На підставі вимог, що пред'являються до захисних покриттів кристалізаторів, були визначені матеріали псевдосплавів для нанесення покриттів з двох дротів. Одним з дротів є мідний, який забезпечує підтримку достатньої теплопровідності шару, а другий складається з матеріалу, що забезпечує зносостійкість покриття. В якості другого дроту використовувалися дроти NiCr, Mo, Ti і порошковий дріт, що складається з сталевої оболонки та наповнювача – порошку FeB. На підставі розрахункових даних по теплопровідності покриттів з урахуванням коефіцієнтів тепловіддачі, виконана розрахункова оцінка впливу цих покриттів на теплові процеси в кристалізаторі (температуру поверхні стінки, інтенсивність відводу тепла від стінки). Електродуговим напиленням отримані псевдосплавні покриття з рівномірним розподілом компонентів, одним з яких є мідь, твердістю 1320–1460 МПа, а другим – зміцнюючий компонент NiCr, твердістю 2440 МПа; Mo, твердістю 5350 МПа; Ti, твердістю 7540 МПа; FeB, твердістю 7050 МПа.

В результаті вимірювань коефіцієнта термічного розширення покриттів встановлено, що найбільш близьким до коефіцієнта термічного розширення міді є покриття Cu-NiCr, далі Cu-ПП (FeB), Cu-Ti і Cu-Mo. Стійкість псевдосплавних покриттів до абразивного зношування при кімнатній температурі перевищує чисту мідь в 1,4–2,3 рази. Випробування псевдосплавних покриттів на опір зношуванню при нагріванні до 350 °C показали, що зносостійкість покриттів Cu-NiCr і Cu-ПП (FeB) перевищує стійкість чистої міді в 4,5 і 22 рази, відповідно. Гаряча твердість покриття Cu-NiCr в діапазоні температур 20–400 °C перевищує твердість чистої міді в 3 рази

Ключові слова: стінка кристалізатора, електродугове напилення, псвдосплавне покриття, тепловий потік

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DEVELOPMENT OF ELECTRIC-ARC PSEUDOALLOY COATINGS FOR THE STRENGTHENING OF COPPER WALLS OF MOLDS

Yu. Borisov
Doctor of Technical Sciences, Professor, Head of Department*
E-mail: borisov@paton.kiev.ua
N. Vigilianska
Junior Researcher*
E-mail: pewinataliya@gmail.com
I. Demianov
Researcher*
E-mail: demianov0415@gmail.com
O. Grishchenko
Junior Researcher*
E-mail: grinya3679@gmail.com
*Department of protective coatings
E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine
Kazymyra Malevycha str., 11, Kyiv, Ukraine, 03150

1. Introduction

The efficient and economical way to increase the service life of parts, operating in difficult conditions of high temperatures, aggressive environment and mechanical wear, is the creation of strong and wear-resistant layers on the surfaces.

Such parts include elements of metallurgical equipment: molds of continuous casting machines (CCM).

In the technological process of continuous casting of steel, mold has one of the most basic functions – formation of an ingot of the required thickness and strength [1]. The main requirement to the mold is to provide a heat removal from solidification of steel and to produce finally a strong shell of the ingot with a surface that would not be destroyed by the heat of the liquid phase and ferrostatic pressure.

The vast majority of surface defects in the ingot (cracks) originate in the mold. The material of working walls should have high thermal conductivity and wear resistance and should maintain the stability of mechanical properties at elevated temperatures. In addition, the material of walls should not be wetted by molten steel and have a harmful effect on the surface of the workpiece as a result of interaction with it at high temperatures [2].

At the present time, to manufacture working walls of molds, copper and copper-based alloys CuAg, CuZrCr, CuNiBe and others are used [3].

When metal moves through the mold in the area of interaction of surfaces, a considerable wear of copper occurs, especially of side walls, which leads to changes in the original geometry of the mold. In addition, the temperature of the wall surface during casting can reach 300–400 °C, and at this temperature, the softening of copper occurs, which reduces its strength properties. Therefore, the service life of pure copper under the mold conditions is clearly insufficient. Copper-based alloys, as compared to copper, have higher strength and softening temperature. However, their thermal conductivity is lower than that of copper, and the manufacture of special alloys is rather expensive and labor-consuming.

The problem of increasing the strength of copper walls of molds is relevant in the area of continuous casting for improvement of CCM performance. An effective way to increase the strength of molds is applying protective coatings. In the world practice, the methods of applying protective coatings are actively developed using more wear-resistant and heat-resistant materials, which do not have a harmful effect on the quality of steel ingot.

2. Literature review and problem statement

The main reasons for the use of mold coatings are increasing the service life of molds (increasing the wear resistance of walls) and the improvement of the quality of workpieces (prevention of defects). The side effects of applying protective coatings include reducing the heat transfer and increasing the wall temperature during casting.

The standard industrial solution to increase the service life of copper walls of molds, which for many years have been used in this industry, is to apply wear-resistant coatings of chromium, nickel and its alloys by the galvanic method [4–6].

The chromium plating allows increasing the hardness of working surfaces of walls of molds, which facilitates increasing the wear resistance, eliminates the penetration of copper into the workpiece and, thus, eliminates the formation of spider-like cracks. The coating is applied either directly on copper walls or on a galvanic nickel coating. However, the chromium coating is not sufficiently effective for CCM molds. Along with a high hardness (from 800 to 1000 HV), it also has a high brittleness and a tendency to spontaneous microcracking because of a high level of inner tensile residual stresses. Therefore, the coating is limited to a thickness of the applied layer of 0.1 mm. With such a thickness of the coating, it is easily damaged, especially during passing the cooled ends of the ingot. At a greater coating thickness due to a large difference in the coefficient of thermal expansion (CTE) of copper and chromium, the chromium layer can be delaminated. A thin layer of chromium is currently used on the mold walls to reduce friction, to protect against initial wear during starting and serves as a visible wear indicator [7].

