THE PROBLEM OF HYDROGEN PERMEATION INTO THE BORON DOPED ELECTRODEPOSITED NICKEL FILMS

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Introduction

It is known [1, 2, 3, 4], that the great hydrogen permeation is typical for iron subgroup metals (Fe, Co, Ni), where the hydrogen evolution overvoltage is not large. The feature of the electrolytic coatings thin layers formation by these metals is the significant hydrogen consumption. The growth centers origin on the cathodic foreign material increases the defects number, where the metal-hydrogen interaction is possible. The more the layer thickness is, the homogeneity degree increases and the number of this interactions decreases, so the hydrogen consumption related to the deposit mass is smaller.

The work aim was the researching of the hydrogen penetration into the Ni and Ni-B coatings and electrodeposition regimes correlation. The investigations were carried out in the sulfamate nickelling electrolyte with the polyhedral borates class dope. The electrolysis regimes: t = 30 – 50 ^{0}C; pH = 3,5 – 4,5; i_k = 0,5 – 4 A/dm^2. The hydrogen penetration (V_{H2}, sm^3/ 100 g) into the films was determined with the vacuum extraction method [5, 6].

Results and discussion

V_{H2} decreases from 260 to 85 sm^3/ 100 g for thin Ni films and from 200 to 65 sm^3/ 100 g for Ni – B films (related to the 100g coating mass) at the same coating thickness when the cathodic current density (i_k) increases (Fig. 1). This fact is connected both with the lower hydrogen power output (VT_{H_2}) (for Ni – B film: VT_{H_2} = 5,39 % at the i_k = = 0,5 A/ dm^2; VT_{H_2} = 3,74 % at the i_k = 4A/ dm^2) and with the smaller coating macro- and microdefects number. For example, the Ni – B film porosity decreases from 25 to 5,7 (pH = 4,0; t = 40 ^{0}C; boron concentration 0,5 %). The crystal lattice microdistortions number decreases and the mosaic blocks size (D_{HKH}) increases and approaches to the nickel size (for example, nickel D_{HKH} changes from ~ 3 – 4 nm at the i_k = 0,5 A/ dm^2 to ~ 9 – 10 nm at the i_k = 4A/ dm^2).

V_{H2} decreasing from 117 to 88 sm^3/ 100 g for nickel coatings and from 90 to 68 sm^3/ 100 g for Ni – B coatings with the temperature (t) growth from 30 to 50 ^{0}C is connected with the changes in the nickel and hydrogen interaction conditions The nickel-hydrogen compounds are characterized by negligible bond energy value (4,5 • 10^{-20} – 5,8 • 10^{-20} J), so the unstable bonds are destroyed with the temperature increasing, and therefore the evidence of hydrogen inclusion into the deposit is decreased. Besides, the smaller V_{H2} in the Ni – B film is determined by VT_{H_2} decreasing from 8,48 to 3,84 % (pH = 4,0; i_k = 2A/ dm^2; boron concentration 0,5 %) at the same conditions.

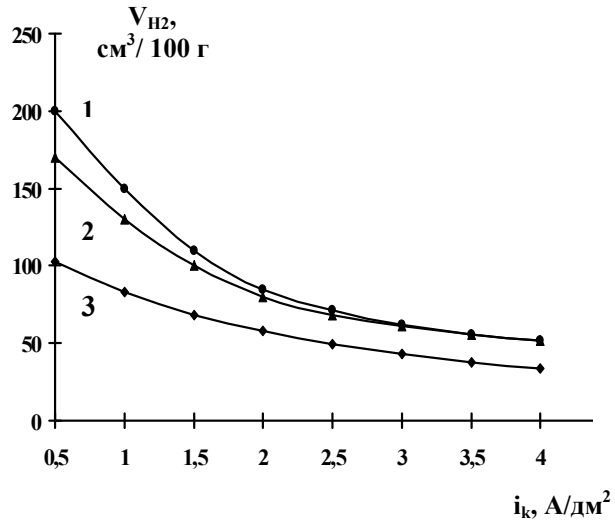

Fig. 1. The coatings hydrogen permeation dependence on i_K:
1 – Ni (pH = 4,0; t = 40 ^{0}C; d = 4 mcm);
2 – Ni – B (pH = 4,0; t = 40 ^{0}C;
C_B = 0,05g/l; d =4 mcm);
3 - Ni – B (pH = 4,0; t = 40 ^{0}C;
C_B = 0,05 g/l; d = 15 mcm)

