

Diffusion coatings formation features, obtained by complex chemical-thermal treatment on the structural steels

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ABSTRACT

Introduction. The main methods of increasing the efficiency of products made from structural steels are considered. A description of diffusion saturation from liquid metal media solutions (*DSLMMMS*) is given. Also, complex diffusion saturation technology (*CDS*), including *DSLMMMS* and carburization is shown. **The purpose of the work** is to reveal the effect of steel composition on the process of formation and elemental composition of diffusion-saturated surface layers (coatings) based on chromium, as well as to establish differences and regularities in the processes of formation of diffusion-saturated coatings after *DSLMMMS* and *CDS*. **The methods of investigation.** Cylindrical specimens 20 mm in diameter and 30 mm long were subjected to *DSLMMMS*. The specimens were made of carbon and alloyed steels: *St3*, *20-Cr13*, *40-Cr*, *40-Cr13*, *12-Cr18-Ni10-Ti*. At the same time, some of the specimens were previously subjected to vacuum cementation. An eutectic *Pb-Bi* with the specified content of *Cr* was used as a transport medium when executing *DSLMMMS*. Metallographic studies were carried out on microsection prepared according to the standard method. Studies to determine the thickness of coatings and its structure were carried out on the *Dura Scan Falcon 500* Microhardness Tester. The elemental composition of the coatings was determined by the method of electron microprobe analysis on a *Tescan Lyra 3* scanning electron microscope with the *Oxford Ultim MAX PCMA* system. **Results and discussion.** As a result of the research, it was revealed that the formation of saturated coatings occurs with *DSLMMMS* and *CDS*. At the same time, the thickness of the coatings and its elemental composition depend on the steel grade and the technology used. After *DSLMMMS* concentration of *Cr* varies from 96.9% to 91.1%. At the same time, the maximum concentration of 96.9% is observed on steel *St3*. After *CDS*, on the surfaces of all steel samples, the concentration of *Cr* decreases in comparison with the coatings obtained by the *DSLMMMS* technology on steels: *St3* from 96.9% to 66.8%; *40-Cr* from 91.1% to 63.18%; *20-Cr13* from 93.18% to 62.54%; *12-Cr18-Ni10-Ti* from 92.92% to 64.77%. The total thickness of diffusion-saturated coatings formed on all the alloys studied ranges from 17 to 17.5 μm.

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Introduction

One of the quite significant reasons of machine parts performance losing is its mechanochemical wear. In this case, the surface layers of parts are subjected to the main destructive effect. In this regard, the use of hardening technologies is one of the most common ways to improve the performance properties of parts [1–4].

Coatings are created on the surface of parts by surface hardening technologies. Usually, coatings base is *Cr*, *Ti*, *W*, *Al*, *Mo*, *Ni* and its chemical compounds with *C* and *N*. Such coatings have a crystalline structure. Coatings make it possible to vary such properties of structural steels surface layers as hardness, corrosion resistance, wear resistance, etc. At the same time, chromium-based coatings should be highlighted

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separately. Chromium is a fairly common metal, has high corrosion resistance, its carbides and nitrides have high microhardness [9–12]. Chromium forms a continuous series of solid solutions with iron and is widely used as an alloying element. In this regard, chromium-based coatings are a fairly common choice for improving the resistance of machine parts to mechanochemical wear.

To apply such coatings, hardening methods such as cladding, flame spraying, electroplating, thermochemical treatment (*TCT*), etc. are used [13–15]. One of the simplest from a technological point of view, industrially implemented and scalable, cost-effective technologies are thermochemical treatment ones.

A method of thermodiffusion chromizing is known, when the surface of a part is coated with a chromium-containing saturating mixture, and then a coated part is subjected to a soaking at 1,000–1,100 °C, followed by cleaning. The disadvantages of this method include a large degree of contamination of the part's surface with the remnants of the saturating mixture and coatings' non-uniformity [16].