Nickel electroplating is the most common protective coating used today in the steel industry. It provides a good adhesion to copper, the service life of molds increases two or three times, as far as the wear decreases due to a higher hardness of nickel (175–250 HV) as compared to copper [8]. In addition, the investigations of the influence of Ni-coating of CCM mold walls on the number of surface defects in slabs showed that the use of nickel-plated walls prevents the formation of star-shaped cracks in workpieces [9]. However, the thermal conductivity of these coatings is 8 times lower than the thermal conductivity of copper, and this can lead to a significant decrease in the rate of steel solidification and the formation of an insufficiently strong crust of the ingot.

It should be noted that in the upper part of the mold, the thermal conductivity of walls plays a big role, since in this region the steel is in a molten state and the tendency to wear is negligible. Whereas at the lower part of the mold, the formed solid steel shell has a high hardness and therefore, the increased resistance of mold walls to wear is required and the thermal conductivity of walls is less significant. Therefore, in some cases, the coating is produced alternating in the height of the mold: thinner in the area of the meniscus and thicker in the lower part of the wall [10]. The thickness of the coating varies from 0.5 to 3 mm. Also, to reduce the cost of coatings only the lower part of the mold wall of 2–6 mm thickness is covered with nickel.

The disadvantage in applying nickel coatings is an increase in the wall temperature by ~15 °C/mm Ni and a decrease in the heat transfer by ~1.5 %/mm Ni [7].

The alternative coatings of pure nickel include the coatings of nickel alloys. The hardness of Ni-Co coatings can vary from 200 to 400 HV depending on the composition, due to which it is possible to increase the wear resistance by 30–40 % [11]. At the same time, the coatings of these alloys are more expensive and the specific thermal conductivity is lower than that for pure nickel, which plays an important role in the heat removal during casting. Thus, for example, Ni-Fe coating (300–450 HV) reduces the thermal conductivity by approximately 4.5 % in the upper part of the working area of the mold at a thickness of the coating being 0.5 mm and up to 17 % in the lower part at a thickness of 1.5 mm [12].

The company "KM Europe Metal" (Germany) uses galvanized coatings of nickel (220 HV, 90 W/m·K), nickel alloys (400–500 HV, 80-86 W/m·K) and chromium (900 HV, 72 W/m·K) [13]. These coatings allow increasing the wear resistance of copper walls several times and improve the surface quality of continuous-cast slabs on the mesh- and spider-shaped cracks.

The method of applying galvanic coatings has several drawbacks. The process of galvanizing occurs extremely slowly and requires the organization of a special area with treatment facilities to apply the coating, which is not always expedient for a metallurgical plant.

The industrial application of gas-thermal spraying in the manufacture of CCM molds with coatings was carried out by the company Mishima Kosan (Japan), beginning from 1990 [14]. To apply coatings on walls of molds, the high-velocity oxygen fuel (HVOF) spraying is used. It provides an opportunity to produce dense coatings of a stable quality. The hardness of Ni-Cr gas-thermal coating is 600 HV, which is 3 times higher than the hardness of Ni electroplating (200 HV) and the hardness of copper (80 HV). As to the value of thermal conductivity, Ni-Cr coating is 7.2 times inferior to the galvanic coating and 33 times inferior to the thermal conductivity of copper.

The complex of measures to increase the resistance of molds using the technology of Mishima Kosan (Japan) provided an increase in the service life of the mold 20 times as compared to walls without a coating and 6 times as compared to Co-Ni-plating. The complex includes a combination of galvanic Co-Ni coating on a wide wall with the spraying of NiCr coating by the method of high-velocity oxygen fuel spraying on a narrow wall of slab molds. A high wear resistance was confirmed by numerous industrial tests at metallurgical plants in Japan and Russia [15]. The operating time of the mold with NiCr gas-thermal coating is 3,984 melts (600 thous. tons of metal). The strength of narrow and wide walls in molds with coatings produced by high-velocity oxygen fuel spraying from the composites based on Ni-Cr, hardened with Cr, W carbides increased 3–12 times as compared to the base variant – walls with wear-resistant galvanic coating [16].

The company "KM Europe Metal" (Germany) [13] offers its customers the metal-ceramic coatings (WC-Co), produced by high-velocity oxygen fuel spraying (hardness is 700–1,200 HV, thermal conductivity is 30 W/m·K). The use of these coatings allows achieving a significant (several times) increase in the service life of mold plates coated applying this method with a narrow end as compared to the plates coated with a layer of nickel.

The spraying of ceramic coatings with high hardness (700–1,600 HV) using the HVOF method can significantly increase the service life of molds, the strength of which can reach 1,200 melts [17]. The coating is applied to both narrow and wide walls. Due to a difference in the CTE of the ceramic coating and the copper wall, a sublayer is applied to prevent the delamination of the coating during operation. The disadvantages of ceramic coatings are their high brittleness, which can lead to cracking and chipping of the coating. In addition, the relation between the cost of the coating and its strength indicates its economic inefficiency.

