

## COMPOSITION COVERAGES CONTAINING Co, C<sub>60</sub>, B, ULTRADISPERSE DIAMOND (UDD)

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### Introduction

Now special interest is represented with the coverings containing particles- clusters which sizes make some units or hundreds nanometers. Clusters have a size which commensurable with size of metal germs. Introduction of such clusters influence process of formation and growth of crystallites, a structure of sediments. It is known, that the quantity of included submicronic particles UDD in a metal matrix is not enough ( $\leq 1$  mass. %). But even these insignificant additives lead to improvement of physicomechanical properties of coverings. In this connection the purpose of the given work is to study influence of C<sub>60</sub> and UDD on process of galvanic sedimentation of cobalt and alloys cobalt-boron; properties of the received coverings; establishment of influence of heat treatment on functional characteristics of composition galvanic coverings (CGC).

### Results and discussion

CGC besieged on steel samples from a solution containing (mol/l): cobalt sulfate - 0,7; cobalt chloride - 0,1; boric acid - 0,6; sodium sulfate - 0,2; sodium tetrahydroborate - 0,005-0,01. NaBH<sub>4</sub> dissolved in 5 ml 1N solution of sodium hydroxide (for prevention of hydrolysis). The electrolysis of solution spent at pH $\approx$ 3-5 and 290-292 K. pH of electrolyte regulated by introduction of a sulfuric acid or sodium hydroxide. The fine-dyspersated particles C<sub>60</sub> dissolved in toluol and added in electrolyte. Particles of UDD entered in electrolyte in an amount 0-10 g/l. Their sizes are 3-6 nm and specific surface is 200-350 m<sup>2</sup>/g. Quantity of boron defined in the covering by potentiometric titration, and UDD – by burning of CGC in oxygen current with the subsequent coulometric titration CO<sub>2</sub>. Phase structure and concentration C<sub>60</sub> defined by diffractational method on ДРОН-3 with Fe-K $\alpha$ -radiation. Calculation of parameters of a crystal lattice, the sizes of area of coherent dispersion (ACD) carried out for crystallographic direction (111) with use of approximating function Koshi. Distribution of elements on depth of CGC spent by means of OZHE-spectrometer Rabin at the set speed of ionic etching certain on standard samples.

It is established, that introduction C<sub>60</sub> and UDD practically does not render influence on speed of sedimentation of cobalt (20 micrometer an hour), however allows to increase the limiting density of current from 2 A/dm<sup>2</sup> (at absence of the disperse phase) up to 4 A/dm<sup>2</sup> (at its presence). It is possible to explain it a high degree of dispersiveness C<sub>60</sub> and UDD, and also theirs structure. It is known, that UDD particles are negatively charged, and the  $\zeta$ -potential of water UDD suspension is equal -5 mV. It is caused by availability of surface of UDD particles the functional groups with oxygen, capable to cooperate with hydrogen selected on the cathode. Particles of C<sub>60</sub> and UDD have the small size, commensurable with thickness of a double electric layer. Therefore they are capable to get in a zone of its influence and to mix electrolyte in the cathode layer, that interfering with increase pH of the electrolyte. Therefore desorption of hydrogen increases on the cathode, and ions of cobalt (II) are unloaded on the released activated surface. This can explain reduction of the hydrogenation degree studied CGC and decrease in a level of internal stress in them.

It has been established by method of phase analysis with X-ray powder diffraction was have established, that UDD particles included in a cobalt covering, represent the crystal diamond with small impurity of carbon. So, the increase of UDD content in electrolyte up to 5 g/l leads to directly proportional increase in its quantity in the covering. The further increase of UDD concentration (to 10 g/l) make for decrease of speed of their including.

Its maximal value 1 mass. % is reached at the maintenance 20 g/l.

The greatest influence on maintenance of UDD and C<sub>60</sub> in the cobalt covering renders the increase in density of the cathodic current  $i_{\text{cathode}}$ . So, increase  $i_{\text{cathode}}$  with 0,5 up to 3 A/dm<sup>2</sup> causes increase in the concentration of UDD and C<sub>60</sub> up to 1 and 0,5 mass. %. Introduction of NaBH<sub>4</sub> in water suspension, and also increase in its concentration with 0,1 up to 2 g/l results to increase of maintenance of UDD and C<sub>60</sub> up to 0,4 and 0,3 mass. % accordingly. Also the concentration of boron increase to 4 mass. %. The  $\zeta$ -potential of particles of UDD (from -5 up to -10 mV) and C<sub>60</sub>

(from 8 up to 20 mV) changes at introduction of  $\text{NaBH}_4$  in water suspension. It, most likely, is caused by interaction between particles and  $\text{BH}_4^-$ . It influences on the process of formation of CGC. Acknowledgement of it is that any hashing of suspension results to deterioration of coverings. It is shown, that qualitative coverings turn out at the long periodic stirring-up of electrolyt-suspension. It is caused by that very fine particles remain in volume, and large agglomerates - at the bottom.