Also known is a method of diffusion saturation of structural steels with chromium from molten salts. A common disadvantage of this type of coating is its low adhesion (compared to diffusion coatings) to the base material. Especially if there is a need to form a coating based on carbides or nitrides [17].

One of the promising technologies for forming coatings based on chromium is diffusion saturation from liquid metal medium solutions (*DSLMMMS*) [18–19]. The technology involves saturating the part in a medium of low-melting metals, in which diffusible elements are dissolved in a certain proportion. Coatings are formed due to isothermal selective mass transfer of diffusing elements to the part's surface and subsequent diffusion and/or chemical interaction with the components of the material being coated. Also, in order to obtain the necessary combination of strength, hardness, wear resistance, and corrosion resistance, the technology of complex diffusion alloying (*CDA*) of parts' material surface layers, including *DSLMMMS* and carburizing technologies [20], are promising.

The purpose of the work is to reveal the effect of steel composition on the process of formation and elemental composition of diffusion-saturated surface layers (coatings) based on chromium, as well as to establish differences and regularities in the processes of formation of diffusion-saturated coatings after *DSLMMMS* and *CDS*.

Methods

Experimental studies were carried out, including the combination of *DSLMMMS* with *TCT* technologies, to achieve the purpose. Cylindrical specimens with a diameter of 20 mm and a length of 30 mm subjected to *DSLMMMS*. The specimens were made of carbon and alloy steels: low-carbon *St3*, *20-Cr13*, medium-carbon *40-Cr*, *40-Cr13*, and austenitic *12-Cr18-Ni10-Ti*. Some of the specimens were previously subjected to vacuum carburization.

The coatings were deposited by diffusion alloying using the originally developed *DSLMMMS* technology. The process was carried out in an inert medium (argon). *DSLMMMS* is based on the phenomenon of isothermal, selective transfer of coating elements, dissolved in a fusible melt, to the surface of the part, followed by diffusion interaction of the coating elements with the main material of the part.

DSLMMMS with chromium was carried out at a temperature of 1,025 °C; the soaking time was 5 hours.

Lead-bismuth eutectic melt was used as a technological medium (transport melt). Chromium was supplied in a given amount into the transport melt. *DSLMMMS* was carried out in a device, designed, produced and patented by us. This device provides the possibility of applying coatings in an open bath with a fusible liquid-metal solution in a cyclic mode, and combines the process of *DSLMMMS* with heat treatment.

Before *DSLMMMS* some specimens were subjected to preparatory vacuum carburization at 950 °C during 5 hours.

Studies to determine the thickness of coatings and its structure were carried out on the *Dura Scan Falcon 500* Microhardness Tester. The elemental composition of the coatings was determined by the method of electron microprobe analysis on a *Tescan Lyra 3* scanning electron microscope with the *Oxford Ultim MAX PCMA* system.

Results and discussion

It is found that the coatings formed by the *DSLMMMS* process significantly differ from the *CDA* coatings. *CDA* led to the formation of diffusion-alloyed coatings of much greater thickness, other elemental composition and operational properties, in particular, mechanical and physicochemical. After *DSLMMMS* and *CDA* multilayer coatings, at least – the main layer and transition layers are formed; but coatings structures differs. The micrographs of the surface layers of *St3* and *40-Cr* steels are showed in figure 1.