The technologies were developed to reduce gaps between the walls and decrease the wear of the working surface of narrow walls of thick-walled molds with their disassembly and without disassembly by electric-arc spraying [18]. As the materials for reducing the gap between the walls, aluminum or copper-nickel alloy were used. To increase wear resistance, the steels Kh18N10T, 40Kh13, as well as a copper-nickel alloy with a sublayer of nickel are used. The developed technologies passed an experimental and industrial testing at metallurgical plants in Russia, which showed an increase in the strength of molds by 25–30 % [19].

In the work [20], the possibility of using wear-resistant nichrome coating of 0.5–0.6 mm thickness is shown produced by electric-arc spraying method to increase the strength of narrow walls of thick-walled CCM molds. To increase the adhesion strength of the coating with the copper base, an aluminum sublayer is applied [21].

The disadvantages of the existing coatings used to increase the resistance of copper walls of CCM molds is the deterioration of heat removal from the mold wall due to the insufficient thermal conductivity of these coatings. This can lead to a decrease in the CCM productivity and the required quality of continuously cast billets because of violation of the conditions for their formation. The use of coatings having an increased wear resistance without a significant reduction in thermal conductivity will increase the strength of walls of molds and provide the conditions for the formation of a high-quality structure of the ingot. The use of the electric-arc spraying method for applying such coatings instead of galvanic methods will reduce the negative impact on the environment.

3. The aim and objectives of the study

The aim of the work is the development of pseudoalloy coatings with the use of the electric-arc spraying method, providing an increased strength of CCM mold walls.

To achieve this aim, it is necessary to accomplish the following tasks:

– to select the compositions of pseudoalloy coatings and to assess the influence of these coatings on thermal processes in CCM molds;

– to produce pseudoalloy coatings by electric-arc spraying and to investigate the structure and phase composition of the produced coatings;

– to investigate the properties of pseudoalloy coatings (CTE, microhardness and wear resistance at room and elevated temperatures).

4. Materials for spraying of pseudoalloy coatings, methods for investigation of properties of coatings

4. 1. Materials and equipment for spraying of pseudoalloy coatings

The choice of materials for producing pseudoalloy coatings on the walls of molds was based on the analysis of the process of CCM operation and the requirements for protective coatings of copper walls. The main requirements for the coatings, in addition to wear resistance in the conditions of abrasion during the movement of the ingot, include providing the necessary thermal conductivity of the coating, the thickness of the coating of 1-3 mm and the homogeneity of the coating properties over the entire area affecting the quality of the ingot.

For spraying of pseudoalloy coatings, Cu, NiCr, Ti wires and flux-cored wire containing FeB of 2 mm diameter and Mo wire of 1.6 mm diameter were used. The pseudoalloy coatings (Cu-NiCr, Cu-Mo, Cu-Ti, Cu-FCW (FeB)) were produced by the simultaneous spraying of dissimilar wires with an electric-arc metallizer EM-14M.

4. 2. Calculation and theoretical analysis of the influence of coatings on thermal processes in molds

In the mold, it is necessary to remove such amount of heat that would provide the formation of a solid shell of the ingot of a certain thickness to withstand the ferrostatic pressure of a liquid metal in the process of casting and withdrawing of the billet from the mold. The processes of heat transfer in the mold affect the beginning of the formation of the solid shell of the continuous ingot and the possibility of various defects in the ingot and the mold wall. The determination of the influence of pseudoalloy coatings on the surface temperature of the working wall and on the heat flux passing through the mold was carried out according to the procedure described in the work [22].

The evaluation of thermal conductivity of pseudoalloy coatings (λ_c, W/m·°C) was carried out using the additivity equation [23], which relates the properties of the coating to the properties of components through the mass concentration:

$$\lambda_c = \lambda_1 \cdot m_1 + \lambda_2 \cdot m_2, \tag{1}$$

where λ_1 and λ_2 are the thermal conductivity of the pseudoalloy coating components, W/m·°C; m_1 and m_2 is the mass concentration, %.

The total coefficient of heat transfer in the upper part (in the region of the meniscus) of the mold (K_l, W/m^2·°C) was determined by the formula:

$$K_l = \frac{1}{\frac{1}{\beta_l} + \frac{\delta_{cop}}{\lambda_{cop}} + \frac{\delta_c}{\lambda_c} + \frac{1}{\alpha_w}}, \tag{2}$$

where β_l is the effective heat transfer coefficient, 2,093 W/m^2·°C; δ_{cop} is the thickness of the copper wall of the mold, 0.045 m; δ_c is the coating thickness, m; λ_{cop} is the thermal conductivity of the copper wall, 395 W/m·°C; α_w is the coefficient of heat transfer from the copper wall to the cooling water, 19,771 W/m^2·°C.

To calculate the temperature of the outer wall surface in the upper part of the mold (T_1, °C) the following formula was used:

$$T_1 = T_l - \frac{(T_l - T_w)\cdot K_l}{\beta_l}, \quad (3)$$

where T_1 and T_w are the temperature of liquid metal and cooling water, 1,550 and 20 °C, respectively.

The maximum heat flux density through the mold wall at the level of meniscus q (W/m^2) was determined by the expression:

$$q = \frac{T_1 - T_w}{\frac{\delta_{cop}}{\lambda_{cop}} + \frac{\delta_c}{\lambda_c} + \frac{1}{\alpha_w}}. \quad (4)$$

These calculations allow establishing the dependence of the heat transfer process on the composition and thickness of coatings.