The hydrogen consumption for the Ni and Ni – B coatings thin films grows with the electrolyte acid value (pH) decreasing. For example, V_{H2} = 49 sm^3/ 100 g at the pH = 3,5 and V_{H2} = = 88 sm^3/ 100 g at the pH = 4,5 for Ni – B. The crystal lattice microdistortions number and D_{HKH} decrease with pH growth. At the same time the decreasing of the evolving cathodic hydrogen volume leads to the less active crystallization centers blocking, resulting to enhance centers number and to the more equal grained deposit structure; the forming coating becomes less strained. This coating structure changing, obviously, is determined by the so called "nomadic" adsorption $Ni(OH)_2$ film production on the growing deposit surface, that

breaks the normal crystallites growth and leads to the fine dispersed coatings formation. Evidently, H_2 consumption in the coating grows because of the hydroxides inclusion into the deposit at high pH values, in spite of the macrodefects number decreasing (the pores number reducing) and the hydrogen power output (VT_{H_2}) decreasing from 6,34 % at the pH = 3,5 to 4,07 % at the pH = 4,5 (t = 40 ^{0}C, i_k = 2A/ dm^2; the boron concentration 0,5 %).

It ought to be noted, that the boron containing dope introduction into the nickelling electrolyte causes the noticeable cathodic hydrogen evolution, that is, obviously, connected with the dope dissociation. The evaluating hydrogen is being adsorbed while metal is electrocrystallized, and then is included into the metal coating, leading to its additional hydrogen permeation. The hydrogen permeation degree of the Ni-B coatings increases from 68 to 113 sm^3/ 100 g (i_k = 2 A/ dm^2; t = = 40 ^{0}C; pH = 4,0) with the boron concentration growth from 0,1 to 1 %, that is represented in the Fig. 2. This dependence is determined by VT_{H_2} changing from 1,96 to 7,05 %, that inlarge the opportunity of the hydrogen inclusion into the coating. The smaller Ni and Ni-B films thickness is, the higher hydrogen permeation degree is. It has been revealed, that the valid alloy boron concentration, when the hydrogen permeation is minimum, is 0,5 %.

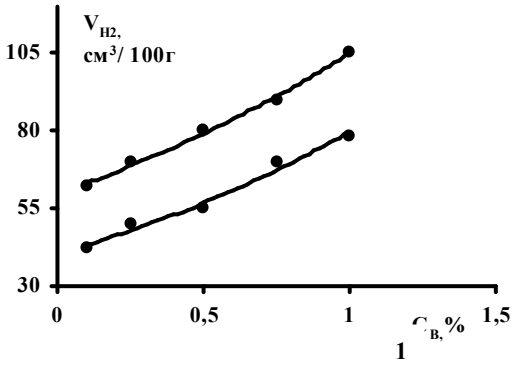

Fig. 2. The Ni - B coatings hydrogen permeation dependence on the alloy boron concentration:
1 – d = 4 mcm; 2 – d = 15 mcm.
Electrodeposition regimes:
pH = 4,0; t = 40° C; i_k = 2 A/ dm^2

Conclusions

The experimental data analysis shows, that the hydrogen consumption in the Ni – B alloy is lower, than in the Ni coating at the same electrolysis regimes. So, when i_k = 4A/ dm^2 for Ni film V_{H2} = = 85 sm^3/ 100 g, and for Ni – B - V_{H2} = = 65 sm^3/ 100 g, that is 1,3 times smaller. This phenomenon can be explained by the particularities of the Ni – B alloy formation mechanism. When i_k achieves the value higher, than 0,5 A/ dm^2, Ni^{2+} ions discharge into $Ni–B^0$ occurs with enhance polarization in comparison with discharge into Ni^0. The breaking of the Ni^{2+} ions discharge rate, when $Ni–B^0$ is electrodeposited (at the E< - 0,75), is connected with this alloy surface coverage by the adsorbed dope boron containing anions. So, for example, cathodic polarization at the i_k = 2 A/ дм^2 maintained the value 30 mV, and at the i_k = = 4 A/ dm^2 - 45 mV.

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