Features and regularities in formation of diffusion nickel-copper coatings on steels in the medium of low-melting liquid-metal solutions

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The paper considers the features and regularities of formation of Ni-Cu based diffusion coatings on the surface of steel products obtained as a result of diffusion metallization from the medium of low-melting liquid metal solutions. It was found out that a solid solution of Ni, Cu, Fe was formed in the main layer of coatings after applying the Ni-Cu coating on armco-iron, steel 20 and tool steel Kh12MF; it was characterized by approximately equal concentration of nickel and copper on the coating surface, it made 55 % Ni and 27 % Cu. As soon as the depth of the base layer increases, concentration of Ni and Cu in it gradually decreases, while the iron content also increases. During formation of Ni–Cu coatings on alloyed steels, selective diffusion of steel alloying elements deep into the coating is observed. It is established that the coatings have two layers – the main and the transition ones. At the same time, the maximal coating thickness constitutes 55 μm at the saturation temperature of 1150 °C and 6 hours duration. It was revealed that the main layer consists of Ni, Cu, Fe solid solution, also contains steel alloying elements and consists of columnar grains elongated in the direction of diffusion of the coating elements, as well as in its surface layer with thickness of about 5 μm. The layer of nano-scale grains with a cross-section size of 80-100 nm is forming. During formation of Ni-Cu based coatings, the phenomenon of displacement of the coating carbon and the steel alloying elements into the transition layer is confirmed; these carbon and steel elements do not interact with the coating elements.

Key words: chemical and thermal treatment, diffusion, coatings, coating formation mechanism, diffusion metallization.
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Introduction

Diffusion metallization as a kind of chemical and thermal treatment is used in machine-building not very widely; it is connected with insufficient information about the processes which are occurring during metallization, as well as with insufficient testing of the technologies. Thereby conduction of fundamental research of the processes and mechanisms of formation of diffusion coatings is rather actual [1-9]. This paper considers the features and regularities of formation of multi-component Ni-Cu based diffusion coatings, providing substantial improvement of operation properties of products which are working at impact and cyclic loads in the aggressive media. The method for diffusion alloying in the medium of low-melting liquid metal solutions (DALMLMS), which was developed by the authors, was used for applying of Ni-Cu coatings [1-4, 9-12]. The passed investigations displayed that this method provides formation of homogenous defect-free coatings on products with extra complicated shape within the range from 10 minutes to 2 hours [10, 12].

The method relates to chemical and thermal treatment, and adsorption and diffusion processes make the base of the mechanism of coating formation [1, 4, 10-12]. However, the processes of mass transfer, activation of coated surface and adsorption have the decisive effect on the mechanisms of formation of diffusion-saturated (alloyed) layers as well as on their elementary, structural and phase composition and operating properties of coated products. It is caused by the fact that DALMLMS method is based on the processes of mass transfer of the elements (with consequent formation of coatings) and elements of coated metal in the liquid metal medium (which is a transporting melt).

Thereby, the aim of this article is description of the features and reveal of the regularities of formation of Ni-Cu based coatings, as well as study of the effect of steel carbon and steel alloying elements, nature of coating elements and conditions of metallization processes on elementary, structural and phase composition and properties of coatings.

Technique of investigations

Investigations for reveal of the features and regularities of formation of Ni-Cu based coatings via DALMLMS method and evaluation of the effect of carbon in steel, physical-chemical properties of coating elements as well as conditions of metallization process on elementary, structural and phase composition and properties of coatings were conducted on the samples manufactured from armco-iron and steels 30KhGSA, 40, 4Kh5MFA, U8, U10, U13A, Kh6VF, Kh12MF as well as R9 and R6M5 high speed steels. Non-carbide forming elements Ni and Cu were used as alloying elements, while Pb and Pb+Bi melts were used as low-melting (transporting) melt.

