Electrodeposition of Nickel, Nickel -Boron Alloy and Nickel -Composite Coatings from Ammonia-Citrate Bath

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Electrodeposition of Ni-B and composites coatings Ni-B-SiC and Ni-B-Al_20_3 from ammonia-citrate baths was studied. Throwing power of these solutions is about 3 to 4 times higher than that of Ni Watts bath. Current efficiency of alloy is higher at higher concentration of boron-containing additive in the solution. Hardness of Ni coatings deposited from ammonia-citrate bath (600 kg/mm^2) is much higher than that of Ni deposited from acid bath (200-400 kg/mm^2). Ni-B coatings have outstanding hardness (>900 kg/mm^2), even at minimum B content in the solution and in the coating. Heat-treatment at 300-400 ^{0}C resulted in additional growth of hardness (up to 1200-1400 kg/mm^2). Ni-B-based composite coatings Ni-B-Al_20_3 and Ni-B-SiC have still better mechanical characteristics and are practically free of pores at thickness of 10 pm. Corrosion resistance of the Ni-B alloy coating is much higher than Ni coatings.

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In the last years more attention is given to the electrodeposition, study of properties and applications of Ni-B alloy [1-6], since Ni-B alloy coating with small content of B (0,1-2 %) has much higher hardness, thermostability and wear resistance, than Ni coatings [6]. Other distinctive properties of Ni-B coatings, such as solderability, high conductivity and low contact resistance promoted their application in electronic industries [6].

The majority of the studies of the electrodeposition of Ni-B were using Watts-type baths, which is characterised by extremely low throwing power. In the literature there is little information on the electrodeposition of Ni and Ni-B alloy from complex ammonia-citrate bath, on throwing power and properties of deposited coatings.

An objective of the present research is an investigation of the electrodeposition of Ni and Ni-B alloy and Ni composite coatings from ammonia citrate bath.

Experimental Procedure

Ni coatings were deposited from ammonia - citrate bath of following composition: $NiSO_4 x 7H_2O$ 20 or 40 g/l, citric acid 70 g/l, NaCl 10 g/l, NH_4OH up to pH 8,0-8,5, at current density 0,5-2,0 A/ м^2, and t 50° Ñ. For the deposition of Ni-B alloy boron-containing additive **(BCA)** $Na_2B_{10}H_{10}$ was introduced into the solution. For the deposition of composite coatings the ultrafine diamonds (UFD) or SiC powder was added.

The boron content was determined in the solution by potentiometric titration method and in the coatings with the use of a ISP spectroscopy. Polarisation curves were taken under galvanostatic conditions. Throwing power was determined in a slot cell. Corrosion resistance of coatings was determined by gravimetric method.

The hardness of coatings with 20-25 μm thick was measured before and after heat treatment using microhardness tester PMT-3 at indenter load – 100 g. Heat treatment of coated samples was carried out at temperatures 100-800 °C during 1 hour.

Experimental Results and Discussion

Dull coatings were deposited at Ni concentration in the solution 20 g/l and current density 0,5-1,5 A/dm^2, while at Ni concentration 40 g/l they were also dull at i_k 2 A/dm^2 and semi-bright at 0,25-1,0 A/dm^2. Coatings had hydrogen pitting on the surface, and look similar to dull deposits, obtained from Watt's bath without additives.

After the introduction of BCA into the bath the quality of deposited coatings was improved: over current density range 0,25 - 1 A/ м^2 Ni-B alloy coatings were bright, and at higher current densities – semi-bright. Addition of BCA to the solution has practically completely eliminated the pitting.

It is well known, that one of the main disadvantages of any acid solutions for Ni plating is their extremely low throwing power both with respect to current and with respect to metal. An important property of ammonia-citrate bath is much higher (by 2,5-3 times) throwing power with respect to current, than for acid solutions (Table 1). Both parameters, which determine throwing power i.e., electroconductivity and polarisability are considerably higher in the case of ammonia-citrate bath (Table 1). Thus highest throwing power values with respect to current correspond to diluted (20 g/l Ni) ammonia-citrate bath.

