

Electroless and electrodeposition of nickel boron composites

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Abstract. It is shown that nickel boron composite coatings can be obtained by electroplating nickel from a bath containing dispersed boron particles. This deposit heated to 300°C forms Ni-Ni₃B composite. Further heating to 400°C converts it into Ni-Ni₂B composite. Mechanical properties, corrosion resistance and wear resistance Ni-Ni₂B composite are better than nickel or the electroless Ni-B composite in the as-deposited condition. The properties of heat-treated electroplated Ni-B composite are similar to that of heat-treated electroless Ni-B composites.

Keywords. Composite; electrocomposite; electroless deposition; electrodeposition.

1. Introduction

Nickel or its alloy coatings are recommended for many industrial applications because of their excellent corrosion resistance, chemical resistance, strength and oxidation resistance at high temperatures; unfortunately, the electroplated nickel coatings are not hard enough and hence cannot be used in applications where resistance to wear is the primary requirement. The electrodeposited nickel composite coatings developed in recent times, however, have proved themselves to combat wear in many industrial applications such as aircraft, automobile and other engineering industries.

A composite contains two or more substances which are blended together homogeneously, but which remains as separate entities in the structure and contribute to the property of the composite. Nickel composites with particulate matter as dispersed phase can be prepared by a variety of methods such as sintering, flame-spraying thermomechanical methods, electrodeposition processes etc.

Electroless or electrodeposition provides a very attractive method of coating composites, since it is a low temperature process and by the proper choice of bath composition and operating conditions the properties of the deposits can be tailored to the particular application. Of recent interest is the electroless deposition of Ni-B composite coatings for electronic and other engineering applications (Mallory 1971).

Auto-catalytic reduction of nickel with sodium borohydride or dimethyl amino borane was employed in the past to get coatings of Ni-B composite (Narcus 1967; Gorbunova *et al* 1973; Mallory 1971; Long and Gonnella 1971). There has been very few attempts (Indira Rajagopal *et al* 1980) to get Ni-B composite by electroplating. In this paper, the results of our study to compare the Ni-B composite coatings obtained both by electroplating and electroless deposition from a borohydride bath are discussed.

2. Experimental

Electroless deposition experiments were carried out in a thermostated bath maintained at $90 \pm 1^\circ\text{C}$ using 75×25 mm mild steel (MS) coupons. A mechanical stirrer was

employed to agitate the solution. The bath composition is shown in table 1.

The coupons were weighed after degreasing, cathodically cleaned in an alkaline phosphate solution and electroless-plated. The increase in weight due to deposition was then recorded.

Electroplating experiments were carried out with a nickel bath of composition as shown in table 1 and the required amount of amorphous boron powder (particle size 2–5 μ) was dispersed by agitating the same with ultrasonic waves generated by a piezoelectric ultrasonic generator (Vibronics Model VPL-P1). An intensity of 0.3 W/cm² was employed. The ultrasonic waves not only kept the particles in suspension but also prevented the formation of agglomerates. The temperature of the bath was kept at $50 \pm 1^\circ\text{C}$. Nickel anodes enclosed in terylene bags were used. Mild steel was employed as cathode. Standard electroplating procedure was used. Thickness and rate of deposition were calculated from weight gain data.

Hardness was measured by the conventional Vickers pyramid diamond indenter using microhardness testing attachment to Neophat 2. In all cases a load of 50 g was used but when the measured hardness was more than 1000 vPN, the results were checked at 70 g load. The measurements were all made on cross-sections of deposits which had been mounted with epoxy resin cured at room temperature. Micro indentations were sufficiently small to avoid errors due to finite boundary. Each hardness value was the average of six measurements. The effect of heat treatment on hardness was studied by heating the specimens in air and withdrawing them from the oven after the required soaking time and cooling in air. Hardness values were reproducible to within ± 50 vPN.

Each deposit was analysed for nickel and the resulting boron content from the electroplated nickel-boron coatings was confirmed by weighing the residue of B after dissolving the nickel in 60% nitric acid.

X-ray diffractograms were obtained with a Philips x-ray unit (PW 1010) using CuK α radiation.

