming regularities with use of liquid metal melts in the conditions of oxidizing effect in electric furnaces with air atmosphere, as well as development of practical recommendations for elimination of harmful influence of high-temperature oxidation of melt and processing product on quality of coatings. Testing of suggested technological routes for forming of diffusion metallic coatings on steel products in low-melting metal melts using electric furnaces with air atmosphere is an actual problem. Protection of final melt and product surface from oxidation using different fluxes is proposed. Use of the mix of NaCl-Na_2CO_3 salts didn't provide protection of liquid metal bath and steel product surface from high-temperature oxidation. Use of $Na_2B_4O_7$ as a protective flux also didn't provide efficient protection from high-temperature oxidation, because porous inhomogeneously distributed diffusion nickel coating with thickness 9-10 µm was obtained. The best result was achieved using CaO-Li_2CO_3-B_2O_3 flux. As a result, single-layered, uniform, porous-free, homogeneously distributed diffusion nickel coating with thickness 20-22 µm was obtained.

Key words: diffusion metallization, liquid metal melts, high-temperature oxidation, protective fluxes, transporting melts, nickel coating, corrosion resistance.
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Introduction

Modern development of petrochemical industry develops directly on availability of materials and technologies which provide high level of corrosion resistance for operating equipment. Details of a pipeline system contact directly with different transported liquids [1-3]. To provide high working capacity in aggressive media, these details are manufactured from high-expensive alloyed steels and alloys.

As soon as operating resource of the components for petrochemical equipment is mainly determined by the service characteristics of their surface layers, use of the special coatings is the most efficient method to provide their high working capacity [4-6]. Thereby, some components of such equipment can be principally manufactured from carbon steels, based on the condition that corrosion-resistant diffusion coatings (in particular in low-melting metal melts) are applied on the surface of these components. Such variant provides possibility of solving the problem of import of auxiliaries for petrochemical industry, which becomes rather actual at present time owing to the foreign sanctions.

There are a lot of methods for application of coatings at present time. Those coatings that are used in machine-building are classified by three principally different groups according to the method of their forming: diffusion-type coatings, covering-type coatings and combined diffusion-covering coatings [7]. Diffusion coatings present an integral part with the basic metal of a component due to diffusion penetration of coating atoms into external layer oc component metal, what makes these coatings more efficient [8]. Diffusion coatings can be formed from gas, liquid or solid phase. The liquid phase variant seems to be the most acceptable from these options for obtaining of uniform corrosion-resistant coating along whole perimeter of components with complicated shape and with internal hollows. It is provided by penetration of diffusing element to all existing surfaces, including all undercuts of processing details [9, 10].

The following advantages of the technology of high-temperature diffusion deposition can be mentioned:

- simplicity and efficiency of technological operations;
- possibility of obtaining of single- and multi-component coatings without pores and cracks, which are uniform in their thickness and are characterized by high density and homogeneity;
- forming of diffusion coatings on the components with complicated shape, on internal and hardly accessible hollows of these components;

- possibility of substantial acceleration of this process and its automation;
- possibility of combining diffusion saturation and heat treatment [11-13].

Materials and methods

At present time, different coatings were obtained with use of liquid metal melts on the following materials: structural and tool steels, cast iron hard alloys of tungsten-cobalt, titanium-tungsten and titanium-tantalum-tungsten-cobalt types [14-16].

Steel 1045 was taken in this work as a basic sample material for high-temperature diffusion deposition in the medium of low-melting melts. Lead of S0 grade was used for obtaining of transporting melt. Nickel of N02200 grade was applied as a diffusing element.

Technological process of obtained diffusion coatings in the medium of low-melting melts includes the following stages: preparing, basic and final.

The preparing stage consists of cleaning of a component surface with oxides removal and degreasing. Low-melting melt, which is a transporting medium for a diffuser, is also prepared during this stage. For this purpose, low-melting metal is heated to melting temperature and obtained melt is saturated with diffusion element. Protective flux is simultaneously molten in a separate crucible, and it covers transporting melt from the top.