4. 3. Investigation of the structure, phase composition and microhardness of pseudoalloy coatings

During investigations, a complex procedure was used, including metallography – the optical microscope Neofot-32 (Germany) with the attachment for digital photography; durometric analysis – durometer PMT-3 (USSR) at a load of 0.49 and 2.94 N; X-ray structural phase analysis (RSFA). The X-ray investigation was carried out in the monochromatic CuKα – radiation in the diffractometer DRON-UM1 (USSR).

4. 4. Measuring the coefficient of thermal expansion of pseudoalloy coatings

The coefficient of thermal expansion is an important characteristic, which affects the development of inner residual stresses in the system "coating-copper". The greater the difference in the CTE of the coating and the base, the higher the risk of cracks in the coating or its delamination.

The coefficient of thermal expansion of coatings was determined using a high-speed quartz dilatometer for measuring elongation in the cross-section of the specimen in accordance with GOST EN 13471-2011. The average coefficient of thermal expansion (α, °C^{-1}) in the temperature range of 20–400 °C was determined by the formula:

$$\alpha = \frac{\Delta L}{k \cdot b \cdot \Delta T},$$

where ΔL is the deviation of the curve on the elongation scale during heating in the temperature range of 20–400 °C; k is the magnification factor on the elongation scale, 1,645 times; b is the width (base) of the specimen (nominal size 6 mm); ΔT is the temperature range, 380 °C.

4. 5. Determination of wear resistance of pseudoalloy coatings at room and elevated temperatures

The abrasive wear resistance of pseudoalloy coatings at a room temperature was investigated using the installation IZA-1, which simulates the wear process with a fixed abrasive according to GOST 17367-71. The tests were carried out at a friction surface load of 3.92; 9.8; 19.6; 29.4 N; the reference is copper of grade M1. During testing, the coefficients of relative weight (*Ew*) and linear (*El*) wear resistance of coatings were determined.

The tests on wear resistance at elevated temperatures were carried out during friction of the specimen with the coating against the counterbody of steel 45 of hardness 40 HRC, heated to the temperature of 350 °C, which corresponds to the operating temperature of the copper wall of the CCM mold. The load on the specimen was 3 kg (linear load was 12 kg). At the end of the tests, the specimens and the counterbody were weighed and the weight wear was determined.

4. 6. Determination of hot hardness

To determine the hot hardness, the method of static indentation of a diamond indenter in the form of a regular tetrahedral pyramid was used in the temperature range of 20–400 °C (the step is 100 °C) in the vacuum installation VIM-1. The measurement of hardness prints was carried out in the metallographic microscope MIM-10 using a digital camera with the subsequent computer processing of information.

5. Results of the estimation of the effect of pseudoalloy coatings on the thermal processes in the mold and investigations of the properties of coatings

To produce protective coatings, which provide a combination of high thermal conductivity and wear resistance, the materials of pseudoalloys were determined for applying coatings from two wires using the electric-arc method. One of the wires is copper, which provides maintaining a sufficient thermal conductivity of the layer, and the second one consists of a material which provides wear resistance of the coating. As the second wire, the wires NiCr, Mo, Ti and the flux-cored wire (FCW) were used, consisting of a steel sheath and a filler – FeB powder. The choice of strengthening components was based on their increased hardness and strength properties (2–5 times) with respect to copper. In addition, NiCr is a heat-resistant material and the CTE is the closest to Cu; Mo has a high strength in melts of ferrous metals and an increased thermal conductivity (162 W/m·K); FeB has characteristic antifriction properties.

The estimation of the influence of the thickness and type of coating on thermal processes in molds was carried out for pseudo-alloy coatings Cu-NiCr, Cu-Mo, Cu-Ti, Cu-FCW (FeB) at a thickness of 1–3 mm. The calculation was carried out in a general form for a flat wall of the mold without taking into account the channels for cooling water. The results were compared with the calculation values for the copper wall of the mold without a coating, with galvanic nickel coating, since it is most often used for protection of molds and NiCr gas-thermal coating.

The calculation values of thermal conductivity of pseudoalloy coatings Cu-NiCr, Cu-Mo, Cu-Ti and Cu-FCW (FeB) are given in Table 1.

Table 1

Thermal conductivity of pseudoalloy coatings

Coating	Mass content of components in the coating, %	λ_c, W/m·°C
Cu–NiCr	Cu – 52; NiCr – 48	213
Cu–Mo	Cu – 58; Mo – 42	297
Cu–Ti	Cu – 67; Ti – 33	271
Cu–FCW(FeB)	Cu – 54; Fe – 35; FeB – 11	241

The results of calculating the total coefficient of heat transfer in the upper part of the mold, depending on the thickness and type of coating, are shown in Fig. 1.

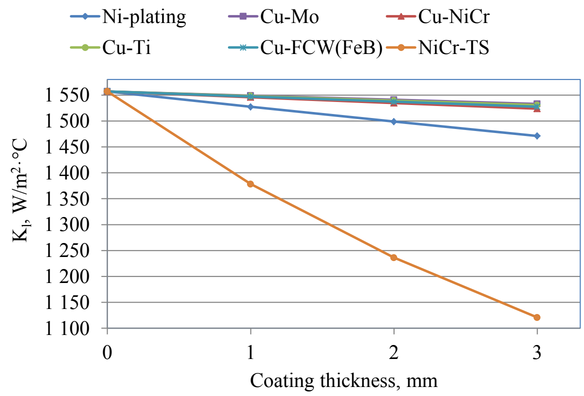

Fig. 1. Dependence of the heat transfer coefficient (K_l) in the upper part of the mold on the thickness and type of coating

The value of the temperature of the outer wall in the upper part of the mold, depending on the thickness and type of coating, is shown in Fig. 2.