Tensile tests were carried out using specimens cut from 250 μ thick electroformed Ni-B composite plates. The strain rate was 2.54 mm per min and the tensile strength values were reproducible to within 2%.

For metallographic studies, electroless or electroplated Ni-B deposits were mounted in epoxy resin, using room temperature for curing, after suitable backing with copper. The deposit was etched in 1:1 acetic acid-nitric acid mixture.

Table 1. Bath composition and operating conditions

(a) Electroless Ni-B coatings		(b) Electroplated Ni-B coating	
Nickel sulphate (gpl)	30	Nickel sulphamate	250
Sodium citrate (gpl)	40	Nickel chloride (gpl)	10
EDTA (tetrasodium salt (gpl)	100	Boric acid (gpl)	20
Sodium borohydride (gpl)	1	Amorphous boron powder (gpl)	10
Sodium hydroxide (gpl)	40	AU size	3–5
Lead acetate (gpl)	0.05	C.D. (Amp/dm ²)	3
pH	14	Temperature	50°C
Temperature (°C)	90	pH	4
Rate of deposition	20 μ /hr	Rate of deposition	50 μ /hr

The wear resistance of the Ni-B deposits was estimated by determining the loss of material per unit time by a jet of abrasive powder.

The corrosion resistance was evaluated by counting the number of rust spots, seen at low magnification, on the sample immersed in 3% sodium chloride solution for 24 hr.

3. Results

3.1 Deposit composition

The nickel deposits formed by chemical reduction with sodium borohydride are alloys of nickel and boron. Nickel and nickel boride were the main phases. The composition of the deposit was a function of pH and bath composition. Under the conditions stated in table 1, the deposits obtained were found to contain 4% B. The boron content of the deposit was essentially independent of the thickness of the deposit. The electro-deposited Ni-B composite coating contained Ni + elemental boron which on heat treatment gave rise to various nickel boride phases. The boron content depended on the amount of boron powder dispersed in the bath and the deposition conditions. The conditions specified in table 1 gave a boron content of 6%.

3.2 Solderability

The Ni-B deposits are readily soldered with non-corrosive resin base fluxes. No activation treatment is necessary and the deposit is easily soldered. The electrical resistivity of heat-treated Ni-B composite coatings was similar to the electroplated nickel and was of the order of 10 Ω cm.

3.3 Tensile strength

Data on tensile strength of electroless Ni-B composite is given in table 2 and that corresponding to electroplated Ni-B composite coating is given in table 3. It is seen that in both cases UTS increases on heating the deposit to 400°C. Although it is known (Graham *et al* 1965) that the tensile strength of electroless Ni-P composite increases after heat treatment, the strength of electroless Ni-B composite coatings has not been studied.

In electroplated composite an increase in UTS of the deposit, in the as-plated condition, is noticed with increase in current density (CD). A similar trend is also seen in pure nickel deposit. Irrespective of the CD at which the composite is plated, the strength of the heat-treated deposit is the same.

Table 2. Mechanical properties of electroless Ni-B composite.

Tensile strength	as-deposited	Heat-treated at 400°C for 1 hr
(kg/mm ²)	40	75
% elongation	2	1.0
Hardness (kg/mm ²)	600	900
Internal stress (kg/mm ²)	20	—

3.4 Hardness

Both electroless and electroplated Ni-B composite coatings exhibit similar behaviour in respect of hardness. In the as-deposited condition they show a hardness of 500–700 VPN at 500°C and the hardness then decreases at higher temperatures (tables 4 and 5). Deposits heated to 800°C exhibit nearly the same hardness as that of samples not treated at all. The results on hardness of electroless Ni-B composite agree with those of Mallory (1971), Gorbunova *et al* (1973).

Table 3. Effect of c.d. on tensile strength of electrodeposited Ni-B coatings (boron 6%).

System	C.D. (A/dm ²)	Tensile strength as plated (kg/mm ²)	Tensile strength after heat treatment at 400°C kg/mm ²
Ni from Niσ bath	1	30	25
	2	35	25
	3	40	28
	4	40	30
	5	44	35
Ni + B from Niσ bath	1	50	70
	2	57	74
	3	59	74
	4	63	75
	5	63	75

Table 4. Effect of heat treatment on hardness of electroless Ni-B coating (boron 4%).