Within the basic stage, product is dipped in transporting melt with diffusion element and is held during definite time at preset technological temperature.

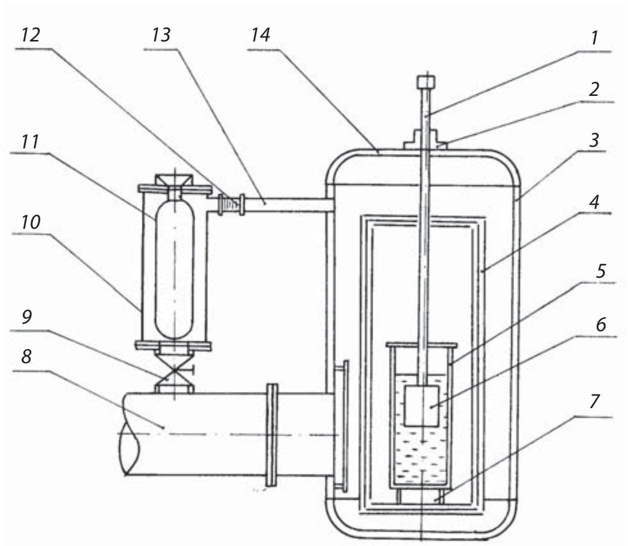

Fig. 1. Route of the unit for container-free method of coatings application:
1 – water-cooled rod; 2 – compacting pipe connection; 3 – water-cooled shell; 4 - heater; 5 – ampoule with transporting melt; 6 - sample; 7 – object table; 8 – discharge tube of vacuum pump; 9 – vacuum gate; 10 – heat exchanger shell; 11 – vessel for liquefied gas; 12 – vacuum bellows; 13 – feeding pipeline; 14 – water-cooled lid

The final stage includes sample extraction and removal of transporting melt residues from its surface (if there are any).

There are different variants for realization of this process. So, container and container-free methods are presented in the work [17]. Application of coatings via container method is conducted using special equipment with operating principle based on creation of protective gas media or vacuum. A capsule with liquid metal melt and sample is located in a hermetic container. This method is not used for diffusion saturation of large-size products due to restricted container size. Container-free method is realized using the unit on the base of vacuum electric furnace (**Fig. 1**). The furnace is modernized by vertically moving plant for charging of products in melt. Argon protective medium in this electric furnace prevents high-temperature oxidation of liquid metal melt.

Despite the above-mentioned advantages of the technology for high-temperature diffusion deposition from the medium of low-melting melts, it has restricted application at present time, because the conventional technology which is used now is based on expensive vacuum equipment of furnaces with protection medium.

To use this process in usual shaft or muffle furnaces, which are widely distributed at the modern machine-building production facilities, it is required to introduce principal innovations in the existing technology. It is connected with the processes of prevention of processing component from oxidizing effect of a furnace air atmosphere. That's why comprehensive examination of the features of coatings forming in liquid metal melt, in the conditions of the effect of furnace oxidizing medium, was the main aim of the investigation which was conducted at the department of material science and technology of artefacts in the St. Petersburg mining university. Another aim was to prepare theoretical