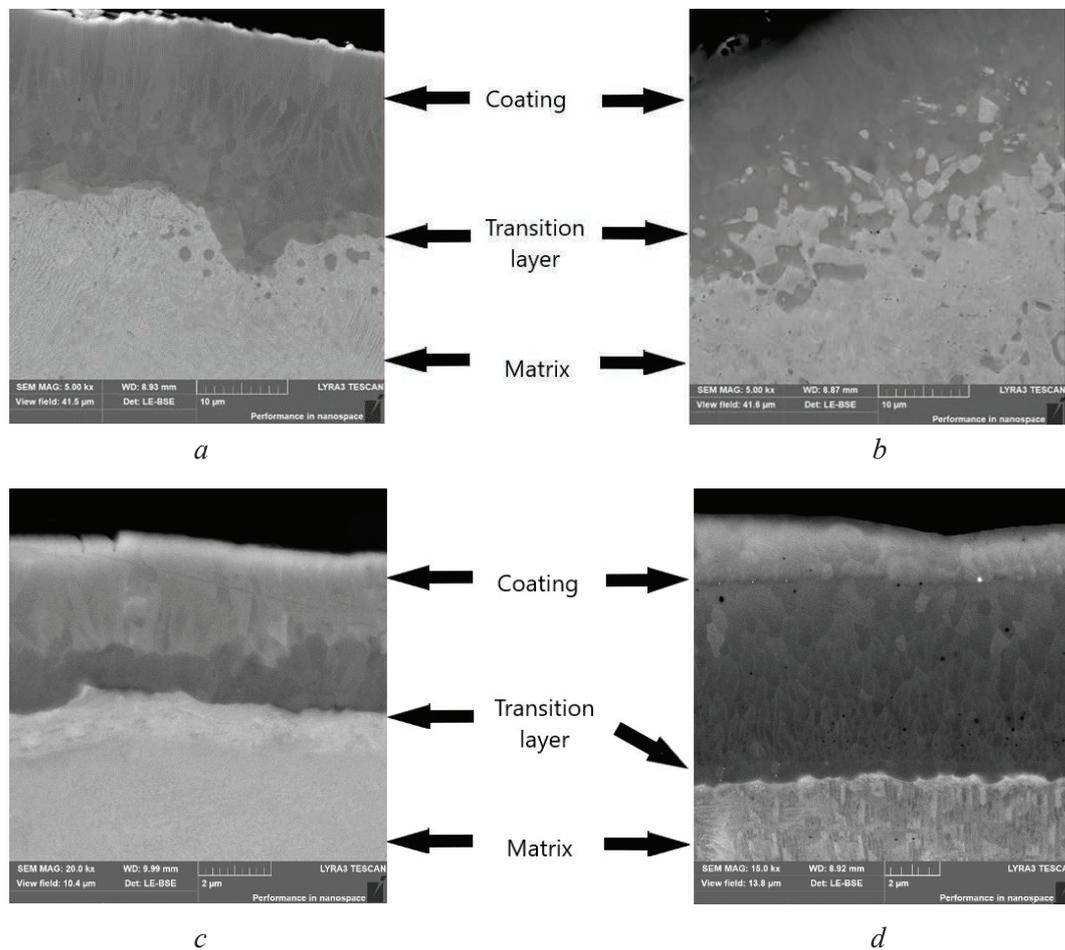


Fig 1. Coating on the surface of steels:
a – *St3 CDS*; *b* – *40-Cr CDS*; *c* – *St3 DSLMMMS*; *d* – *40-Cr DSLMMMS*

Analyzing the data of micrographs, it can be concluded that *TCT* makes it possible to obtain coatings of a greater thickness than *DSLMMMS*.

More details about the thickness and elemental composition of the layers are provided by X-ray microanalysis. The elemental composition and distribution of elements in the coatings being formed using *DSLMMMS* and *TCT* technologies differ in many respects not only in the thickness of the resulting diffusion coatings, but also in the elemental composition, and, consequently, in the properties. The results of electron microprobe analysis made it possible to compare the elemental composition of the coatings, formed by the *DSLMMMS* and *TCT* in order to further reveal the features of the formation of diffusion-alloyed coatings. The diffusion penetration depth of chromium and its concentration in different areas of the formed diffusion-alloyed coating is compared.

The results of X-ray microanalysis of diffusion-alloyed chromium *DSLMMMS* coatings are shown in figure 2.

As follows from the X-ray microanalysis of the chromium distribution in the coating, despite the different composition of the coated steels, the chromium content at the surface layers is from 96.9 to 91.1 %.

