Formation mechanism of Ni-Cu-base coatings with diffusion alloying into low-melting liquid metal media solutions

A G Sokolov¹, E E Bobylyov¹* and I D Storogenko¹

¹ Kuban State Technological University, Russia

* ebobylev@mail.ru

Abstract. The paper shows the mechanism and kinetics of the formation of diffusion coatings deposited in the medium of low-melting liquid metal melts depend on the nature of the interaction of the elements forming the coatings with the elements of the coated steel. When applying a coating based on Ni-Cu, the following features were revealed: the presence of a process of carbon displacement by the coating elements deep into the coated material; the practical absence of the influence of the carbon concentration in steel on the coating formation process; the elements of the coated material that do not interact with the coating elements are pushed deep into the product. The paper presents a scheme for the formation of diffusion coatings. Formulas for calculating the diffusion fluxes and the coating thickness are presented.

1. Introduction

Diffusion coatings are such common in modern mechanical engineering [1-10]. At the same time, the diffusion alloying of steels is one of the most promising areas for improving the performance of products [6-14]. This is due to the fact that the surface alloying of products with metals that occurs during diffusion alloying makes it possible to give their surface layers special physical and chemical properties (corrosion resistance, heat resistance) with minimal consumption of alloying elements and while maintaining the resistance of the base to corrosion cracking, to the formation of cracks of the height [12-20]. In addition, diffusion alloying can increase the wear resistance, contact, fatigue strength of products, etc. However, at present, diffusion alloying in mechanical engineering is used very limited, which is due to the lack of technology and insufficient knowledge of the processes occurring during alloying, and their duration. Nevertheless, the studies of the processes and mechanisms of coating formation using the method of diffusion alloying into the medium of low-melting liquid metal solutions (DALMMS) [6, 7, 11, 12, 19, 20] showed that this method simultaneously provides the formation of uniform defect-free coatings on batches of parts of the most complex configuration with a process duration of 10 minutes to 2 hours.

The method of diffusion alloying in a medium of low-melting liquid metal solutions is based on the processes of selective isothermal and (or) thermal transfer of alloying elements dissolved in a low-melting liquid metal medium (transport melt) to the surface of products with subsequent diffusion of alloying elements into the surface layers of the product material [6-12].

This method refers to the methods of chemical-thermal treatment (CTT). It based on the adsorption and diffusion processes common to all types of CTT, which determine the mechanisms of formation of diffusion-saturated layers, their elemental, structural and phase composition and, ultimately, operational properties. At the same time, each of the CTT methods also has features in the mechanism of formation of these layers (diffusion coatings).
The purpose of this article is to describe the features of the mechanism of formation of coatings based on Ni-Cu, as well as the influence of the carbon concentration in steel, the nature of the coating elements and the modes of the alloying process on the composition, structure and properties of coatings.

2. Methods
Studies to assess the effect of DALMMS on the mechanism of coating formation, as well as the effect of the carbon concentration in steel, the nature of the coating elements and the modes of the DALMMS process on the composition, structure and properties of coatings were carried out on the samples of round and rectangular cross-sections made of structural and tool steels with different carbon content and alloying elements, in particular, samples of armco-iron, steels: AISI 1017, AISI D2, AISI 5140. Ni+Cu was used as an alloying element, and Pb+Li, Pb+Bi+Li melts were used as a low-melting (transport) melt.

The formation of diffusion-doped layers on the surfaces of the samples was carried out by immersion and holding the samples for a specified time in a bath with a low-melting melt. The process was carried out in a modernized electric furnace SGV–2,4–2/15–IZ, which allows heating of products in an environment of inert gases [6]. The modernization of the furnace was carried out in order to provide the possibility of coating in an open liquid metal bath and heat treatment of the coated material of the parts.

The diffusion coatings were applied in the temperature range from 1000°C to 1220°C in the isothermal cycle and in the thermal cycling cycle. The duration of exposure varied from 10 minutes to 10 hours.