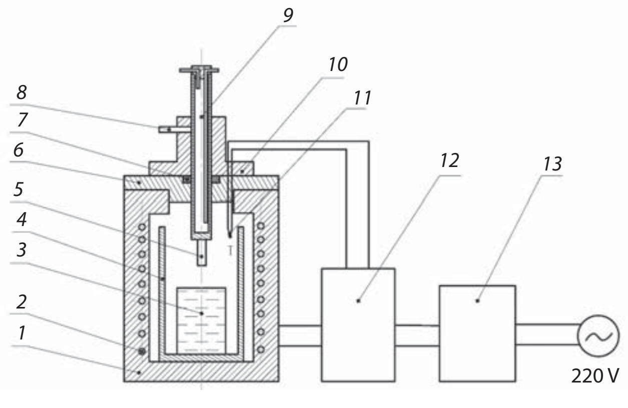

Fig. 2. Principal scheme of the plant for surface alloying from the medium of low-melting metals using shaft electric furnace with air atmosphere:
1 – shaft electric resistance furnace; 2 – heating element (spiral); 3 – liquid metal melt; 4 – protection screen; 5 – fixation of sample; 6 – thermal furnace lid; 7 – thermal stable flange from refractory wool; 8 – fixing element; 9 – water-cooled rod; 10 – device for charge of processing samples; 11 - thermocouples; 12 – temperature controller; 13 - variator of current adjusting

and practical recommendations for elimination of harmful influence of the processes of high-temperature oxidation of melt and processing product on quality of coatings. Study of the process of diffusion alloying of the sample surface was conducted using the laboratiorial plant (**Fig. 2**), which was specially developed on the base of shaft thermal furnace with air atmosphere [18,19.].

Influence of oxidizing atmosphere on state of transporting melt and on surface quality of a processing component, as well as development of efficient method of its protection using fluxes was determined with assistance of this plant. It was mentioned in the works [20, 21] that transporting melt of lead has insufficient reducibility of oxides which are forming on the surface of coated steel components. Additionally, transporting melt itself is partly oxidizing, what retards transition of diffuser atoms from the melt to the component surface.

Research part

This investigation used both fluxes which were applied in the industry for welding and heat treatment, and the flux with special composition.

Simultaneously with removal of oxide film, flux should meet the following requirements:

- its melting temperature should be by 50-100 °C higher than the melting temperature of transporting melt;
- speed of oxides dissolution should exceed their forming speed;
- liquid flux should have maximal level of intra-phase tension on the boundary with liquid metal;
- flux should not arise interaction between its components and transporting melt;
- flux should not cause corrosion of furnace components;
- flux should float easily on the surface of transporting melt [22, 23].

Possibility of high-quality coating obtaining when using the technology of high-temperature diffusion saturation in the air atmosphere of an electric furnace depends mainly on correct flux choice. Saturation temperature and duration should be determined correctly during this choice. Flux reaction ability should allow removal of oxide films without any corrosion effect on product and on transporting melt, and it should be indifferent relating to the crucible material [24].

The fluxes which are used in the industry have definite temperature intervals of their activity. The minimal temperature of interaction beginning between flux and oxides on metal surface is considered as the lower limit of this interval. As soon as temperature rises, flux activity increases too. When the upper temperature limit is achieved, flux activity begins to decrease due to burn-out, evaporation or volatilization of its separate component [25].

Flux can be less active in the conditions of long-term diffusion saturation, but at the same time it should have resistance against decomposition and sufficient refining ability [26].

The optimal temperature conditions for realization of diffusion metallization process include holding at 950 °C during 4 hours; it was tested successfully in the works [22, 23].

The mix of salts $NaCl$-Na_2CO_3 was selected as the flux for preliminary testing. Percent relationship of its components, such as NaCl (35 %)-Na_2CO_3 (65 %), was chosen in order to obtain relative neutrality to product material and to components of transporting melt. Heat treatment of machine components and tools was conducted in metallurgy using sodium chloride. Sodium carbonate is widely used in quenching baths as water solution for rinsing of components after heat treatment. The mix of sodium chloride and sodium carbonate is melting under high temperature conditions and forms carbonates with metal oxides; these carbonates elevate on the surface as slags.

Sodium tetraborate $Na_2B_4O_7$ (borax) is selected as the following pilot flux. In molten form it is presented as vitreous mass, which protects metal from oxygen influence, interacts actively with oxides with forming sodium metaborate and boron anhydride.