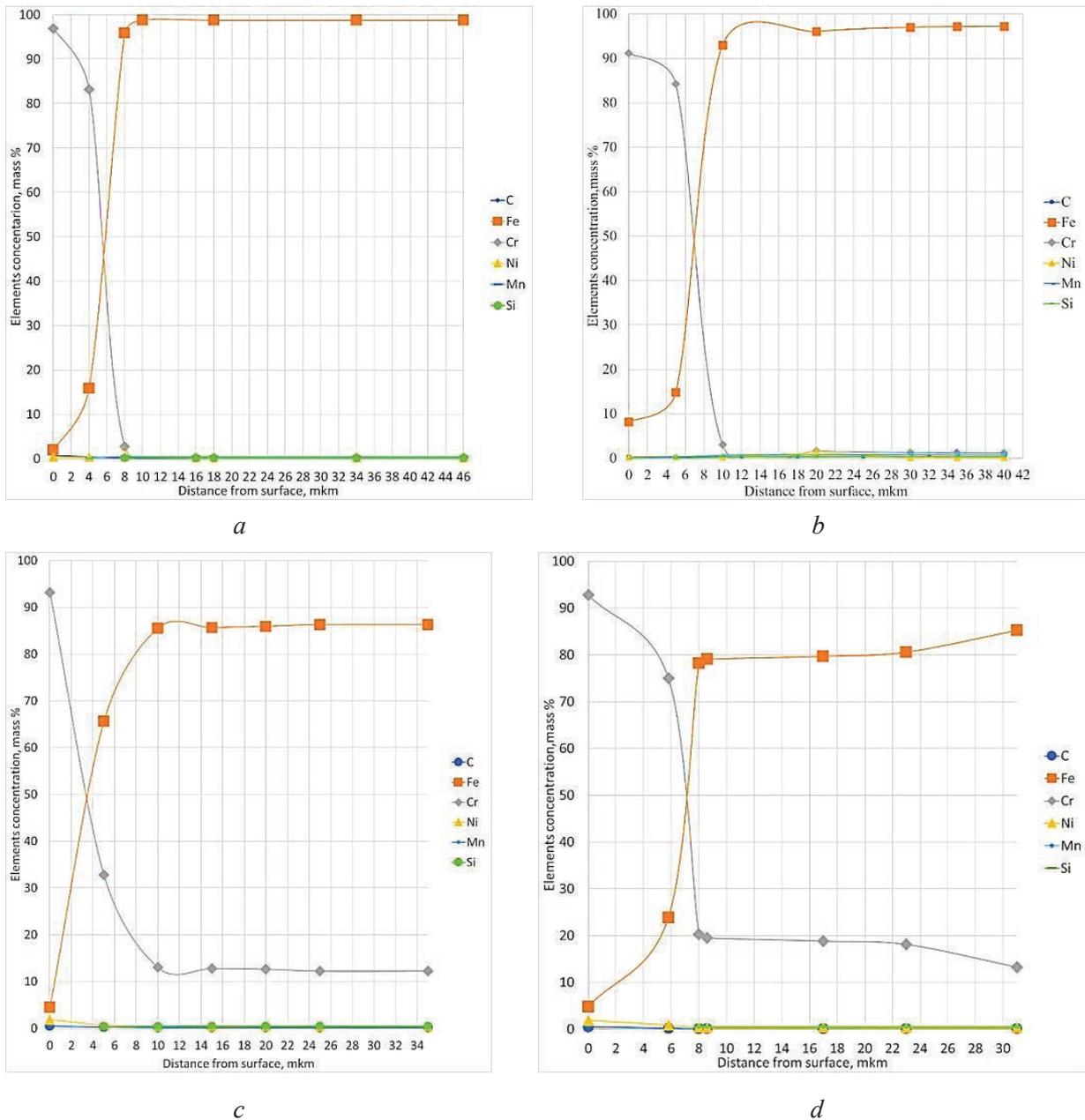


Fig. 2. Results of electron microprobe analysis of diffusion-saturated chromium coatings formed by DSLMMS, temperature 1 025 °C, duration 5 h:
 a – St3; b – 40-Cr; c – 20-Cr13; d – 12-Cr18-Ni10-Ti

The maximum concentration of 96.9 % is observed in unalloyed, low-carbon steel *St3*. On the surface of other coatings, formed on alloy steels *40-Cr*, *20-Cr13*, *12-Cr18-Ni10-Ti*, the concentration of chromium decreases by almost 6 %. Such decrease in the concentration of chromium in the coating indicates the steels' alloying elements influence.