Temperature	Microhardness (VPN)	Temperature	Microhardness (VPN)
30	600	600	1000
100	800	700	800
200	900	800	500
300	1050	900	350
400	1100		
500	1100		

Table 5. Effect of heat treatment on hardness and tensile strength of electroplated nickel-boron composite (6% boron).

Temperature	Microhardness (VPN)	Tensile strength (kg/mm ²)	% Elongation
R.T.	600	50	2
100	550	55	1.5
200	600	60	1.3
300	780	62	1.3
400	950	70	1.1
500	1100	72	1.0
600	1000	70	1.0
700	700	58	1.8
800	450	38	5

3.5 X-ray studies

The electroless nickel-boron coating does not give any x-ray diffraction pattern indicating that the deposit is either amorphous or has grain size smaller than the coherent scattering domain size of x-rays. On heating the sample to 300°C x-ray studies revealed the presence of Ni and Ni₃B. The samples heated to 425°C show the presence of Ni and Ni₂B. These results agree with those reported by Gorbunova and Nikiforova (1963).

Electroplated Ni-B composite containing 6% B (in the as-plated state) gives an x-ray diffraction pattern corresponding to nickel. No pattern of B or any of nickel boride is seen. However, the x-ray diffraction pattern of electroplated Ni-B composite reveals Ni₃B and Ni₂B phases after heating respectively to 300 and 425°C. Even though the electroless and electroplated compositions differ in their x-ray structure in the as-deposited state, their x-ray structure, qualitatively speaking, is similar after heat treatment. The Ni₃B and Ni₂B content which increases with boron content is as high as 20% by weight in electroplated composite.

3.6 DTA studies

Electroless Ni-B composite shows exothermic peaks at 300, 400 and 425°C which agrees with the results of Gorbunova *et al* (1973) for Ni-B coatings obtained from a borohydride bath of a composition different from the one reported here. Similar exothermic peaks are also noticed in the DTA of electroplated Ni-B composite.

On comparing these observations with the x-ray diffraction results the peaks at 300 and 425°C appear to be due to the formation of Ni₃B and Ni₂B. X-ray diffractograms of deposits heated to 400°C are similar to those heated to 300°C. Hence the peak at 400°C may not be due to any new phase formation. However, its origin is not clear.

3.7 Corrosion resistance

Electroless and electroplated Ni-B composite coatings stand corrosion better than electroplated nickel due to immersion in 3% NaCl solution. Both electroless and electroplated Ni-B composites when heated to 400°C exhibit much better corrosion resistance than the as-plated Ni-B coatings. This could be due to the presence of Ni₂B phase which might bring down the local corrosion current density. No sign of corrosion spots is observed on the heat-treated Ni-B deposits even after immersion for 100 hr, whereas corrosion spots were observed for electroplated nickel of similar thickness (10 μ) after 20 hr of immersion test.

Although it is generally believed that electroless nickel deposits resist corrosion better due to lower porosity (Mallory 1974; Stephen *et al* 1981), corrosion resistance has been studied only on Ni-P deposits. It has been pointed out that in Ni-P deposit, corrosion resistance improves on heating (Vojtiskova 1961). However the improvement in corrosion resistance brought about by heating Ni-B composite coating is reported here for the first time.

3.8 Abrasion resistance

The abrasion resistance of heat-treated (400°C) electroless and electroplated Ni-B composite coating is 3×10^{-4} mm³/hr as against 25×10^{-4} mm³/hr in the case of plated nickel.

3.9 Microstructure

The electroless Ni-B coating showed a lamellar structure as seen in figure 1. This seems to arise from the periodic change in the ratio of nickel to boron caused by pH changes near the substrate. At 400°C heating, the structure remained the same, except that the laminations became broad and pronounced. The laminations could not be seen after 800°C heating and the microstructure revealed typical grain pattern. Such a banded structure for electroless nickel boron deposit has been reported by Gorbunova *et al* (1973).