Formation of diffusion alloying layers on the surface of samples was implemented via their dipping in the bath with low-melting melt and holding there during preset time. The process was conducted in the unit for diffusion alloying of

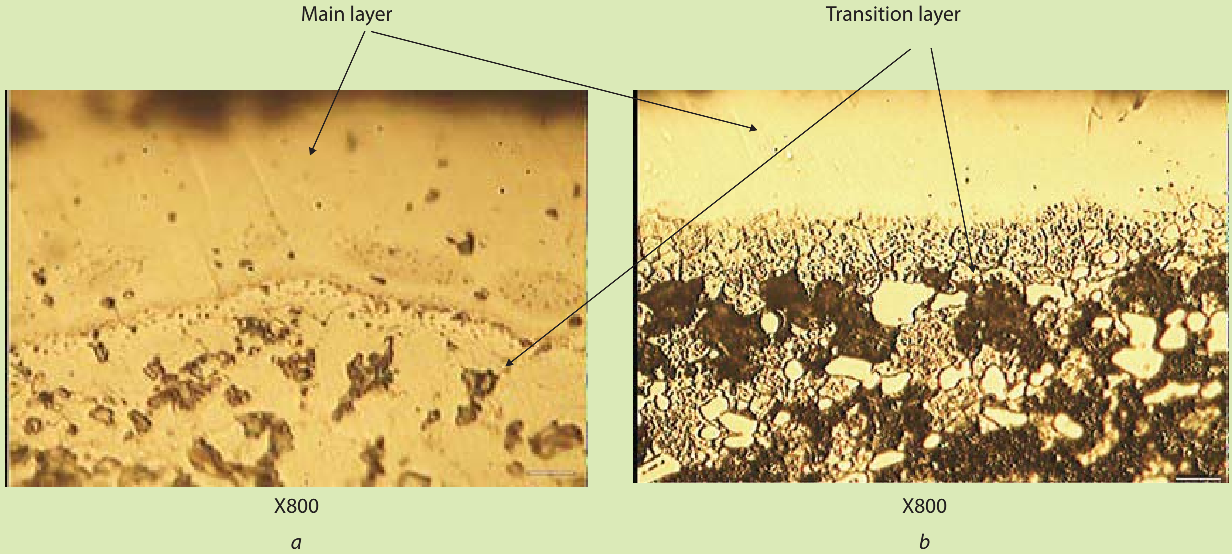

Fig. 1. Electron microscopic image of the structure of Ni-Cu coating:
a – steel 20; *b* – steel Kh12MF

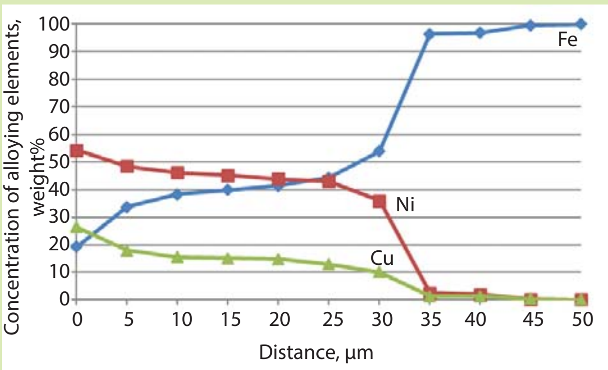

Fig. 2. Distribution of alloying elements in the nickel-copper coating on Armco-iron,
t = 1100 °C, τ = 2 hours, melt Pb + Li + Ni +Cu)

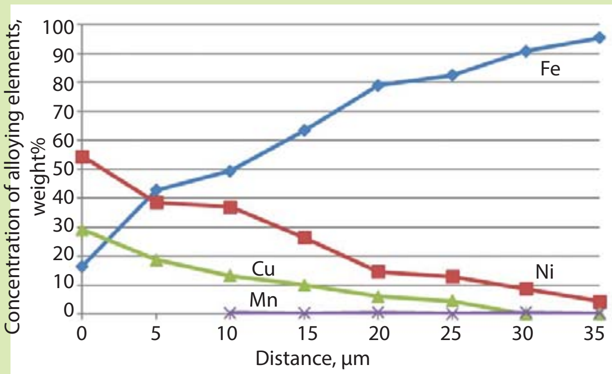

Fig. 3. Distribution of alloying elements in the nickel-copper coating on steel 20,
t = 1100 °C, τ = 2 hours, melt Pb + Li + Ni +Cu)

metal products in the medium of low-melting liquid metal solutions, which had been developed, patented and fabricated by the authors. It allows to provide coatings application in the opened liquid metal bath and consequent heat treatment of the coated material for the components [12].