Table 1. Electrochemical parameters of solutions

Electrochemical parameters	Watts bath		Ammonia-citrate bath			
			Ni 20 g/l		Ni 40 g/l	
	0.5 A/dm^2	0.75 A/dm^2	0.5 A/dm^2	0.75 A/dm^2	0.5 A/dm^2	0.75 A/dm^2
Electroconductivity, Om$^{-1}\cdot$ cm^{-1}	0.053		0.070		0.057	
Polarizability, dE/di	0.036	0.033	0.017	0.067	0.063	0.059
DE/di $\cdot\chi$, cm	0.19	0.18	0.50	0.47	0.36	0.34
TPcur*, %	8.20	7.30	20.15	19.95	15.20	15.00
TPmet**, %	5.2	4.7	18.2	20.4	15.1	14.5

** TPcur Throwing power of solutions with respect to current*
*** TPmet Throwing power of solutions with respect to metal*

As current efficiency in Watt's bath grows up with an increase in the current density, its throwing power with respect to metal should be lower, than that with respect to current. Data, presented in Table 1 confirm this conclusion. For ammonia-citrate bath throwing power with respect to both metal and current is nearly the same and is much higher than that for Watt's bath.

Current efficiency in ammonia-citrate bath with BCA decreased with increase in current density (Fig.1). Hence, the throwing power with respect to metal should be better, than throwing power with respect to current. Comparison of data, presented in Table 2 with those in the Table 1 confirmed the above assumption. Adding of B to the solution and increase in its concentration, also improve throwing power with respect to metal. At BCA content in the solution 1 g/l throwing power with respect to metal (Table 2) becomes higher than that with respect to current (Table 1) by more than 50 %.

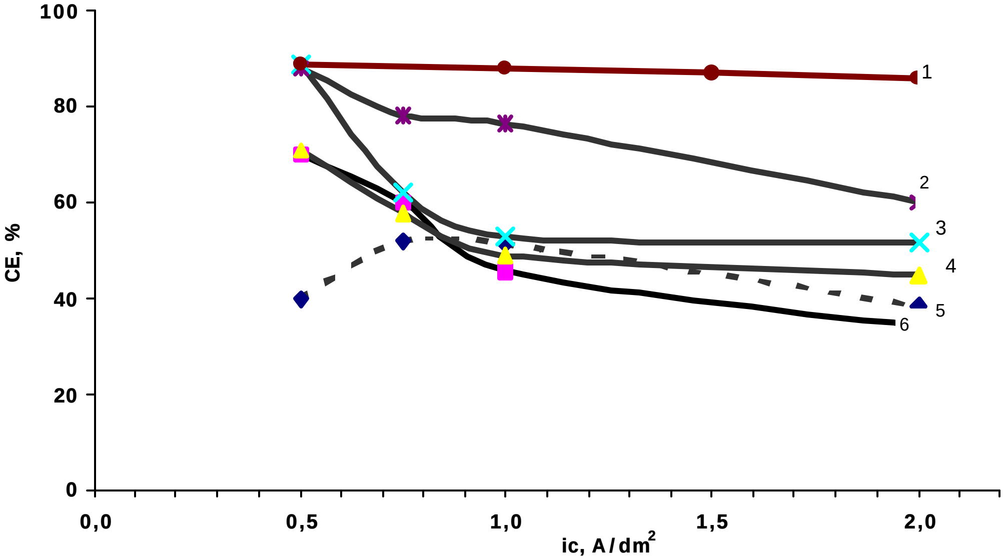

Fig.1 Current efficiency vs current density. Solutions without BCA: 1.-40 g/l Ni; 5.-20 g/l; solutions (20 g/l); with BCA: 2.-1g/l; 3.-0,5 g/l; 4.-0,25 g/l; 6.-0,1 g/l.