The smallest coating thickness of 8 μm is observed on steels *20-Cr13* and *12-Cr18-Ni10-Ti*. The thickness of the coatings on *40-Cr* and *St3* steels is greater and amounts to 10–12 μm.

There is a dependence of the chromium distribution on the composition of the coated steel, which is especially evident for steel *20-Cr13*. A significantly faster drop of chromium concentration in the coating surface/base material area is observed on *20-Cr13* steel. So the chromium concentration in the amount of 60 % in the coating formed on this steel corresponds to a distance from the surface equal to 3 μm, and in steels *12-Cr18-Ni10-Ti*, *St3*, *40-Cr* 60 % chromium concentration is observed in the coatings of these steels at distances: 6.5, 8 and 10 μm, respectively. This feature during the coating formation can be explained by the presence in steel *20-Cr13* of a sufficiently large amount of chromium not bound by carbon in steel.

The elemental composition of the coated steels has a significant effect on the coating formation by *DSLMMMS*. The formation of coatings is influenced by the content of such elements in the steel being coated, as carbon and chromium. When processing steels *20-Cr13*, *12-Cr18-Ni10-Ti* steels, containing chromium in a concentration of more than 10%, the formation of rather thin coatings is observed. This is due to the peculiarities of the interaction of diffusing chromium and the components of steels that already contain chromium. Thus, the formation of a coating requires the formation of chemical compounds, or solid solutions. In the presence of carbon bound into carbides as well as the presence of solid solutions with the participation of chromium, the chromium concentration gradient at the boundary material being coated/diffusive element decreased, and as a result, the chromium diffusion rate decreases. In steels, containing chromium in small amounts, there is a different pattern of coatings formation. Carbon contained in steel in the form of a solid solution in iron, or in the cementite, actively diffuses to chromium due to the fact that chromium is a strong carbide-forming element, compared with iron, tending to form chromium carbides. The probable diffusion mechanism is grain-boundary diffusion.

The results of X-ray microanalysis of diffusion-alloyed chromium *CDA* coatings are shown in figure 3.

As studies have shown, after *CDA*, under the same modes, the elemental composition and elements distribution in the coatings being formed are determined both by the elemental composition of the alloyed steel and by a significant increase of the carbon concentration in the surface layers of the coated steels from 2.4 % carbon obtained on steel *40-Cr13* to 0.7 % carbon on austenitic steel *12-Cr18-Ni10-Ti* (figure 3).

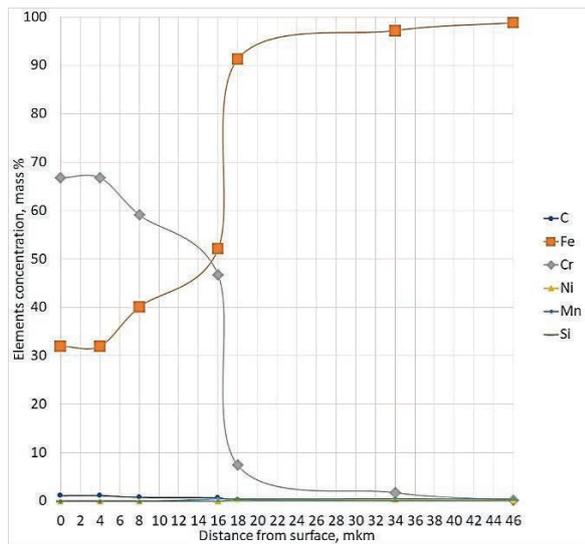
The resulting coatings consist of several layers. Figure 4 shows a multilayer *EDS* image after the *40-Cr* steel, *CDA*. It can be concluded that the coatings consist of several layers. The surface layer is characterized by high chromium content and is formed due to the diffusion of chromium into the surface layers of the material being coated. A transition zone formed between the coating and the base material is characterized by a decrease in the concentration of chromium, an increase in the concentration of iron and the presence of a sublayer with an increased concentration of nickel. The formation of a zone with high nickel content can be explained by the fact that nickel, having a low mutual solubility with chromium carbides formed during *CDA*, is pushed into the transition zone.