The complex CaO-Li_2CO_3-B_2O_3, which was developed by Yu. D. Brusnitsyn from the Central research institute of structural materials “Prometey”, was used as the third pilot flux composition. Percent relationship of its components, such as (CaO (20 %)-Li_2CO_3 (30 %)-B_2O_3 (50 %), is chosen in such way to provide the temperature of flux softening be more close to the temperature of intensive high-temperature oxidation and evaporation of the transporting melt, then flux will be in molten state during sample dipping in this melt. In this case the better result is achieved, because the process of interaction with liquid phase is seriously accelerated.

Calcium oxide, which is widely used in metallurgy, is characterized by glass-forming effect. Its existence in composition is determined by necessity of flux structure stabilization, what is required during long-term high-temperature heating. Melting of this glass-forming component promotes restriction of oxygen diffusion in a flux layer, providing in such way leak tightness of metallization [27].

Lithium carbon dioxide is a surface-active substance, it provides lowering of melt surface tension, improvement of the component surface softening and decrease of melt toughness, testifying the ability to flux spreading over the coating surface of the component. Lithium carbon dioxide has the advantage as a flux component, which consists of its non-interaction with saturating material and its components and no chemical compounds or solid solutions are formed; it is not toxic as well [28].

Boron anhydride is characterized by acidic properties, it provides interaction with the main oxides of the transporting melt and the sample. It is widely used at high temperatures, has low volatility and weak reaction ability with iron. Boron anhydride also provides protection from secondary oxidation of the processing surface. When interacting with metallic oxides on the surface of the sample and transporting melt, it forms glass-form borates which are transferred to the surface of a liquid metal bath; in such way additional protective layer on the surface is created [29].

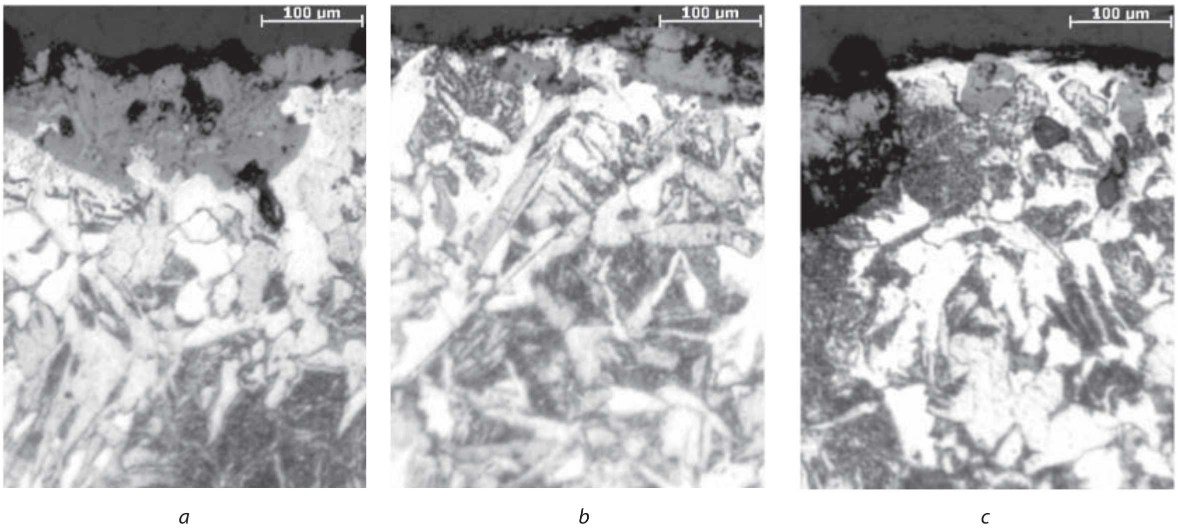

Fig. 3. Steel 1045 microstructure after surface diffusion saturation without flux use (950 °C, 4 h) (×200): *a*) violated surface geometry of the samples; *b*) areas not saturated by nickel; *c*) small coating areas