Application of diffusion coatings was carried out in isothermal cycle and in thermal cycling cycle, within the temperature range 1000-1200 ºC. Holding duration varied from 10 minutes to 10 hours.

The properties of surface layers of samples material, which were formed after DALMLMS process and consequent heat treatment, were examined in accordance with the requirements of GOST 21905 for products after chemical and thermal treatment. These investigations included:

- metallographic investigations were based on qualitative and quantitative metallography (determination and analysis of thickness, structure and building of diffusion coatings and structure of substrate) and were conducted on the research metallographic microscope AxioObferever A1.m of Zeiss company; microhardness was determined on electronic hardness meter Dura Scan 80;

- micro-X-ray spectral analysis was carried out on micro analyzer Camebax micro, which was equipped with energy dispersion spectrometer INCA ENERGY 350, while probe electron energy was 15 keV and determination locality made 2 µm;

- phase composition of coating and coated material was examined via the method of X-ray phase structural analysis using diffractometer DRON-UM2;

- variations of mass, shape and geometric dimensions, surface roughness of the samples and components were undertaken after diffusion metallization using analytical scales HT-84CE, instrumental microscope MIR-2, profilograph of 201 model.

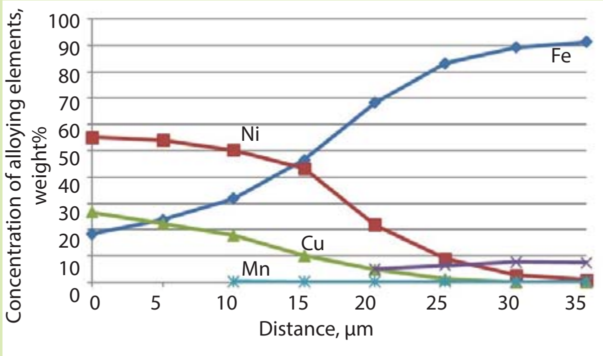

Fig. 4. Distribution of alloying elements in the nickel-copper coating on steel Kh12MF, t = 1100 °C, τ = 2 hours, melt Pb + Li + Ni +Cu)

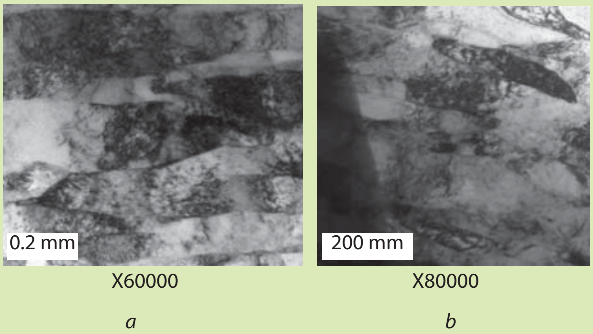

Fig. 5. Electron microscopic analysis of Ni-Cu coating on steel Kh12MF after diffusion metallization, t = 1050 °C, τ = 2 hours

Results and discussion

The conducted investigations displayed that the mechanism of formation of elementary and phase composition in obtained coatings via diffusion alloying of the surface layers of steel products with nickel and copper using DALMLMS technology has its own features and regularities. Dual-component steel alloying with nickel and copper leads to formation of diffusion coatings with two layers. The first main (external) layer consists of solid solution of nickel, iron, copper and alloying elements which are included in steel composition, while the second layer is located between the main layer and substrate material and can be considered as transition one (**Fig. 1**).