It is shown from data of the x-ray analysis, that the crystal lattice parameter does not change at inclusion of nanodiamond or  $\text{C}_{60}$  in small concentration (up to 0,3 %) (table). The parameter of a lattice increases slightly at the further increase in the maintenance of particles in CGC. Apparently, inclusion of the most active particles of nanodiamond or  $\text{C}_{60}$  occurs on the surface of growing crystals Co on crystal boundary. On the contrary, the parameter of a crystal lattice and the size of grains decreases at introduction of the boron in a covering up to 2,8 %. These coverings represent the solid solution of boron in cobalt with enough generated crystal structure. To it testify the sharp diffraction peaks which correspond to planes of the reflecting planes of Co (111), (200), (220), (311). Sediments with concentration of boron more than 2,8 % are radioamorphous. The most intensive reflex Co (111) disappears and appears wide halo in the field of corners 2Q, equal 45-60°. Most likely, inclusion of boron occurs at adsorption  $\text{NaBH}_4$  to its subsequent disintegration up to an elementary boron. Introduction of UDD particles up to 0,5 % in covering Co-B results to reduction of the size of grain up to 7 nanometers and parameter of a crystal lattice up to  $a=3,5069$  Å. It can be caused by interaction between boron and UDD, introduced in a lattice of Co. CGC turn out radioamorphous at concentration of UDD 0,5 % and boron more than 3,5 %.

Measurements of microhardness of the covering (H10) have shown, that the increase in the percentage of UDD results to its increase. Microhardness of cobalt-diamond CGC exceeds on 35 % the microhardness of cobalt coverings. The further increase of microhardness at introduction of ultradisperse particles of boron, probably, is connected with introduction of hard particles in the Co matrix, and also with its dispersive solidification. The last is observed at presence of the submicronic particles which interfere of recrystallization and formation of coarse grains. According to the roentgen phase analysis, its atoms take root into the Co lattice and reduce its grain. Microhardness of Co-UDD coverings exceeds on 30 % those for cobaltous. This effect is connected with introduction of solid nanoparticles in Co-matrix and its dispersive solidification. For coverings with boron H10 increases in 2-3 times in comparison with cobaltous. According to the roentgen phase analysis, introduction of atoms of boron in the Co lattice results to reduction of grain. Introduction of  $\text{C}_{60}$  in Co-covering practically does not influence it H10, but essentially increases their corrosion stability to solutions of 20 % sodium hydrate and the sulfuric acid. We also spent heat treatment of the studied coverings at 350°C within 1-2 hours per an atmosphere of argon or in vacuum. Microhardness of such coverings increases on 20 % that is caused by disintegration of the solid solution of cobalt with formation  $\text{Co}_3\text{B}$  and ordering of the structure of these coverings.

### Conclusions

There are certain the optimum conditions of CGC reception on the Co basis. It is established, that microhardness of the studied coverings increases in liner:  $\text{Co-C}_{60}\sim\text{Co-UDD}\rightarrow\text{Co-B}\rightarrow\text{Co-B-UDD}$ .

Table. Phase composition, the periods of the lattice and the sizes of grains

| UDD,<br>mass. % | Cont. of boron,<br>mass. % | Phase composition            | ACD,<br>nanometer | a, Å   |
|-----------------|----------------------------|------------------------------|-------------------|--------|
| 0               | 0                          | cryst. Co                    | 24                | 3,5122 |
| 0,3-0,8         | 0                          | cryst. Co                    | 24                | 3,5122 |
| 1,0             | 0                          | cryst. Co                    | 29                | 3,5122 |
| 0               | 1,5                        | solid solution<br>of B in Co | 17                | 3,5105 |
| 0               | 2,9                        | radio-amorphous              | 10                | 3,5101 |
| 0,4             | 0,7                        | solid solution<br>of B in Co | 18                | 3,5080 |
| 0,5             | 2,3                        | solid solution<br>of B in Co | 7,2               | 3,5010 |
| 0,6             | 3,2                        | radioamorphous               | -                 | -      |