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Research/Technical Note

The Use of Coatings to Obtain the Diffusion Layer on the Walls of Molds

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Abstract: In this work diffusion layers on narrow walls of crystallizers removed from service were created by aluminium spraying on M1 copper and MH2, 5KoKpX copper alloy with subsequent heat treatment for increasing of life time of crystallizers in continuous casting machines. Layer thickness and microhardness have been assumed as basic measure of serviceability. To clarify the reasons of reducing the thickness of the diffusion layer on the copper alloy MH2, 5KoKpX were conducted metallographic and microengineering research. The coating was applied on the wall alloy MH2, 5KoKpX, the diffusion layer microhardness was measured on microthermometry PMT–3. The analysis found that increasing the thickness of the deposited coating and the temperature rise of the heat treatment, as a rule, lead to an increase in the thickness of the diffusion layer; change the security environment with 95%N_2+5%H_2 100%H_2 does not change the thickness of the diffusion layer; a diffusion layer microhardness of 2-6 times higher than the microhardness of copper and is 1140-3880 MPa against 460-590 MPa on copper base. It is reasonable to spray aluminium thermal coating on narrow crystallizer walls with subsequent heat treatment in protective atmosphere using adjusted modes and proofing of a crystallizer in a continuous casting machine for estimation of wall state during exploitation and change of cast metal quality.

Keywords: Crystallizer, Narrow Wall, Coating, Diffusion Layer, Sample

1. Introduction

Numerous parts of metallurgical equipment (crystallizers, converter and blast furnace lances etc.) are made from copper and copper alloys which have high electro- and thermal conductivity [1]. Nevertheless copper has low heat and wear resistances [2]. Experiments have revealed that copper oxides don't withstand thermal shocks and break down after first thermal cycle, as well as peel off during a friction test.

Thermal-diffusion saturation of a surface by alloying elements is one of methods to improve copper part performances [3]. Aluminium is one of basic elements used for saturation. For example, it is possible to carry out an aluminizing by saturation in powder mixture containing 50% Al-powder, 1% Al_2O_3, and 1% NH_4Cl [4].

An oxidation test of M1 grade copper with a coating at 850°C in air atmosphere have revealed that thermal-diffusion aluminizing is a perspective oxidation protection for copper [5]. Aluminized samples are oxidized considerably slower, a process is stabilized quickly. It seems likely that oxidation goes on by logarithmic dependence. After oxidation samples of aluminized copper have a compact and durable oxide layer, which is not peeled off during thermal cycles.

As for wear resistance of aluminized copper, it increases by a factor of 1.3 [6].

However, diffusion saturation in powder mixtures is significantly labor-intensive and low-productive. At present gas-thermal spraying with subsequent heat treatment is used for obtaining of diffusion layers on metallurgical machinery elements [7]. Standard equipment for such coating spraying is relatively compact and low-price, dimensions of parts under treatment are not limited by anything, and it is possible to form local and double-side coatings [8, 9]. A technological process of spraying allows obtaining necessary productivity and is characterized by relatively low labor content [10].

A result of thermal spraying of coatings on copper and copper alloys with subsequent heat treatment is diffusion layer with heat- and wear resistance necessary for improvement of metallurgical facilities life cycle [11]. Heat- and wear resistance of thermal sprayed coatings are highly competitive with that of coatings obtained by thermal diffusion saturation in powder mixtures.

Purpose of the study: The aim is to improve the quality of the cast metal by applying thermal coatings on the working surface of the mold of continuous casting of steel billets.

2. Methods and Materials

At present M1 grade copper and a copper-nickel allow MH2, 5KoKpX are used for production of crystallizer walls in continuous casting machines at some domestic plants. So outspent narrow walls of crystallizers made from those materials were used for investigations.

Table 1. *The microhardness of the diffusion layer.*

No. of sample	The coating composition	Microhardness, kg/mm^2			
		The surface of the diffusion layer	The middle of the diffusion layer	Boundary layer-metal	Main metal
1	Al	367	272	190	110

Table 2. *The results of the microprobe analysis of the diffusion layer.*

No. of sample	The coating composition	The content of chemical elements, %									
		phase closer to the surface of the diffusion layer			phase in the middle of the diffusion layer				phase closer to the boundary layer-metal		
		A1	Ni	Cr	A1	Ni	Cr	Si	Al	Ni	Si
1	A1	18, 1-2, 3	1, 5-1, 6	0	14, 0-14, 8	3, 5-4, 1	0	0, 1-0, 3	11, 5-11, 8	4, 0-4, 2	0, 8-1, 7

Diffusion layers on M1 copper and MH2, 5KoKpX copper alloy were created by spraying of aluminium of 1.5 mm thickness and subsequent diffusion annealing at 800°C for 10 hours in oxidizing atmosphere1.

It was determined that reinforcing diffusion layer on a M1 copper surface if of 1.5 mm thickness, and on MH2, 5KoKpX alloy surface – 0.6 to 1.4 mm respectively. The latter is because of restraint of diffusion process by alloying elements containing in alloy. In any case diffusion layer thickness doesn't exceed thickness of a sprayed coating.

To clarify the reasons of reducing the thickness of the diffusion layer on the alloy MH2, 5KoKpX were conducted metallographic and microengineering research. The coating was applied on the wall alloy MH2, 5KoKpX, the diffusion layer microhardness was measured on microthermometry PMT–3 (table 1).