In the electrodeposited Ni-B coatings, the microstructure revealed a matrix with included particles (figure 2). In figure 3, the microstructure of Ni-B composite plated with ultrasonic agitation is shown. Comparing the two microstructures, it is seen that ultrasonic agitation has minimised the agglomeration of boron particles. Figure 4 shows the microstructure of electroplated Ni-B composite heated to 450°C and

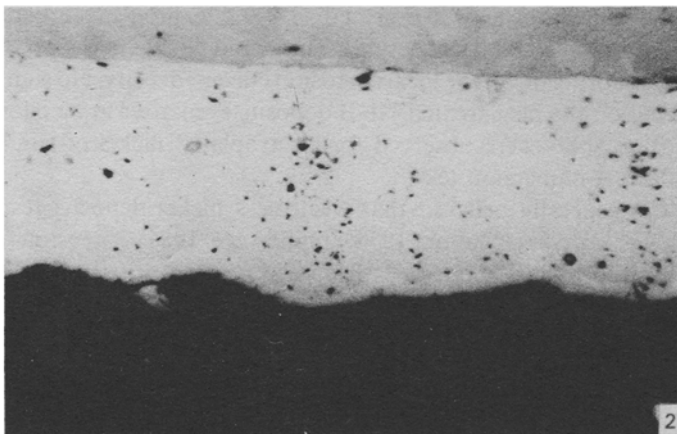
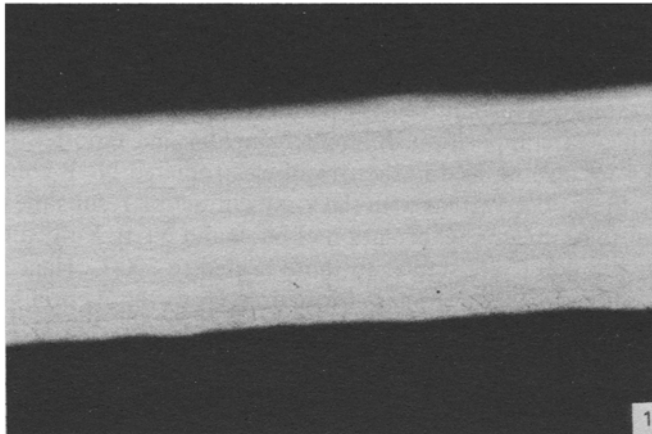


Figure 1. Cross-section of electroless Ni-B deposit ($\times 400$).

Figure 2. Cross-section of electroplated Ni-B composite deposited without ultrasonic agitation ($\times 500$).

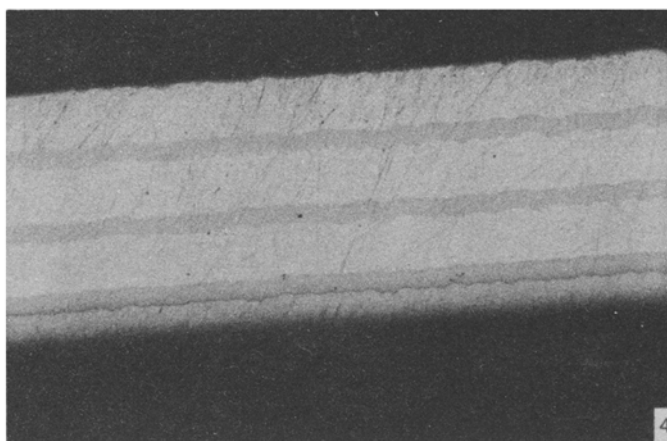
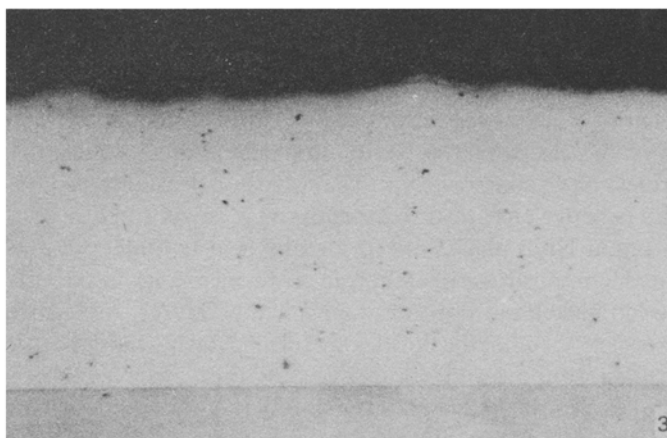


Figure 3. Cross-section of electroplated Ni-B composite deposited with ultrasonic agitation ($\times 500$).