Table.2 Throwing power of solutions with respect to metal (ThPme)

Solution	Ni 20 g/l	Ni 40 g/l
C.D. 0.50 A/dm^2		
Ni	18.2	15.1
Ni-B (0,1 g/l)	23.0	
Ni - B (0,25 g/l)	28,6	22,0
Ni - B (0,5 g/l)	31,9	24,2
Ni - B (1 g/l)	31,5	24,0
C.D. 0,75 A/dm^2		
Ni	20,4	14,5
Ni - B (0,1 g/l)	23,3	
Ni - B (0,25 g/l)	29,3	21,1
Ni - B (0,5 g/l)	30,8	22,7
Ni - B (1 g/l)	30,0	22,8

Current efficiency in ammonia-citrate bath (20 g/l Ni) is low (40-50 %.). Introduction of BCA into this bath has resulted in the increase in current efficiency under all conditions of electrolysis. Thus, with an increase in BCA concentration current efficiency increased and reached 80-90 % at B contents in the solution 1g/l (2,8% B in a coating) (Fig .2). Ni-B alloy, deposited at i_c 0,75 A/ м^2 from the bath with B concentration 0,1 g/l, contained 1,9 % of B. With an increase in B concentration in the bath from 0,1 g/l up to 1,0 g/l, its concentration in the deposit was also increasing and reached 2,8 % (Fig. 2, curve 4).

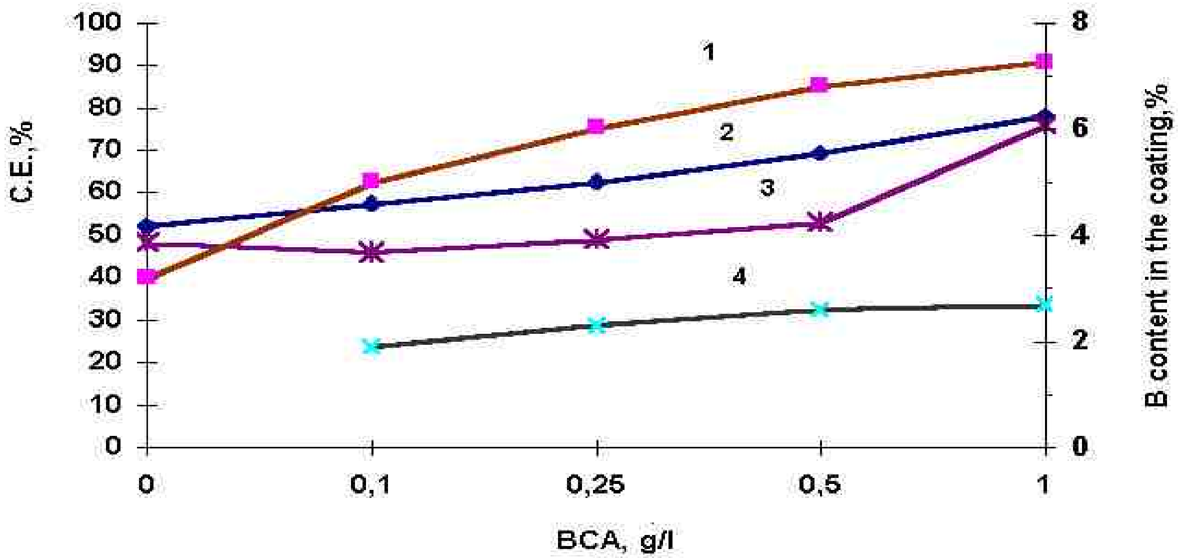

Fig.2. Dependence of C.E. on DCA in the solution (20 g/l) at current density (A/dm^2);
1. *–0.5; 2. – 0.75; 3. –1.0; 4. –Dependence of B content in the coatings on BCA content in the bath.*

Hardness of Ni deposits, obtained from the ammonia-citrate bath is around 600 kg/mm^2, that is much higher than hardness of deposits obtained from Watt’s bath (200-300 кг/мм^2). Increased hardness of coatings in the first case can be connected with the inclusion of carbon-containing decomposition products of citrate into the deposit. This effect is well known from the literature.