Studies of the properties of the surface layers of the material of samples formed after the DLMMS study included: metallographic studies—determination of the coating thickness, microhardness and the nature of its changes in the coating, the study of the structural and phase composition of the coating and the coated material; X-ray microanalysis, analysis—study of the concentration distribution of elements in the coating and in the layers under the coating; investigation of the phase composition of the coating and the coated material, as well as studies of changes in mass, shape and geometric dimensions, surface roughness of samples and parts after DLMMS.

Metallographic studies, including qualitative and quantitative metallography—determination and analysis of the thickness, structure and structure of diffusion coatings, as well as the structure of the base, were carried out on the research metallographic microscope AxioObservever A1.m of the company "Zeiss", which has a digital photo and video shooting system.

The microhardness was determined using the DuraScan 80 electronic hardness tester. The microhardness of the coatings, as well as the transition layers and the base material, was measured at a load of 2 to 50 g.

The composition of the coatings and the adjacent areas was determined by X-ray spectral microanalysis using a Camebax micro microanalyzer equipped with an INCA ENERGY 350 energy dispersive spectrometer at the electron energy of the probe of 15 keV. The locality of the determination is 2 microns.

3. Results and discussion
When obtaining coatings based on Ni+Cu by diffusion metallization, if we do not consider the possibility of dissolving the elements of the coated material in the transport melt, the mechanism of coating formation is classical, characteristic of CTT. This mechanism includes the stages of adsorption, diffusion of the coating element and the formation of solid solutions, intermetallides and chemical compounds in the coating, which are the product of the interaction of the coating elements with iron and alloying elements of the coated steel. In the case of two-component alloying with nickel and copper, diffusion coatings are also single-layer coatings consisting of a solid solution of nickel, iron, copper, as well as alloying elements that are part of steel (Figure1).
When forming coatings based on non-carbide-forming elements, the concentration of carbon in steel practically does not affect the kinetics of coating formation and the nature of the concentration distribution of coating elements in it. As follows from the analysis of the graphical dependences of the distribution of alloying elements in the nickel-copper coating, which is shown in Figure 2, the concentration curves of the distribution of nickel and copper in the coatings obtained on armco-iron and on high-carbon steel AISI D2 practically overlap.

Thus, the main features of the formation of coatings based on non-carbide-forming elements are:
- the presence of the process of carbon displacement by the coating elements deep into the coated material;
- the practical absence of the influence of the carbon concentration in the steel on the coating formation process;
- elements of the coated material that do not interact with the coating elements are pushed deep into the product.

The process of DALMMS with Ni-Cu is schematically presented in Figure 3.
In contrast to the processes of diffusion saturation carried out in solid, vapor and gas media, DALMMS is characterized by the presence of reverse diffusion flows in the transport melt of iron (jFe,0) and alloying elements of the product material (jFe,0). The presence of these flows, as well as the high activation capacity of the transport melt inherent in the liquid metal melt, have a significant impact on the mechanisms of adsorption, diffusion, and the kinetics of coating formation.

The high ability of the transport melt to activate the coated surface, the presence of the process of entrainment of elements of the coated material and the resulting diffusion porosity in the base material provide an intensification of adsorption and diffusion processes. This intensification of processes, which is a feature of the technology under consideration, provides a significant reduction in the metallization time, which has a positive effect not only on energy costs, but also reduces the harmful effect of high diffusion metallization temperatures on the structure of the coated material. Working diffusion coatings with the use of this technology can be obtained in 10-30 minutes.

The composition of these steels has a special influence on the process of obtaining coatings on steels. When coating is applied, the coating formation process in most of the transport melts used is inhibited by the shielding effect of the coating. The shielding effect of the coating is manifested by a decrease in the intensity of adsorption processes due to a decrease in the chemical potential difference of the coating element in the transport melt and in the coating itself. As a result of these phenomena, the growth rate of coatings decreases sharply with increasing exposure time. So, if when applying nickel-copper coatings to armco-iron from a lead-lithium melt at a temperature of 1100 °C, a coating with a thickness of 22 microns was formed in the first 30 minutes, then in the next 30 minutes it increased to 30 microns, i.e. by 8 microns, and to increase the coating thickness by another 30 microns, i.e. to 60 microns, an increase in the process duration of up to 8 hours would be required.

