Obtaining of combined hardening coatings of copper molds of machines for continuous-casting of billets


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Received May 7, 2018

The article is devoted to study of the problem of improving of durability of surfaces of copper plates of molds of machines for continuous casting of billets. Presented here are the results of investigations of combined Ni-coatings on Cu that are a thin Ni-sublayer obtained by electric spark alloying method and a working Ni-layer deposited by arc plasma-spraying. Complex analysis (optical microscopy, durometric analysis and SEM) of the coatings is conducted and their mechanical characteristics are also studied. The using of Ni-sublayer is shown to increase the adherence of coatings considerably. Resulted in the work are the values of adhesion and other characteristics of the coatings obtained.

Keywords: Ni-coating, electric spark alloying, arc plasma spraying, cohesion, adhesion.

Исследован вопрос повышения стойкости поверхностей медных плит кристаллизаторов машин непрерывного литья заготовок. Представлены результаты исследований комбинированных покрытий никеля на меди, представляющих собой тонкий подслой никеля, полученный методом электродугового легирования, и рабочий слой никеля, нанесенный методом плазменно-дугового напыления. Проведен комплексный анализ покрытий (оптическая микроскопия, дуromетрический анализ и СЭМ), изучены их механические характеристики. Показано, что применение никелевого подслоя значительно увеличивает сцепление покрытий. Приведены значения сцепления и другие характеристики полученных покрытий.

Отримання комбінованих зміднюючих покриттів мідних кристалізаторів машин безперервного литья заготовок. А.В.Паустовський, В.Г.Христов, В.Є.Шелудко, І.В.Доценко, В.І.Зеленін, М.А.Полещук, В.М.Теплюк, Е.В.Зеленін.

Досліджено питання підвищення стійкості поверхонь мідних плит кристалізаторів машин безперервного литья заготовок. Представлені результати досліджень комбінованих покриттів нікелем на міді, що являють собою тонкий підшар нікелю, отриманий методом електродугового легування, і рабочий шар нікелю, нанесений методом плазменно-дугового напилення. Проведено комплексний аналіз покриттів (оптична мікро скопія, дуromетричний аналіз та СЕМ), вивчено їх механічні характеристики. Показано, що застосування нікелевого підшару значно збільшує зчеплення покриттів. Наведені значення зчеплення і інші характеристики одержаних покриттів.
1. Introduction

In metallurgy industry the increase of durability of wear surfaces of Cu-plates of molds of machines for continuous-casting of billets (MCCB) in dozens of times is attained mainly by application of Ni-coatings [1, 2]. The basic technology of depositing of such coatings is electropolishing [3] having a number of larks, the main of which are big consumption of electric power and environmental contamination. So, the working out of alternative technologies [4, 5] of Ni-coating obtaining on Cu-plates is of current importance. The technology of electrospark alloying (ESA) in a combination with arc plasma-spraying [6, 7] can be referred to such technologies.

The formation of the alloyed surface layer at ESA is defined by anode metal transfer on a metal cathode at a spark discharge and their active interaction among themselves [8]. Repeated influence of spark discharges between the anode (Ni-wire) and the cathode (Cu-plate) leads to the formation of dense Ni-coating alloyed with Cu-plate.

However owing to high heat conductivity of Cu, the thickness of dense fused Ni-base is limited but it's quite enough to produce Ni-sublayer by ESA followed by arc plasma-spraying of the base coating.

The technology of arc plasma-spraying with the remote wire anode allows to deposit Ni-coating up to 2 and more millimeters in thick. Without Ni-sublayer such coating has the low value of adherence with Cu-surface [9–11].

The use of plasma spraying can considerably accelerate the process of obtaining of protective Ni-coating on the big areas of Cu-plates of cooling and integration of ESA and arc plasma-spraying can serve as the basis for new combined technologies possessing several advantages to work out.

The aim of the work is to obtain and investigate the complex coating consisting of Ni-sublayer deposited by ESA on a working surface of Cu-plate and the working Ni-coating deposited by arc plasma-spraying method.

As it's researched, some aspects of forming of ESA- and arc plasma-sprayed-coatings by wire Ni-materials and also their mechanical characteristics namely adhesive strength, cohesion, porosity are studied.

2. Experimental

ESA Ni-coating was deposited on the samples of M1 copper at "0" mode on "ELITRON-52" or EEV-2 installations in Ar medium. Pulse energy — 4–7.5 J, processing time — 0.6 Ms/cm², impulses frequency — 100 Hz. After ESA-coatings were washed in degreasing solvent and processed by jet-abrasive method with electrocorundum (fraction 0.5–12).

Then arc plasma-sprayed Ni-coating was deposited on the obtained in that way Ni-sublayer with UN-26 unit. A spraying was carried out at an optimal distance between the spraying anode and a surface of Cu-samples. The mode of coating application determined depending on the necessity of the maximal adhesive strength, cohesion and porosity is presented in Table 1.

Plasma forming Ar-gas flow at the pressure of 0.3 MPa is within 2 m³/h and the compressed air cooling plasmatorn — 20 m³/h at the pressure of 0.5–0.7 MPa. The wire feed speed is no more than 5 m/min and that of plasmatorn horizontal moving relative to the samples — 1 mm/min with vertical step — 20 mm.

The working capacity of Ni-coatings on Cu-plates of molds in MCCB is defined by their adhesion to Cu-base, cohesion and porosity. In the given work adhesive strength of Ni-coatings with Cu-base was defined by a pin test [11, 12]. In Fig. 1 the scheme of the work tool for adhesion of Ni-coatings to Cu base to define is presented.