The hardness of Ni-B alloys is in its turn much higher than the hardness of Ni deposits. As it is seen from Fig. 3, the hardness of coating is 950 kg/mm^2 already at the lowest BCA concentration in the bath (0,1 g/l). With an increase of B content in the bath and, hence, in the coating, the hardness is a little higher and reaches 1000-1050 kg/mm^2 (Fig.3).

It is known, that the hardness of Ni deposits sharply reduces after heat treatment. The hardness of Cr coatings does not change after heat treatment up to 400 ^{0}C, and at higher temperature falls sharply (Fig. 4, curve 5). Unlike Ni and Cr, hardness of Ni-B alloy grows up with increasing temperature of heat treatment from 100 ^{0}C to 400 ^{0}C and only at higher temperature begins to reduce (Fig. 4, curves 1-4). Maximum hardness of about 1350 kg/mm^2 is reached at 400 ^{0}C (at BCA concentration 0,5 g/l), that is much higher than the hardness of Cr coatings (900-1000 kg/mm^2).

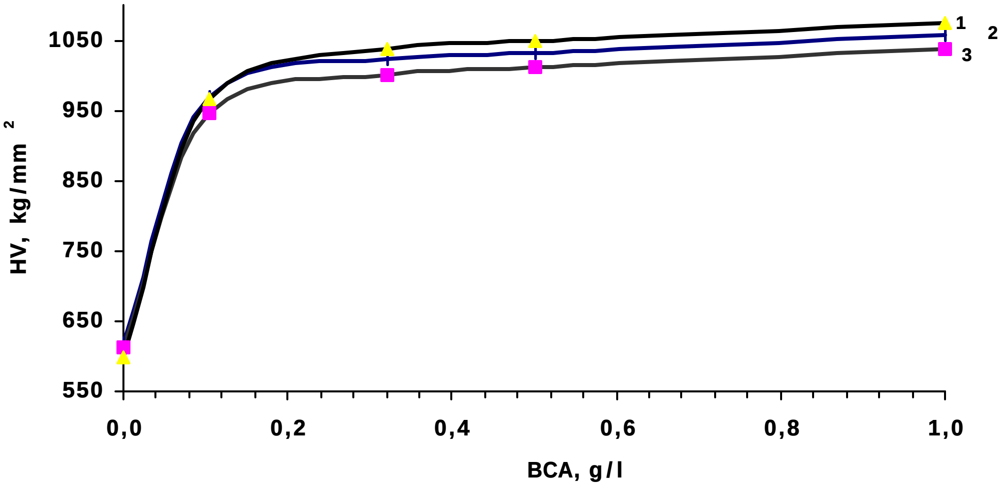

Fig. 3 Hardness of Ni-B coatings depending on BCA concentration in the solution: 1.- 0,5 A/dm^2 ; 2.-0,75 A/dm^2 ; 3.- 1,0 A/dm^2 .

Ni-B-SiC composite coatings turned to be the hardest ones (curve 6 in Fig.4), and even after heat treatment at 600°C their hardness was close to 1200 kg/mm^2.

The quality of Ni-B coatings surface after heat treatment depends on its temperature and BCA content. At BCA content in the bath 0,2 g/l the coating changes from bright to semi-bright. As a result of heat treatment and at the BCA content 0,5-1 g/l (400°) the coating remains still bright. With further increase in temperature the brightness of the coating gradually decreases. At 700-800°C the quality of a deposit is much worsened, its surface darkens and visible oxide film appears.

The porosity of Ni-B coatings is lower, than the porosity of Ni coatings (Table 3). As one can see from Table 3 Ni-B coatings at 2 µm thickness have insignificant porosity. Poroless Ni-B coatings were obtained at thickness 10 µm, while bright Ni coatings deposited from Watt's bath, were poroless only at 15-20 µm thickness. Lower porosity of Ni-B coatings corresponds to their better protective ability in comparison with deposits obtained from Watt's bath.