When forming coatings based on elements (without considering reverse isothermal transfer), the absence of the process of interaction of carbon of the coated steel with the coating elements allows us to describe accurately describe the processes of transfer and diffusion interaction of the coating elements and the product material using the equations of Fick's laws, which ultimately makes it possible to predict the kinetics of coating formation and their composition.

The kinetics of coating formation, as well as their composition, depend on the ratio of the diffusion fluxes of the coating element to the surface of the product j1.0, the diffusion fluxes of the coating element deep into the product j1.2 and diffusion flows of iron jFe, 2 and alloying elements of the product jFe, 2. The diffusion flow j1. 2 can be determined from the solution of the diffusion equation:

Figure 3. Scheme of the process of forming diffusion coatings with DALMMS

Me1 – coverage elements; Me0 – transport melt; Me2 – material products.

j1.0 – flow coverage element transport in the melt; j1.2 – flow coverage element in the product; jFe,2 – the flow of iron in the product; jFe,0 – flow of iron in the melt; jdiff2 – flow of alloying elements in the product; jdiff0 – flow of alloying elements in the melt transport; jc – carbon in the product.
\[
\frac{\partial n}{\partial T} - D_{1,2} \frac{\partial^2 n}{\partial x^2} = 0
\]

(1)

under boundary and initial conditions

\[
x = 0, t = 0, j_0 - kn = -D_{1,2} \frac{\partial n}{\partial x}, n_1 = 0
\]

(2)

where \(j_0\) and \(kn\) are the forward and reverse chaotic flows of the atoms of the product elements from the melt and into the melt. Under the boundary conditions \(x=0; n=n1, 2\), the diffusion flow of the coating element deep into the product can be determined by the formula [3,5,7]:

\[
j_{1,2} = \frac{n_{1,2}}{\sqrt{10\pi}} \frac{D_{1,2}}{a}
\]

(3)

where \(n_{1,2}\) is the concentration of the coating element in the product material;

\(D_{1,2}\) – the diffusion coefficient of the coating element in the product material;

The diffusion flow of the coating element in the transport melt \(j_{1.0}\) can be represented as the difference between the chaotic flow of the coating element from the melt to the coated surface and the flow back to it. In this case, the diffusion flow can be determined by the formula [3]:

\[
j_{1.0} = \frac{n_{2.0}D_{1.0}}{2\sqrt{D_{2.0}t}} \beta
\]

(4)

where \(n_{2.0}\) is the concentration of the product element in the transport melt;

\(D_{1.0}\) – diffusion coefficient of the coating element in the transport melt;

\(D_{2.0}\) – the diffusion coefficient of the product element in the transport melt;

\(t\) - time of the metallization process;

\[
\beta = \exp \left[ -\frac{\Delta \psi}{kTn_1a} \right] - 1.
\]

(5)

The thickness of the diffusion layer, which is determined by the ratio of the values of the diffusion fluxes \(j_{1.2}/ j_{1.0}\), can be determined by the formula [3]:

\[
h = \frac{n_{2.0}D_{1.0}}{n_{1.1}D_{2.0}} \beta \sqrt{t}
\]

(6)

\(t\) is the time of the DALMMS.

4. Summary

The mechanism of formation of coatings based on Ni+Cu has the following features:

1. The short duration of the delay period of adsorption processes due to the high ability of liquid metal melts to activate the coated surface of the product, which accelerates the process of starting the formation of coatings;
2. The presence of entrainment by the transport melt (saturation medium) of the elements of the coated material, which intensifies the diffusion processes and, thereby, increases the rate of coating formation;

3. The intensification of diffusion processes depends on the parameters and conditions of the saturation process, the degree of doping and the nature of the alloying elements of the coated material, as well as the nature of their interaction with the coating element;

4. The main features of the coating formation are: the presence of the process of carbon displacement by the coating elements deep into the coated material; the practical absence of the influence of the carbon concentration in the steel on the coating formation process; the elements of the coated material that do not interact with the coating elements are pushed deep into the product.

5. References

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