The microstructure of the diffusion layer consists of eutectoid (α+γ2), and secretions of the α-phase and γ2-phase at the grain boundaries. In the layer structure can be divided into several zones:

- in the surface area on the background of eutectoid observed grain gray γ2-phase;
- the middle zone consists of bright grains of α-phase and dark field eutectoid (α+γ2) different degrees of dispersion (figure 1);
- the area adjacent to the boundary layer-metal, is a light grains of α - phase.

The surface layer of the samples is characterized by the presence of pores with a depth of 0.1 to 0.4 mm.

The phase composition of the diffusion layer, the distribution of A1 and other chemical elements in the area adjacent to the boundary layer-metal, defined microengineering method on the device "Camebax". The results of the study are shown in table 2.

Figure 1. *The microstructure of the diffusion layer (sample No. 1), X500.*

It is known that service life of diffusion layer formed on copper parts of metallurgical facilities is determined, for the first time, by its thickness. As a rule, increasing of sprayed coating thickness as well as temperature and duration of heat treatment results in increasing of diffusion layer thickness. However, increasing of sprayed coating thickness is accompanied by degradation of its adhesion, and heat treatment temperature rise – by intense oxidation of coating and uncovered areas of copper base, respectively. Thereby diffusion annealing of coatings on copper was carried out in protective atmosphere (95%N_2 + 5%H_2 or pure H_2) at 800 – 900°C for 10 hours for increasing of diffusion layer thickness.

Samples from M1 copper with an aluminium coating were investigated in this work. Sample marking-off is the following: # 1 – without diffusion annealing, others – after diffusion annealing (table 3).

[1] Alexander Kuznetsov took part in this work.

Main results of investigation for samples with coating 2 are presented in the table 3.

Table 3. *The influence of aluminium coating thickness, heat treatment mode and protective atmosphere on thickness and microhardness of diffusion layer.*

#	h_C, mm	t, °C / τ, h	Atmosphere	$h_{D.L.}$, mm	Microhardness, H_μ, MPa
1	1.1 – 1.5	–	–	–	310
2	1.0	800/10	$95\%N_2+5\%H_2$	0.7 – 0.9	1650 – 3010
3	1.5	850/10	H_2	3.8 – 4.0	1490 – 3880
4	1.0	900/10	$95\%N_2+5\%H_2$	2.3 – 2.4	1180 – 2100
5	1.0	900/10	H_2	2.6 – 3.0	1420 – 1510
6	1.5	900/10	H_2	3.3 – 4.0	1350 – 2750
7	2.5	900/10	$95\%N_2+5\%H_2$	4.0 – 4.6	1140 – 3330

3. Conclusions

The study is aimed to improve the quality of the cast metal by applying thermal coatings on the working surface of the mold of continuous casting of steel billets. To clarify the reasons of reducing the thickness of the diffusion layer on the copper alloy MH2, 5КоКрХ were conducted metallographic and microengineering research.

In the course of analysis it has been found that:

- The are heat treatment modes, ensured obtaining of a diffusion layer of 4.0 mm thickness and high hardness without dimples on copper sample surface;
- As a rule, increasing of sprayed costing thickness and heat treatment temperature rise result in diffusion layer thickness;
- Protective atmosphere changing from 95 %N2 + 5 %H2 to pure H2 does not change diffusion layer thickness;
- Maximum diffusion layer thickness hD.L.= 4.0 – 4.6 mm is obtained at t = 900°C and hC = 2.5 mm;
- Diffusion layer microhardness exceeds the one of copper by a factor 2–6 (1140 – 3880 MPa as compared with 460 – 590 MPa).

Subsequently aluminium thermal spray coating of 2.0 mm thickness [3] was sprayed on a surface of two pairs of narrow crystallizer walls removed from service. The first pair was heat treated in protective atmosphere ($95\%N_2$ + $5\%H_2$) at 800°C for 10 h, and the second pair – in pure H_2 at 900°C for 10 ч [4] respectively (see the figure 2).

Sample investigation has revealed that for the first pair diffusion layer thickness was 0.9 – 1.2 мм, and microhardness was 1650 – 3250 MPa. Nevertheless such thickness is not sufficient for mechanical treatment of wall surfaces from coating side and obtaining of residual thickness ensured significant increasing of their life cycle.

Examination of second pair of crystallizer walls has showed that their heat treatment in protective atmosphere at 900°C for 10 h results in distortion which can not be eliminated by mechanical means [5].

It is reasonable to spray aluminium thermal coating on narrow crystallizer walls with subsequent heat treatment in protective atmosphere using adjusted modes and proofing of a crystallizer in a continuous casting machine for estimation of wall state during exploitation and change of cast metal quality.

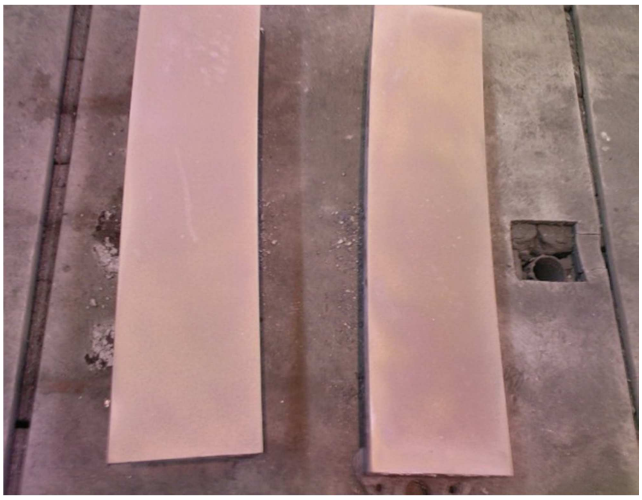

Figure 2. *Crystallizer walls after heat treatment in protective atmosphere (H2) at 900°C for 10 h.*

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