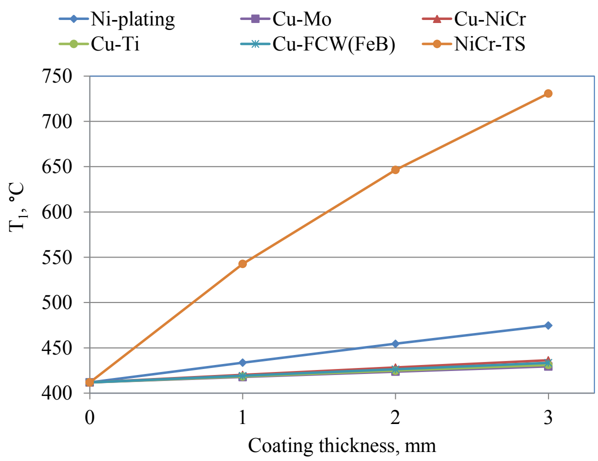

Fig. 2. Value of the temperature of the outer wall of the mold (T_1) depending on the thickness and type of coating

Table 2 shows the values of the heat flux through the wall of the mold, calculated by this procedure.

Table 2

Values of the heat flux through the wall of the mold with the coating

Type of coating	Heat flux through the mold wall, $q \cdot 10^6$, W/m^2 at the coating thickness $\delta_c \cdot 10^{-3}$, m		
	1	2	3
Ni-galv.	2.34	2.29	2.25
Cu-Mo	2.37	2.36	2.35
Cu-NiCr	2.37	2.35	2.33
Cu-Ti	2.37	2.36	2.34
Cu-FCW(FeB)	2.37	2.35	2.34
NiCr-TS	2.11	1.89	1.71
Without coating	2.38		

For investigations of the microstructure, the electric-arc spraying on copper specimens of pseudoalloy coatings Cu-NiCr, Cu-Mo, Cu-Ti, Cu-FCW (FeB) of up to 6 mm thickness was carried out. The microstructure of pseudoalloy coatings is shown in Fig. 3.

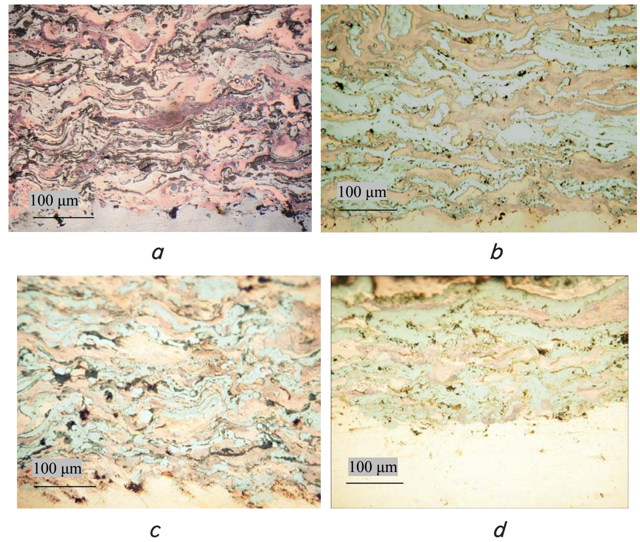

Fig. 3. Microstructure of electric-arc pseudoalloy coatings: *a* – Cu-NiCr; *b* – Cu-Mo; *c* – Cu-Ti; *d* – Cu-FCW(FeB)

Pseudoalloy coatings have a heterogeneous lamellar structure, are adjacent densely to the copper base and uniform across the thickness. In the coatings, thin oxide interlayers along the boundaries of lamellas and tiny round particles (1–3 µm) of oxides across the whole cross-section of coatings are observed. According to the data of X-ray spectroscopic fluorescence analysis (RSFA), during the process of applying coatings some oxidation of coating components takes place. During spraying of the coating Cu-Mo, only the copper component is oxidized forming Cu_2O oxide (Fig. 4, *b*). During spraying of coatings Cu-NiCr and Cu-Ti, both coatings are oxidized, resulting in the formation of copper oxides Cu_2O, spinel $NiCr_2O_4$ (Fig. 4, *a*) and titanium oxide TiO_2 (Fig. 4, *c*). In case of spraying the coating Cu-FCW (FeB), the oxidation of copper does not occur and only the second component of the heterogeneous coating is oxidized. In this case, it is Fe from the sheath of the flux-cored wire (Fig. 4, *d*).

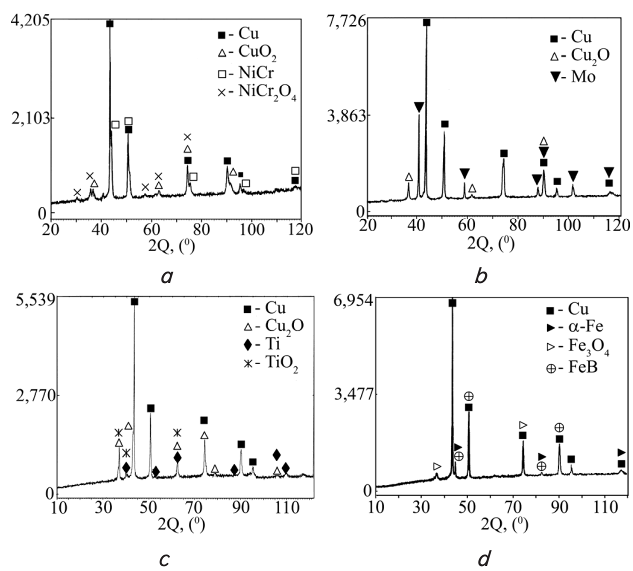

Fig. 4. X-ray patterns of electric-arc pseudoalloy coatings: *a* – Cu-NiCr, *b* – Cu-Mo, *c* – Cu-Ti, *d* – Cu-FCW(FeB)

Table 3 shows the results of measuring the microhardness of pseudoalloy coatings.