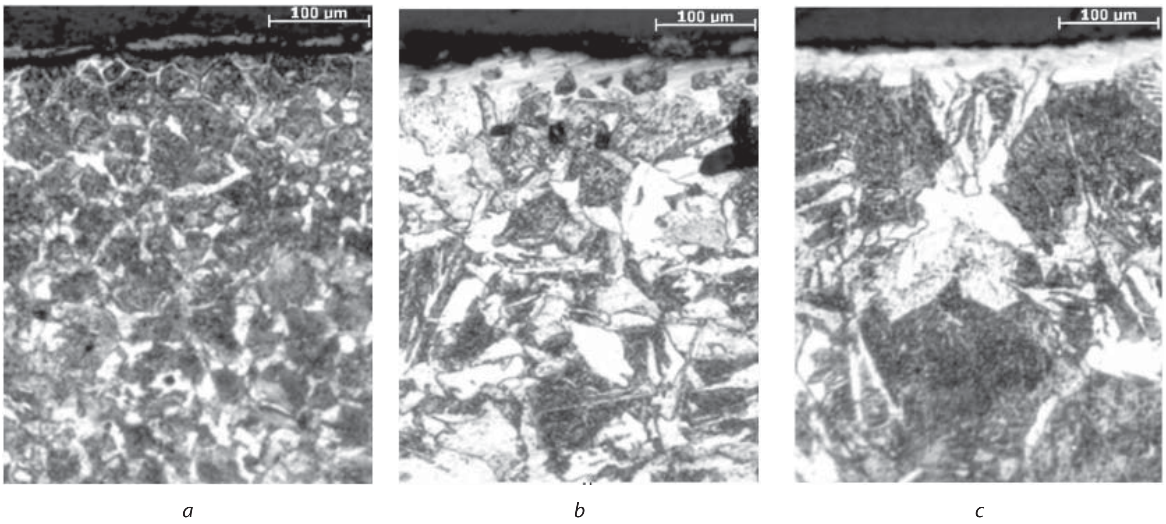

Fig. 4. Microstructure of nickel diffusion coating using the complexes: *a*) NaCl-Na_2CO_3 (800 °C, 4.5 h) (×200); *b*) $Na_2B_4O_7$ (950° C, 4 h) (×200); *c*) CaO-Li_2CO_3-B_2O_3 (950 °C, 4 h) (×200)

Table 1. **Influence of fluxes on nickel coating thickness on Steel 45**

No.	Flux	Flux composition, %		Coating thickness, µm
1	Without flux	–		–
2	Mix of salts	NaCl Na_2CO_3	35 65	–
3	Borax	$Na_2B_4O_7$	100	9-10
4	CaO-Li_2CO_3-B_2O_3	CaO Li_2CO_3 B_2O_3	20 30 50	20-22

Experimental part

The surface layer structure of the sample, which was subjected to the whole cycle of diffusion saturation by nickel in a lead melt, but without protection by flux, was examined initially to provide possibility of comparative assessment of efficiency of protective action for used fluxes. Analysis of microstructure of coatings, which were obtained without use of protective fluxes, displays violated surface geometry of the samples (**Fig, 3,** *a*), the areas which are not saturated by nickel (Fig. 3, *b*) and small coating areas under corrosion effect (Fig. 3, c).

The results of examination of coatings microstructure with use of selected protective fluxes, such as complexes NaCl-Na_2CO_3, $Na_2B_4O_7$ и CaO-Li_2CO_3-B_2O_3, showed that their efficiency to protect the coating surface differ seriously (**Fig. 4**).

Use of the complex NaCl-Na_2CO_3 for protection from high-temperature oxidation is not recommended due to active evaporation and absence of nickel coating (see Fig. 4, *a*).