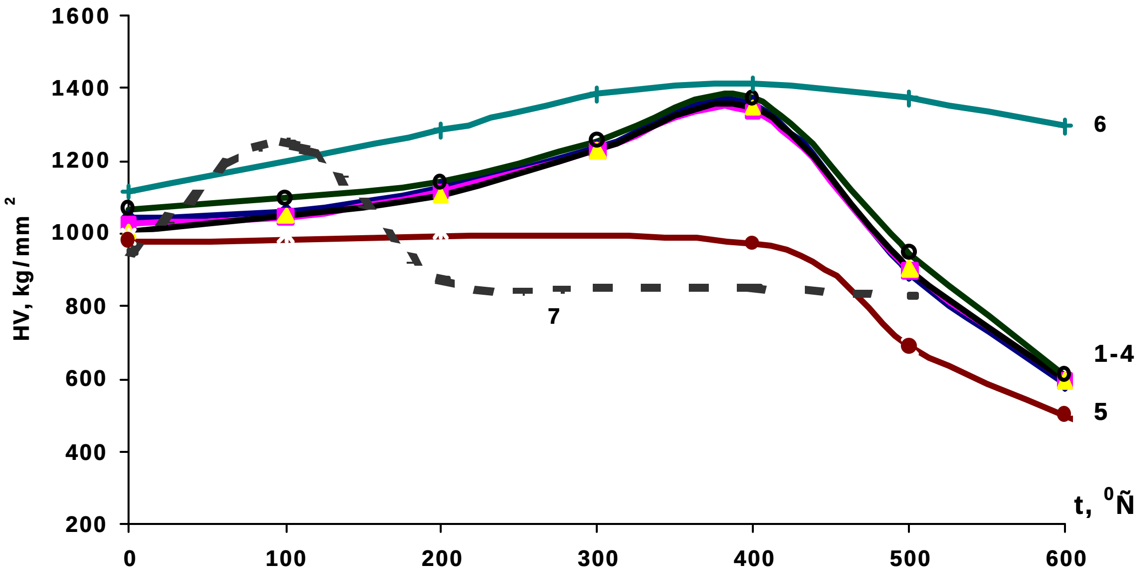

Fig.4 Hardness Ni-B coatings vs heat treatment temperature; 1.-0,5 A/dm ^{2} ; 2.-0,75 A/dm ^{2} ; 3.-1 A/dm ^{2} ; 4.-2 A/dm ^{2} ; 5.- Cr; 6.- Ni-B-SiC; 7.- Ni-UFD.

Table 3. Number of pores (N/cm^2) in Ni and Ni-B coatings.

Thickness	N-B	Watts
2	4,31	20
5	2,9	10
10	0,92	5

Ni-B alloy coatings have rather high corrosion properties in strongly agressive environments. Rate of their corrosion is much lower, than that of Cr and Ni coatings (Table 4). It is obvious, that higher corrosion resistance of Ni-B coatings in acid media is due to several factors. First of all, due to amorphization, increased structural uniformity of coatings and formation of corrosion-resistant intermetallic phases substances. Secondly, due to the interaction of these factors which results in accelerated transition of Ni-B coatings into passive state in acidic and other agressive environments and, accordingly, is responsible for the reduction of corrosion rate.

Table 4. Corrosion rate of coatings mm/year (gravimetry)

Conditions	Coatings		
	Cr	Ni-Watts	Ni-B (0,52)
25% HCl, 100°C	>2000	>14,00	4,90
25% H_2SO_4, 100°C	>2500	6,30	0,15

Conclusion

Experimental data have demonstrated much higher throwing power of citrate-ammonia baths for the deposition of Ni and Ni-B coatings in comparison with conventional acid baths. Hardness of Ni-B coatings is of the same order or even higher than that of chromium coatings and does not depend on current density while their porosity is lower than porosity of pure nickel coatings deposited from acid baths. Ni-B coatings have also higher corrosion resistance in aggressive media.

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