As follows from the X-ray microanalysis of the distribution of chromium in the coating, despite the fact that all the steels under study were carburized under the same conditions, the distribution of chromium in the coating is determined by the amount of carbon in the surface layers of the steel being coated. Thus, comparing the percentage of chromium in the coatings obtained after the *CDA* and in the coatings obtained after the *DSLMMMS*, it can be seen that the concentration of chromium is significantly reduced: for *St3* – from 96.9 to 66.8 %; for *40-Cr* – from 91.1 to 63.18 %; for *20-Cr13* – from 93.18 to 62.54 %; for *12-Cr18-Ni10-Ti* – from 92.92 to 64.77 %. Such decrease in the concentration of chromium in the surface layers can be explained by an increased content of carbon in the coatings obtained as a result of carburizing, which binds chromium into carbide compounds.

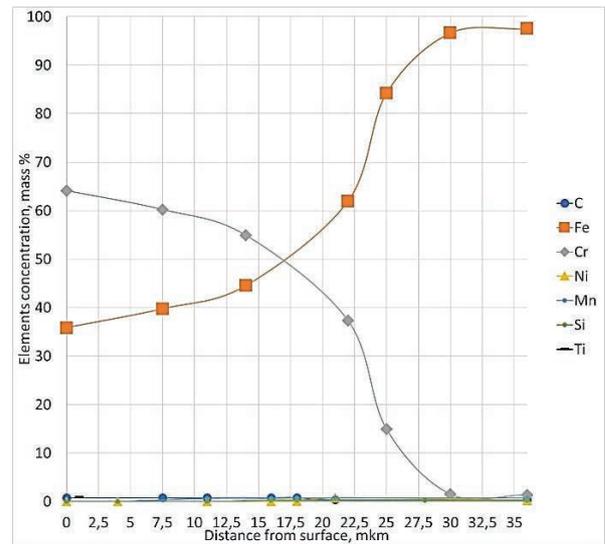
The influence of the composition of steels being coated on the coating formation process is manifested due to the influence of its composition both on the carburizing process and on the *DSLMMMS*. Carburization influence on the composition of the coated steels occurred according to the already sufficiently studied mechanism. But the effect of cementation to the *DSLMMMS* technology is still practically unstudied.

The carbon content after *DSLMMMS*, despite the presence of high-temperature soaking, remains high in the range from 1.2% C to 0.8% C, throughout the entire thickness of the main coating layer. After that, the carbon concentration in the transition layer gradually decreased to the carbon concentration of the steel being coated. Such stability of the carbon concentration in the main layer is explained by the chromium carbides formation in this layer.

