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Laser Modification of the Microstructure of Zn-Co Electroplating Alloys

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In this study we report the experimental results of researches of the effect on the microstructure of the Zn-Co coatings with laser radiation generated by a ruby laser operating of free oscillators regime (1.2 ms pulse duration, wavelength $0.69\mu m$ and the power density of 10^4 to 10^6 W/cm²). It is shown how the microstructure of the investigating alloys after its modification by an impulse laser radiation depends on the power density.

Keywords: Electrodeposition, Zn-Co alloys, Laser radiation, Microstructure.

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1. INTRODUCTION

The Zn-Co alloys coating on a steel from a bath are widely used in a tech industry as protective coatings. The Zn-Co alloys has a number of characteristics that make it a well-suited corrosion protective coatings for iron and steel products and have an exigency to search and to develop new ways for it modification to form layers, having the required performance properties. There has been a growing interest to methods of modification of the structure and properties with energy effect, particularly, the method of laser interaction allowing a thermally stable layers with the required properties. The laser treatment of coatings is an efficient method of their hardening due to change in the defect structure and in the some case it's can decrease the degree of atomic ordering or distortion of crystals structure under laser irradiation[1-3].

The aim of present work is to of the laser radiation on the structure of the Zn-Co electroplatings using with the free oscillators regime of a treatment.

2. MAIN PART

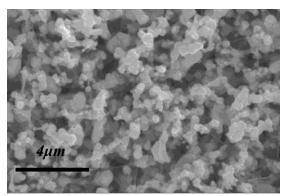
The Zn-Co coatings were irradiated by laser beams generated by a GOR-100M laser with a wavelength of 0,69 μ m. In the case of free oscillators regime (100ns) the duration of a generating pulse was ~1.2 μ sec with an energy varying within the range 5-50J. The laser beam was focused to a relatively homogeneous spot. The diameter of an irradiation area was varied from 2 to 5 mm. The laser radiation power density was charged form 10^4 to 10^6 W/sm².

The Zn-Co coatings have been electrodeposited from an additive-free sulfate electrolyte with following composition: $CoSO_4 \cdot 7H_2O - 200 \, g \, l$, $ZnSO_4 \cdot 7H_2O - 200 \, g \, l$, $NaSO_4 \cdot 7H_2O - 45 \, g \, l$. Deposition was performed with a preliminary reverse onto 08kp low-carbon steel for 1h and at controlled temperature of 25 °C. Current density was equal 1 A/dm². The average thickness of the coating, measured with help of magnetic thickness gage MTTs-3 was 19.8 microns.

The elemental composition which was determined by scanning electron microscopy (SEM) LEO 1455VP with a X-Max $^{\rm N}$ OXFORD INSTRUMENTS microanalyzer was 8.5 at% cobalt, 91.1 at.% zinc, and 0.4 at.% iron [4]. It was obtained the distribution of elements

along a scan line was sufficiently uniform. It should be noted, that iron ions enter to a bath owing to the erosion of a substrate (steel 08kp) during a preliminary reverse of a current. The phase composition of the coatings was studied by X-ray diffraction analysis with the X-ray diffractometer DRON 4.0 (Cu $K\alpha$ radiation). The X-ray diffraction analysis demonstrated that phase composition of the reference sample consists from several phase systems and representing a mixture of zinc and phase solid solution of zinc with cobalt.

Figure 1 shows the relief of the surface of the reference nonirradiated by laser beams coatings.



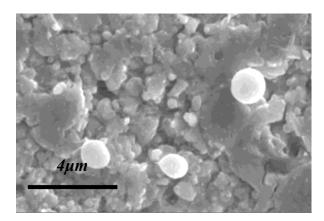
 $\textbf{Fig.}\ 1-Surface\ morphology\ of\ a\ reference\ sample$

It is evident that the reference coatings have developed surfaces. It can be seen, surface of Zn-Co coatings electrodeposited on the steel is a conglomerate of nanotubes with the balls on their end.

3. DISCUSSION OF THE RESULTS

It is found that under laser treatment the structure of the alloys were modificated. In particular, the laser treatment coatings hardly modifies the coatings surface. The surface morphology of irradiated samples was investigated on two points: in the center and in the edge of area of the laser treatment.

The fig. 2 shows the surface morphology of the coating in the central irradiated zone i.e. in the center of a crater processing laser.



 ${f Fig.\,2}$ – Surface morphology of center of the irradiated sample by laser operating of free oscillators regime

Compare with the reference coatings (Fig. 1), it is evident that the crystallinity of the irradiated zone increases. Besides that irradiated by laser coatings in the zone of the crater processing laser have the results of a recrystallization. These modifications are similar to those produced by furnace annealing.

The next figure shows another picture (Fig.3).

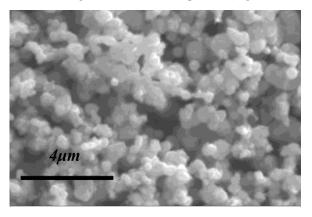


Fig. 3 – Coating's surface morphology of an edge of an area irradiated by laser operating of free oscillators regime

On the edge of the area irradiated by laser operating of free oscillators regime almost places without signs of melting and recrystallization [5].

Results of the study of the elemental treated by laser irradiation Zn-Co alloys are presented on the fig.4. It is

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shown a non-uniform distribution of alloying elements in the area of laser exposure of the investigated coating. Specifically with irradiating by laser operating of free oscillators regime the iron concentration in coatings increases in a direction from the edge of area exposure by laser irradiation to the central area of the crater processing laser.

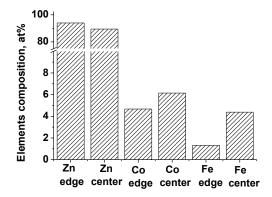


Fig. 4 – Elemental composition (in at. percent) in two point of the alloys prepared at cathode current density $1~{\rm A/dm^2}$ irradiated by laser operating of free oscillators regime

Increased iron in a direction from the edge of area exposure by laser irradiation to the central area of the crater processing laser, can be related with an inhomogeneous thinness of coatings. Besides an impulse laser irradiation induced heating of coatings occurs to leading to the diffusion of iron ions from a substrate into the coating [6]. A similar pattern is observed for cobalt: the concentration of a few more in the central area of the crater processing laser than in the edge of the irradiated area due to the decrease of the zinc concentration in the coating owing to its high volatility.

4. CONCLUSION

The effect of high intensity laser irradiation on the microstructure of Zn-Co coatings electrodeposited from sulfate baths is investigated. It is obtained dependences of the surface geometry and the element's concentration included in alloys on a power density of an impulse laser radiation (1.2 ms pulse duration, wavelength $0.69\mu m$, the power density of 10^4 to 10^6 W / cm²).

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