Table 3

Microhardness of electric-arc pseudoalloy coatings

Type of coating	Microhardness of the structural components of the coating $HV_{0.49}$, MPa	Average microhardness of the coating $HV_{2.94}$, MPa
Cu-NiCr	Cu – 1,390±190; NiCr – 2,440±240	1,850±300
Cu-Mo	Cu – 1,460±260; Mo – 5,350±240	1,890±230
Cu-Ti	Cu – 1,320±190; Ti – 7,540±200	2,750±1,130
Cu-FCW(FeB)	Cu – 1,450±280; FeB – 7,050±500	2,490±760

Table 4 shows the values of the CTE of pseudoalloy coatings Cu-NiCr, Cu-Mo, Cu-Ti and Cu-FCW (FeB) (×10^6, °C^{-1}). For comparison, the CTE of copper is also given, determined experimentally by the same method.

Table 4

Results of measuring the coefficient of thermal expansion for electric-arc pseudoalloy coatings

Type of coating	CTE ×10^6, °C^{-1}	Difference between the CTE of pure copper and the coating ×10^6, °C^{-1}
Cu	15.1	–
Cu-NiCr	14.5	0.6
Cu-Mo	6.65	8.45
Cu-Ti	11.8	3.3
Cu-FCW(FeB)	13.5	1.6

The results of tests of coatings Cu-NiCr, Cu-Mo, Cu-Ti and Cu-FeB for abrasive wear resistance at a room temperature are given in Table 5.

Table 5

Relative abrasive wear resistance of pseudoalloy coatings at a room temperature

Type of coating	Coefficient of relative weight wear resistance – E_w at the load on specimens, N				Coefficient of relative linear wear resistance – E_l at the load on specimens, N			
	3.92	9.8	19.6	22.4	3.92	9.8	19.6	22.4
Cu-NiCr	1.69	1.55	1.29	1.47	1.64	1.50	1.25	1.43
Cu-Mo	–	1.24	1.32	1.38	–	1.32	1.40	1.46
Cu-Ti	–	3.175	2.95	2.4	–	2.39	2.22	1.805
Cu-FCW(FeB)	1.91	–	1.93	3.40	1.80	–	1.82	3.21

Fig. 5 shows a histogram of the results of testing coatings Cu-NiCr, Cu-FCW (FeB) and pure copper for wear at elevated temperature.

The results of measuring the hardness of Cu-NiCr coating at an elevated temperature (hot hardness) are presented in Table 6. The data are presented as the average of 10–12 measurements and the scatter of values (±S) is indicated.

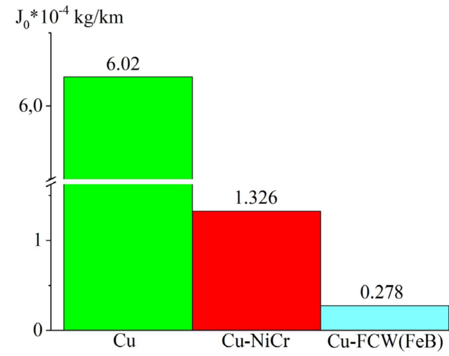

Fig. 5. Results of tests of pseudoalloy coatings for wear at the temperature of (J_o) as compared to pure copper

Table 6

Hardness of Cu-NiCr coating at different temperatures

t, °C	HV, MPa	±S, MPa
20	2,120	72
125	2,000	56
205	1,720	82
307	1,350	89
410	1,200	84

Fig. 6 shows a diagram of the change in the hot hardness of the Cu-NiCr pseudoalloy coating with the temperature change.

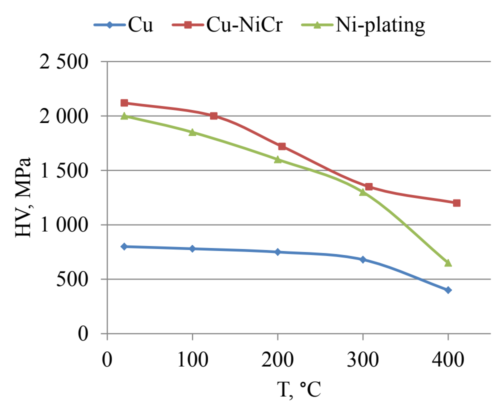

Fig. 6. Dependence of the hot hardness (HV) of pure copper, Ni-plating and pseudoalloy coating of Cu-NiCr on the temperature (T)

For comparison, the diagram shows the values of the hot hardness of pure copper and Ni-plating [16].

6. Discussion of the results of the evaluation of thermal energy of the mold and investigations of the properties of coatings

It follows from the results of calculations of thermal processes in the mold, that pseudoalloy coatings (while using the calculation data on thermal conductivity) have a greater intensity of heat removal from the mold wall than galvanic nickel and gas thermal nichrome coatings. The highest value belongs to the coating Cu-Mo, since it has a higher value of thermal conductivity (~75 % of the thermal conductivity of copper). The thermal conductivity of coatings Cu-Ti, Cu-FCW (FeB) and Cu-NiCr amounts to ~70 %, ~60 % and ~55 % of the thermal conductivity of copper, respectively.