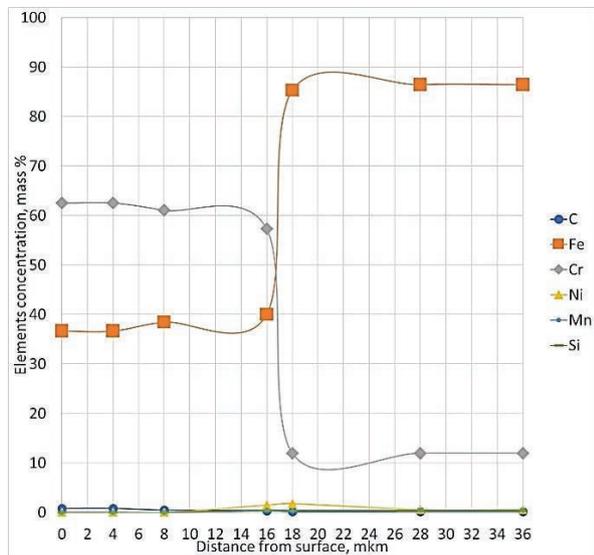
In addition to carbon, the diffusion of chromium into the depth of the coating is also influenced by alloying elements. In the case of steel *20-Cr13* surface *CDA* with chromium, the chromium concentration remains almost constant (more than 60 %) at a depth of 15 μm . With *CDA*, the chromium concentration of more than 60 % in steel *St3* does not exceed a depth of 8 μm , in steel *40-Cr* – 7.5 μm , in steel *40-Cr13* – 7 μm , in steel *12-Cr18-Ni10-Ti* – 6 μm . These phenomena occurring during the formation of diffusion-alloyed chromium coatings on steels containing carbide-forming elements, such as chromium, are explained



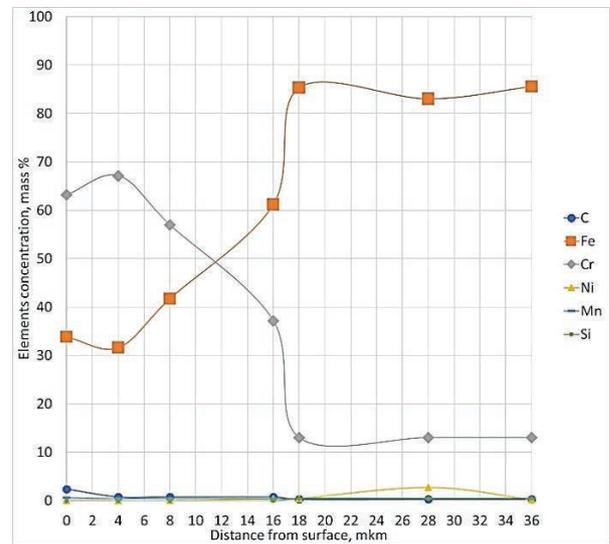
a



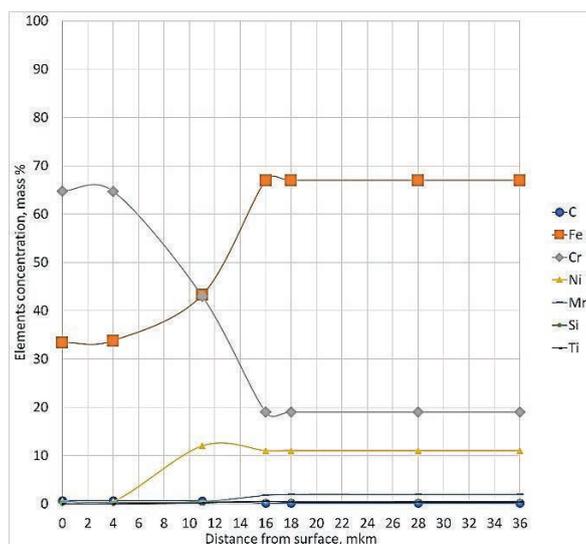
b



c



d



e

Fig. 3. Results of electron microprobe analysis of diffusion-saturated chromium coatings formed using the CDS technology:

a – St3; b – 40-Cr; c – 20-Cr13; d – 40-Cr13; e – 12-Cr18-Ni10-Ti

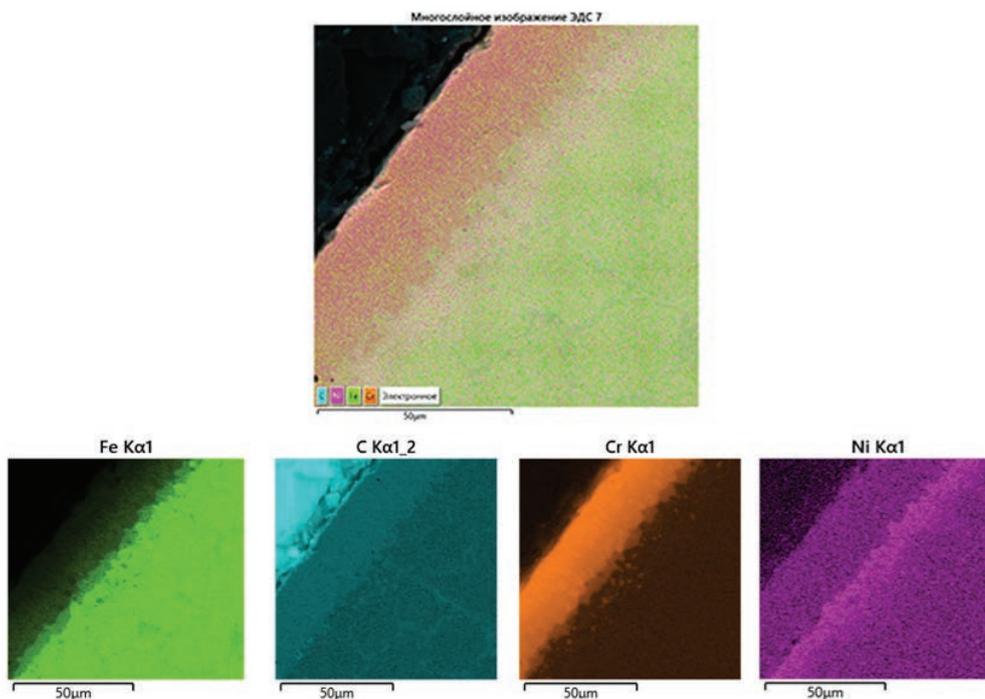


Fig. 4. EDS of 40-Cr steel after CDS

by the formation of chromium carbides diffusing from the process medium, in this case, from a fusible liquid metal solution.

Also, despite the fact that during *CDA*, the diffusion of the chromium alloying element depends on the elemental composition of the steels being coated, the chromium content on the surface has approximately the same percentage. The chromium concentration on the surface of *St3* steel is 66.8 %; on the surface of steel 40-Cr – 64.22 %; on the surface of steel 20-Cr13 – 62.54 %; on the surface of steel 40-Cr13 – 63.18 %; steel 12-Cr18-Ni10-Ti – 64.77 %. This is due to approximately the same carbon concentration in the surface layers of the steels being coated due to the fact that it was subjected to preliminary carburizing under the same conditions. This also explains the reduced chromium content on the surface of the coatings.

There is no effect of the composition of steel after *CDA* on the total thickness of the diffusion-alloyed coating. The total thickness of the coatings formed on all the steels lies in the range from 17 to 17.5 µm.

Conclusions

1. It is established that the coatings formed by the process of *DSLMMMS* differ significantly from the coatings obtained by *CDA*. Under the same chromizing modes, multilayer coatings are formed in the *DSLMMMS* and *CDA* processes, at least the base layer and transition layers, however, the elemental-phase composition, the concentration distribution of alloying elements in the coatings being formed are different.

2. *CDA* led to the formation of coatings of a much greater thickness than *DSLMMMS*. There is no influence of the composition of the steel being coated on the overall thickness of the diffusion-alloyed coating.

3. The chromium concentration in the surface layers of the coating after *DSLMMMS* is quite large for diffusion coatings, and lies, depending on the composition of the steel being coated, in the range from 96.9 to 91.1 % Cr. After *CDA*, the Cr concentration on the surface of the coating is much less and ranges from 66.8 to 62.54 %.

After the *CDA*, under the same conditions, the elemental composition and concentration distribution of elements in the formed coatings are determined both by the elemental composition of the alloyed steel and by a significant increase in the carbon concentration in the surface layers of the steels being coated from 2.4 % carbon obtained on steel 40-Cr13 to 0.7 % carbon obtained on austenitic steel 12-Cr18-Ni10-Ti.

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Conflicts of Interest

The authors declare no conflict of interest.

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