The conducted investigations and analysis of structural, phase and elementary coating compositions, presented on the **Fig. 1-4**, showed that solid solution of nickel, copper and iron formed in the main coating layer after application of Ni-Cu coating on armco-iron, steel 20 and tool steel Kh12MF. In this case nickel and copper concentration on the coating surface is approximately equal and makes 55 % Ni, 27 % Cu. As soon as depth of the main layer increases, Ni and Cu concentration in this layer smoothly decreases and Fe content elevates, what provides good compatibility of the coating and substrate. After formation of Ni-Cu coatings in alloyed steels, selective diffusion of steel alloying elements inside the coating is observed. Steel alloying elements, which are forming solid solutions and/or intermetallic compounds with Ni and Cu, diffuse inside the coating, while alloying elements which are not interacting with the coating elements are pushing away in the depth of steel substrate. The results of investigations showed that metallic elements Cr, Mn, Mo, V, W etc. are diffusing inside the coating, while such elements as C, Si etc. are pushing away in the depth of substrate material.

Structural analysis of the main layer (**Fig. 5**) displays that this layer consists of columnar grains extended in the direction of coating elements diffusion. It was established additionally that the layer with nano-scale grains is forming in the surface layer with thickness about 5 μm; size of these grains in their cross-section is 80-100 nm.

The most strong influence of concentrations of carbon and steel alloying elements on structural, phase and elementary coating composition is appeared in the transition later (**Fig. 6**).

Metallographic analysis of transition or so-called interface layer testifies that structural, phase and elementary composition of this layer in the process of coatings formation on carbon non-alloyed steels is characterized by increase of pearlite amount. It can be explained by pushing away of carbon inside the surface layers of steel by diffusing non-carbide forming elements of Ni-Cu coating. When Ni-Cu coatings are formed on alloyed steel, containing carbide-forming elements, such as Cr, Mo, V, W etc., phase composition of transition layer is more various. So, Ni-Cu coating on steel Kh12MF leads to forming of the transition layer containing sorbite, secondary carbides, intermetallic compounds, Ni-Cu-Fe solid solution.

Such complicated composition of the transition layer is forming as a result of meeting the opposite flows of alloying elements and coating elements; deposition of cubic carbide $M_{23}C6$ i.e. $(Cr, Fe, Mo)_{23}C_6$ and σ-phase FeCr with approximately equal content of Fe (50-55 %) and Cr (45-50 %) is observed in the transition layer. Forming of the transition layer is a multi-stage process including formation of atomic segregations, 2D and 3D formations such as Guinier-Preston-Bagaryatskiy zones, different intermediate states of forming phase as well as equilibrial carbide $M_{23}C_6$ and intermetallic compound FeCr. In this case such phases are characterized by distinct separation surface with connecting matrix solid solution. The stage of forming the preliminary extraction of carbide and intermetallic compound phases is accompanied with strengthening of the transition layer; it can be explained by the processes of fixing dislocations and inevitable origination of essential structural stresses, as a result of concentration and dimensional non-conformities on the separation boundary “forming phase – matrix”.

Structural, phase and elementary composition, as well as kinetics of Ni-Cu coatings formation on steel is mainly determined by DALMLMS technological conditions. So, if DALMLMS process is conducted at the temperature

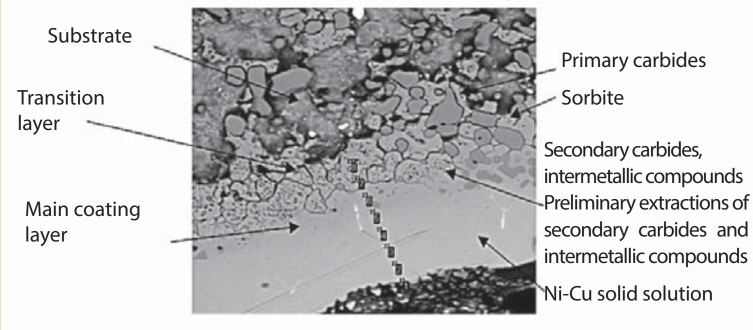

Fig. 6. Electron microscopic image of the structure of Ni-Cu coating on steel Kh12MF