Figure 4. Cross-section of electroplated Ni-B composite heat treated at 450°C for 3 hr ($\times 500$).

laminations similar to those exhibited by electroless Ni-B composite are seen in the heat treated sample.

3.10 Adhesion

Adhesion of electroless or electrodeposited Ni-B composite coatings is excellent in various substrates if proper cleaning procedures are employed. Adhesion in steel is better than 344.75 MPa as confirmed by the shear adhesion test (Dini and Johnson 1977). An improvement in adhesion is seen after heat treatment. This may be due to further strengthening of adhesion by diffusion.

3.11 Internal stress

Internal stress of electroless and electroplated Ni-B coating was measured using the stress meters developed by Rajagopalan *et al* (1981).

4. Discussion

The results presented above show that (i) the mechanical properties such as hardness and tensile strength are improved when the deposit is heated at 400–500°C. (ii) The tensile strength of the electroplated Ni–B composite is greater than that of the as-deposited electroless Ni–B composite. (iii) The corrosion resistance of both the types of Ni–B composites is better after heat treatment. (iv) X-ray diffraction and DTA studies reveal that Ni₃-B and Ni₂B phases are formed by heat treatment.

In electroplated composite, nickel boride is formed as a result of a chemical interaction between nickel and boron at higher temperatures. As regards electroless composite it is not clear whether the borides are formed during the deposition or during the heat treatment. Gorbunova and Nikiforova (1963) also observed these phases in the heat-treated samples. However, there is a possibility that the borides may form during the deposition if the mechanism suggested by Schoenberg (1971) is true.

Whatever be the origin of nickel borides, the experimental results on electroless Ni–B composite so far published and presently reported as well as the present results on electroplated Ni–B composites demonstrate that borides improve mechanical properties. This may be understood in terms of strengthening due to dispersion of precipitation. However, the improvement in strength noticed in electroplated Ni–B composite (in the as-plated condition) is difficult to understand in terms of the same mechanism because the particles are coarse.

Comparing the properties of Ni–B composites formed by electroless and electroplating technique, it is seen that they are similar. For deriving the maximum benefit both the types of composites have to be heat-treated.

In electroless deposition of Ni–B one notices that only 75% of the borohydride consumed is effective in bringing about the reduction of nickel ions. Twentyfive percent of the borohydride consumed produces only hydrogen and sodium perborate. This is an unwanted side reaction leading to the accumulation of NaBO₂ which has a deleterious effect on the rate. The solution is susceptible to spontaneous decomposition due to lowering of pH or formation of catalytically active particles. Because of the high operating pH of the bath, substrates like Al, Mg, Zn etc., cannot be plated. Besides these limitations, it is not easy to vary the boron content of the deposit. None of these limitations is exhibited by the electroplating process in the formation of composite. The bath is operated at a pH of 4 and is very stable. Deposits with boron content at any level from 0–20% can be produced. In view of these advantages, and the fact that the properties of electroplated Ni–B composite are as good or even better than electroless Ni–B coatings, it is clear that electroplating would be a preferred method for getting Ni–B composites. The results presented here demonstrate that newer types of composites could be prepared by electroplating and subsequent heat treatment. Using this idea, metal-metal boride, metal-metal phosphide composites have been prepared and the results will be reported elsewhere.

Acknowledgements

The author sincerely thanks Prof. S Ramaseshan, for many stimulating discussions without which this work would not have been possible. Thanks are due to Miss S Usha Devi, Dr V Srinivasan and Mr Lakshminarasimham for assistance in x-ray diffraction, tensile strength and DTA data.

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