The determination of the temperature value of the outer surface of the mold wall showed that the wall temperature increases with an increase in the coating thickness. With nickel coating, the wall temperature is higher by 15–40 °C, and with gas-thermal nichrome coating – by 120–300 °C than with pseudoalloy coatings Cu-NiCr, Cu-Mo, Cu-Ti and Cu-FCW (FeB). The wall temperature with the coating of 3 mm thickness as compared to the copper wall without the coating is increased by ~20 °C with the coating Cu-Mo, Cu-Ti, Cu-FeB and by ~25 °C with the Cu-NiCr coating. In turn, with galvanic nickel coating, the wall temperature increases by ~60 °C, and with gas-thermal nichrome one the temperature increases by ~320 °C.

The effect of pseudoalloy coatings on the total heat flux through the mold wall depends mainly on the thickness of coatings and depends little on the selected compositions. At the coating thickness of 1 mm, the reduction is <1 %, with 3 mm it is 1–2 %. In the case of galvanic Ni coating, this reduction is 2 and 6 %, and in the case of gas-thermal nichrome one it is 11 and 28 %, respectively.

The consequence of a decrease in the heat transfer and an increase in the temperature of the mold wall is an increase in the thermal stresses in the ingot. This can cause the formation of ingot defects such as cracks, axial looseness, etc. It also leads to an increase in stresses at the coating-base interface, a decrease in the adhesion strength of the coating and the risk of its delamination or cracking. Moreover, an increase in the wall temperature can lead to thermal deformation of the walls of molds during operation.

The investigation of the structure of coatings showed that in the electric-arc spraying of dissimilar wires, mainly a two-phase coating of a pseudoalloy type with a uniform distribution of components is formed, which guarantees uniformity of the coating properties throughout its entire area. In coatings, there is a small number of oxidation products of the sprayed materials. The microhardness of the strengthening phase of NiCr, Mo, Ti and FeB is 1.5–3 times higher than that of the Cu phase, and due to the presence of these components, the total hardness of pseudoalloy coatings increases. The produced coatings densely adhere to the copper base and do not delaminate at a thickness of 6 mm.

As a result of measurements of the CTE of coatings, it was established (Table 4) that Cu-NiCr coating is the closest to the CTE of copper. Then it is followed by Cu-FCW (FeB), Cu-Ti, and Cu-Mo. The proximity of the CTE of the copper base of the mold and the coating should be a positive factor in terms of reducing the level of stresses at the interface and, as a result, reducing the negative effect on the adhesion strength and deformation of the base. From this point of view, due to a high difference in the CTE of copper and Cu-Mo coating, there is a risk of delamination of the coating during casting.

From the data obtained from the results of tests for abrasive wear resistance at a room temperature (Table 5), it follows that as compared to pure copper, on average, the linear wear of coatings decreases with Cu-Mo 1.4, with Cu-NiCr 1.5; with Cu-Ti 2.1 and with Cu-FCW (FeB) 2.3 times.

The determination of the hot hardness of Cu-NiCr pseudoalloy coating showed that the coating has a sufficiently high hardness at elevated temperatures (Table 6). Thus, in these conditions the hardness of the coating at 400 °C exceeds the hardness of copper 3 times and of galvanic nickel coating – 2 times (Fig. 6). With an increase in temperature, there is no sharp decrease in hardness, but a monotonic decrease for the entire temperature range of 20–400 °C is observed. These values of the hot hardness of the coating are an important characteristic for the operation of walls of CCM molds with the coating, since they increase the service life of walls with a pseudoalloy coating as compared to the wall with electric plating.

The tests at a temperature of 350 °C showed that the wear resistance of coatings at a given temperature by wear mass exceeds the wear resistance of pure copper 4.5 times for Cu-NiCr coating and 22 times for Cu-FCW coating (FeB) (Fig. 5).

Based on the experiments on electric-arc spraying of pseudoalloy coatings and the obtained results of the investigation of properties, the developed coatings can be recommended for applying on the walls of CCM molds. The pseudoalloy electric-arc coatings can be an alternative to the existing technologies of galvanic nickel plating because of a higher strength of these coatings in the conditions of steel casting. The electric-arc spraying method also has technological and economic advantages over the methods of galvanic coating. According to its technological characteristics, the method of electric-arc spraying allows applying coatings of variable thickness, repairing the walls by applying pseudoalloy coatings both over the entire surface and in the case of local wear spots without dismantling the mold. To test the developed technology, the pseudoalloy coating Cu-NiCr was applied to the inner surface of the fragment of the liner of CCM mold (Fig. 7). The coating showed a good machining quality when using turning.

Fig. 7. Fragment of the CCM mold liner with the inner Cu-NiCr coating after machining

To implement the practical application of the developed coatings, it is necessary to carry out pilot-industrial tests in order to choose the most effective variant.

The drawback of the electric-arc spraying process used for application of pseudoalloy coatings is associated with a limited range of materials supplied as a wire for spraying. This does not allow regulating the composition of pseudoalloy coatings in wide ranges and introducing non-metallic materials into the composition of coatings. Therefore, the further ways of development of investigations in this field are associated with the use of flux-cored wires for producing coatings with a composite structure. This will allow producing coatings of variable composition on the mold walls (with a decrease in the copper content from meniscus to the lower part of the mold). Another way of development of these investigations is associated with the use of high-velocity gas-thermal spraying technology, in particular activated arc metallization.