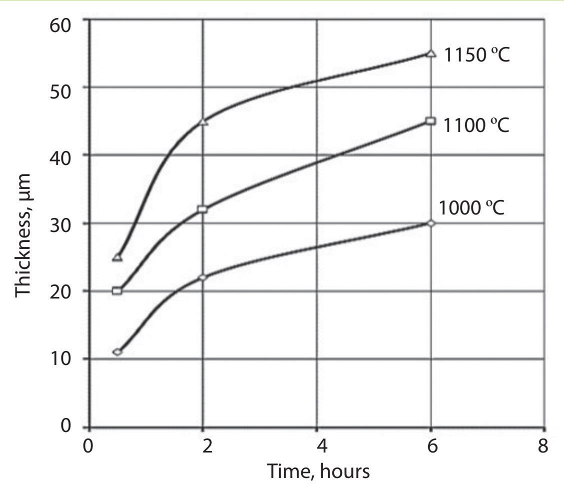

Fig. 7. Dependence between thickness of nickel-copper coatings on steel Kh12MF (from one side) and temperature and duration of saturation process (from other side)

1100 °C, nickel and copper concentration on the surface reaches 44 % and 27 % respectively. Lowering of the process temperature down to 1000 °C leads to increase of copper concentration in the coating up to 58 % and decrease of nickel concentration in the coating down to 22 %. Such relationship of concentrations of the main alloying elements Ni and Cu in the forming coating from the process temperature is very important, because it allows to change the coating composition and, respectively, their properties via variation of DALMLMS process temperatures.

Additionally, kinetics and thickness of the forming coatings depends on the temperature and duration of DALMLMS process during formation of nickel-copper coatings on steels. As soon as the process temperature increases, elevation of growth rate for coatings thickness is observed, and visualization of this process depending on time has parabolic features (**Fig. 7**).

Increase of the process temperature leads also to enlargement of the component dimensions. So, coatings thickness on steel Kh6VF increased from 28 µm to 55 µm after process temperature rise from 1000 °C to 1150 °C with 5 hour holding of the samples in the melt; it led to increase of samples diameters by 28 µm and 55 µm respectively.

Enlargement of the component dimensions during application of nickel-copper coatings is observed even at the temperature 1200 °C, what testifies about absence of reverse isothermal transfer of the elements of coated steel. If we apply nickel-copper coatings on steel R6M5 at the temperature 1200 °C, enlargement of the sample dimensions makes 0.02 mm for the coating thickness 20-22 µm, i.e. enlargement for a side is approximately equal to half of the coating thickness.

Conclusions

1. In the case of dual-component steel alloying by nickel and copper, diffusion coatings consist of main and transition layers. The main layer consists of columnar grains of Ni, Fe and Cu solid solution and steel alloying elements. The zone with thickness 5 µm from nano-scale grains (80-100 nm) is forming on the surface of the main layer.

2. The transition layer on carbon steels is characterized by increased carbon content, what is explained by pushing away of Ni and Cu carbon on alloyed steels containing Cr, Mo, V, W etc. The layer phase composition can contain sorbite, secondary carbides, intermetallic compounds, Ni-Cu-Fe solid solution.

3. When forming Ni-Cu coatings on alloyed steels, selective diffusion of steel alloying elements is observed. The elements which are forming solid solutions and/or intermetallic compounds with Ni and Cu, diffuse inside the coating, while the elements which don't interact with Ni and Cu are pushing away inside the steel substrate.

4. Structural, phase and elementary composition as well as kinetic of formation of Ni-Cu coatings on steels are determined by DALMLMS technological conditions. Copper and nickel content in the surface layer achieve 58 % and 22 % respectively for the process temperature 1000 oC, while at the temperature exceeding 1100 °C nickel concentration increases and copper concentration decreases.

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