Table 2. **Distribution of chemical elements in different points through the depth of nickel coating of the sample**

Distance from the coating surface inside	O	Si	S	Mn	Fe	Ni	Total
0 µm	–	–	–	–	57.87	42.13	100.00
5 µm	0.70	–	0.14	–	61.68	37.48	100.00
10 µm	–	–	–	–	70.07	29.93	100.00
15 µm	–	0.47	–	0.60	77.45	21.48	100.00
20 µm	1.05	–	–	–	86.14	12.81	100.00
25 µm	–	–	–	–	96.32	3.68	100.00

Table 3. **Corrosion resistance of the samples from Steel 1045 with nickel coating and without it**

Type of sample	Corrosion speed in the testing environment				
	10% KOH	40% KOH	10% NaCl	5% HCl	5 % H_2SO_4
	mm/year	mm/year	mm/year	mm/year	mm/year
without coating	0.0173	0.0317	0.0483	6.9713	5.0471
Resistance group	Resistant	Resistant	Resistant	Low-resistant	Low-resistant
with coating	0.003	0.0029	00183	0.4496	0.4833
Resistance group	Absolutely resistant	Very resistant	Resistant	Reduced resistant	Reduced resistant

Use of borax for protection from the effect of oxides provided obtaining of nickel coatings with average thickness 9-10 µm. However, the coatings were porous owing to insufficient flux gas tightness (see Fig. 4, *b*).

When using the flux $CaO-Li_2CO_3-B_2O_3$, the single-layered, uniform, porous-free coating was obtained, it was homogeneously distributed along the whole sample surface (see Fig. 4, *c*). Absence of pores in the nickel coating testifies on sufficient flux gas tightness, what is especially important in the case of nickel use as a diffusing element due to its high sensitivity to dissolved gases and tendency to forming pores. Average thickness of the nickel coating is 20-22 µm.

The values of nickel coatings with use of different fluxes are compared in the **Table 1**.

Based on the data of spectral analysis using micro-analyzer Inca X-Act, the obtained coatings contain from 42.13 % Ni on the surface to 12.81 % on the distance 20 µm from the surface (**Table 2**). Such variation of the content of saturating element testifies that the coating basis contains solid solutions Fe-Ni with variable concentration (corresponding to the Fe-Ni state equilibrium diagram).

Testing for general corrosion of the examined steels with diffusion nickel coatings and without coatings was conducted at normal temperature in accordance with the GOST P 9.905-2007. Corrosion resistance of the investigated samples was evaluated in 10 % and 40 % KOH water solutions at the temperature 20 °C during 2016 hours. The studies of corrosion resistance for steels with nickel coatings and without coatings were also conducted in 10 % water solution of NaCl and 5 % water solutions of HCl and H_2SO_4 at the temperature 20 °C during 720 hours. The results of testing on corrosion resistance are presented in the **Table 3**.

Application of nickel coating increases resistance of carbon steels in 10 % KOH water solution by 5 times; in 40 % KOH water solution by 10 times; in 10 % NaCl water solution by 2 times; in 5 % HCl water solution by 15 times; in 5 % H_2SO_4 water solution by 10 times.

Conclusion

When using the mix of salts $NaCl-Na_2CO_3$, active evaporation, weak protection of a liquid metal bath from the effect of environment protection were observed, as well as absence of removal of oxide films form the sample surface. These factors make the salt mix invalid as a complex for protection from high-temperature oxidation.

Using borax as flux leads to obtaining nickel coating with thickness 9-10 µm, which is porous and inhomogeneously distributed. Thereby borax is unacceptable as protective flux.

Use of $CaO-Li_2CO_3-B_2O_3$ flux for protection from high-temperature oxidation provides obtaining of single-layered, homogeneous, porous-free diffusion nickel coating with uniform thickness 15-22 µm, and it precisely reproduces shape of coating sample.

Application of nickel coating increases resistance of carbon steels in 10 % KOH water solution by 5 times; in 40 % KOH water solution by 10 times; in 10 % NaCl water solution by 2 times; in 5 % HCl water solution by 15 times; in 5 % H2SO4 water solution by 10 times.

Use of $CaO-Li_2CO_3-B_2O_3$ flux for surface protection of the transporting melt and processing components from high-temperature oxidation allows to obtain diffusion nickel coatings in liquid metal lead melts, using electric furnaces with air atmosphere. These coatings provide improvement of corrosion resistance for such components in different media.

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