7. Conclusions

1. Based on the requirements for the coatings on walls of CCM molds, the compositions of pseudoalloy coatings for electric-arc spraying were developed, containing a combination of copper with a metal, which has a greater resistance to wear than copper. As a wear-resistant component, NiCr, Mo, Ti and FCW (FeB) were used. The influence of the composition and thickness of pseudoalloy coatings on the mold wall temperature and the heat flux was determined by calculation. It is shown that pseudoalloy coatings Cu-NiCr, Cu-Mo, Cu-Ti, Cu-FCW (FeB) have a smaller effect on these characteristics of the casting process than galvanic nickel and gas-thermal nichrome coatings due to preserving a high thermal conductivity of coatings (~ 55 %, 75 %, 70 % and 60 % of the thermal conductivity of copper, respectively).

2. As a result of electric-arc spraying using wires of two dissimilar metals, the pseudoalloy coatings with a uniform distribution of components were produced, one of which is copper, with the hardness of 1,320–1,460 MPa, and the second one is a strengthening component NiCr with a hardness of 2,440 MPa; Mo, with a hardness of 5,350 MPa; Ti, with a hardness of 7,540 MPa; FeB, with a hardness of 7,050 MPa.

3. The CTE of the coatings Cu-NiCr, Cu-Mo, Cu-Ti, Cu-FeB was measured. As a result of measurements, it was found that the coating Cu-NiCr ($14.5 \cdot 10^6$, $^{\circ}C^{-1}$) is the closest to the CTE of copper ($15.1 \cdot 10^6$, $^{\circ}C^{-1}$). Then it is followed by Cu-FCW(FeB) ($13.5 \cdot 10^6$, $^{\circ}C^{-1}$), Cu–Ti ($11.8 \cdot 10^6$, $^{\circ}C^{-1}$) and Cu–Mo ($6.65 \cdot 10^6$, $^{\circ}C^{-1}$). The abrasive wear resistance of pseudoalloy coatings at a room temperature is more than 1.4–2.3 times higher than that of pure copper. The tests of pseudoalloy coatings for wear resistance during heating to 350 °C showed that the wear resistance of Cu-NiCr and Cu-FCW coatings (FeB) exceeds the strength of pure copper in these conditions 4.5 and 22 times, respectively. The determination of the hot hardness of the Cu-NiCr coating showed that at 400 °C the hardness of the coating exceeds the hardness of pure copper 3 times and that of galvanic nickel coating – 2 times.

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STUDYING THE EFFECT OF THE COMBINED TECHNOLOGY ON DURABILITY OF THE SHAFT-TYPE PARTS

N. Miedviedieva
PhD, Associate Professor*
E-mail: natalya.miedvedeva@gmail.com
M. Levytsky
PhD, Associate Professor, General Director
Limited Liability Company "TMS Ukraine"
Vozdvyzhenska str., 44, Kyiv, Ukraine, 04071
E-mail: m.levitskij@tms-ua.com
V. Sukhenko
Doctor of Technical Sciences, Professor, Head of Department*
E-mail: vladsuhenko@gmail.com
*Department of Standardization and certifying of agricultural products
National University of Life and Environmental Sciences of Ukraine
Heroiv Oborony str., 15, Kyiv, Ukraine, 03041

Відновлення деталей типу «вал» при одночасному підвищенні їх ресурсу – важливий резерв розвитку та підвищення ефективності ремонтного виробництва. Підвищення зносостійкості та довговічності деталей сільськогосподарської техніки і машин є пріоритетним напрямком сучасного машинобудування. З цією метою виконаний аналіз та розглянуто процес електроконтактного зміцнення напилених зносостійких покриттів деталей типу «вал».

Проведені експериментальні дослідження фізико-механічних властивостей зносостійких покриттів, отриманих комбінованою технологією. Встановлені залежності міцності зчеплення, пористості напилених зносостійких покриттів від струму і тиску процесу електроконтактного зміцнення. Зі збільшенням тиску зміцнення до 30–40 МПа і сили струму до 14–16 кА спостерігається зростання міцності зчеплення напиленого покриття до 180...220 МПа та зниження пористості до 2...5 %.

Зносостійкість покриттів, отриманих за комбінованою технологією, у всьому діапазоні досліджених навантажень і швидкостей виявилася вищою, ніж у покриттів, отриманих окремо за класичними технологіями газополуменевого і електродугового напилення. Найвищі показники зносостійкості виявлено у покриття з матеріалу ФМІ-2, отриманого комбінованою технологією.

Дослідження втомної міцності зміцнених деталей показали, що покриття отримані комбінованою технологією підвищили межу витривалості деталей, відновлених напиленням, на 20 %, а деталей без покриттів – на 50 %.

Проведена порівняльна оцінка фізико-механічних і експлуатаційних властивостей покриттів отриманих електродуговим, газополуменевим напиленням та комбінованою технологією. Встановлено, що застосування електроконтактного зміцнення напилених зносостійких покриттів при тиску 20...40 МПа, силі струму 11...16 кА, тривалості імпульсів струму і пауз 0,02...0,04 с, значно підвищилися їх фізико-механічні властивості та експлуатаційні характеристики.

Ключові слова: напилені покриття, пористість, міцність зчеплення, зносостійкість, електроконтактне зміцнення, довговічність, витривалість, комбінована технологія, відновлення

1. Introduction

Wear of parts is the main cause of declining reliability of machine operating parameters. It leads to surface damage, loss of power and worsening of reliability and durability of a machine in general. The mechanical, physical and electrochemical processes taking place in tribologically conjugated assemblies and units result in damaged and deteriorated friction surfaces [1].