Into Cu-disk (220 mm) having a hole (23.8 mm) M1-Cu-rod was inserted. Face-plates of details were grinded in one plane and ESA Ni-coating of 0.1–0.15 mm in thick was deposited on it. As at a separation of a pin sample, the coating is exposed to influence both tearing and cutting loadings, the rod in the disk was turned up to ESA-coating shear throughout the diameter of 3.8 mm so that the strength of ESA-coating wasn't overlaid on the value of adhesive strength of the following arc plasma-sprayed coating.

On the surface of the samples obtained in such way, arc plasma-sprayed coating about 2 mm in thick was deposited. Further the

<table>
<thead>
<tr>
<th>Material</th>
<th>Distance to sample, mm</th>
<th>Current, A</th>
<th>Arc voltage, V</th>
<th>Wire diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>120</td>
<td>200</td>
<td>70</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 1. Mode of coating deposition with UN-26 unit
samples were tested by IR100 rupture-test machine where the rod was torn out from a disk with a hole. Then the samples were investigated metallographically and their mechanical and other properties were also defined.

While carrying out metallographic analysis of the samples, the complex technique including metallography (NEOPHOT-32 optical microscope (Karl Zeiss, Jena, Germany)), durometric analysis and structure investigation on SEM REM-1061 (SELMI, Ukraine) was applied.

For the structure of investigated compounds to find out, chemicals [13] and the conditions of etching resulted in Table 2 were used. The microstructure of cross-section of the compounds obtained by complex Ni depositing was investigated.

To define cohesion, Ni-layer of 2 mm in thick was sprayed on Cu-plate. After that it was separated and the samples — strips of 4 mm in width for mechanical properties to define were cut out from it by electroerosion cutting. The surface of the strips was grinded to remove its irregularities up to 1.6—2.0 mm in thick. The samples were made of the strips (type MI96, COST 696-66) for the coating rupture strength to define. Then the samples were torn by IR100 rupture-test machine with the use of self-aligning grips.

### Table 2. Chemicals and etching conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical mixture</th>
<th>Method of using</th>
<th>Notice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (M1)</td>
<td>Nitric acid (50 ml) + water (50 ml)</td>
<td>Chemical etching at intensive stirring of chemical, ( \tau = 5...30 \text{ s}, T = 20^\circ\text{C} )</td>
<td>To remove oxide film, hydrochloric acid (50 ml) and water (20 ml) at ( T = 30^\circ\text{C}, \tau = 1...3 \text{ s are used} )</td>
</tr>
<tr>
<td>Ni (H1)</td>
<td>Sulfuric ammonium (20 g) + water (100 ml)</td>
<td>Electroetching, ( U = 6...15 \text{ V}, \tau = 3...10 \text{ s} )</td>
<td></td>
</tr>
</tbody>
</table>

### 3. Results and discussion

As stated earlier, the technology of arc plasma-spraying with the remote anode allows to deposit with high efficiency a coating to several millimeters in thick. Such a coating without sublayer has low adhesive strength with Cu-surface [14, 15].

Resulted in Fig. 2 is the microstructure of plasma Ni-coating on Cu-plate. Chips and discontinuities between Cu-surface and Ni-coating are seen well. The value of adhesive strength of Ni with Cu at direct its depositing by plasma spraying on Cu-substrate after grit blasting of Cu-surface comes to 6—8 MPa. This is evidence of the absence of chemical-metallurgical interaction at the phase boundary. In all cases the coating break occurs through line — Cu-substrate — an arc plasma-sprayed coating.

Somewhat different picture is observed in case of application of Ni-sublayer deposited by ESA. Resulted in Fig. 3 is cross-section of Cu-sample with the combined coating. One can see Ni-sublayer having considerable adhesion to processed Cu-surface owing to mixing of the melted Ni-electrode with fused Cu-surface. The absence of obvious defects in the adherence area is ob-
Fig. 3. Microstructure of cross-section of Cu-sample with combined coating (×100).

served. The coating break occurs through boundary lines with arc plasma-sprayed coating.

SEM data confirm the presence of Cu in Ni-sublayer that is mixing of Ni with Cu (Fig. 4). Its content can amount to 70 and more percent.

Adhesive strength of arc plasma-sprayed Ni-coating with ESA Ni-sublayer has turned out within 24–36 MPa. This is significantly more than the value of adhesion of arc plasma-sprayed Ni-coating deposited directly on Cu without Ni-sublayer (6–8 MPa).

Thus, the application of Ni-sublayer deposited by ESA allows to increase adhesive strength of coatings considerably.

Investigations have shown that in practice dense Ni-coatings deposited on Cu by ESA can be obtained no more than 0.15 mm in thickness, then fusion locks and porosities arise. It’s caused by a number of the factors [16] one of which may be that the heat of electrospray discharge to a greater extent goes to the body of Cu-detail instead of processed surface fusion.

Another important feature of the coatings is cohesion of a working layer of arc plasma-sprayed Ni-coating which is connected directly with its porosity. Porosity was defined by hydrostatic method and it came to 10.2–12 % for the given samples. At such porosity coating strength came to 100–110 MPa which is quite a high characteristic for arc plasma-sprayed coating [17].

4. Conclusions

The technology of depositing of the combined coatings of Ni on Cu providing for depositing of Ni-sublayer by ESA and a working Ni-layer by arc plasma spraying is developed. The possibility of obtaining sufficiently dense Ni-coatings on Cu-plates of molds in MCCB is shown. At that adhesive strength of arc plasma-spraying coatings on Cu, at the use of ESA sublayer, can amount to high values (24–36 MPa), cohesion — 100–110 MPa at the porosity of 10.2–12 %.

References