

# Studies on development of electroless Ni–B bath for corrosion resistance and wear resistance applications

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Electroless deposition process has undergone numerous changes to meet the challenging needs for a variety of industrial applications ever since the invention of the process during 1947. Among the various metals that can be electrolessly plated, electroless nickel has proved its supremacy for producing coatings with high corrosion resistance, hardness, wear resistance and uniformity. Electroless nickel can be deposited from a variety of baths and the coating properties depends upon the type of reducing agents and other deposition conditions. Electroless nickel–boron coatings have received considerable interest nowadays because of the superior hardness, corrosion and wear resistance characteristics. In this paper, the authors have reported on the development of a biodegradable electroless Ni–B bath and evaluated its characteristic properties. The influence of bath constituents, temperature and pH on the rate of deposition was studied. Scanning electron microscopy, X-ray diffraction, X-ray fluorescence spectroscopy and atomic absorption spectroscopy techniques were employed to find out the deposit morphology and boron content in the deposits. The hardness and wear resistance of the deposits were evaluated in the as deposited and heat treated conditions. The influence of sodium hypophosphite as reducing agent on the Ni–B deposit has also been studied. The use of nickel methane sulphonate as the metal ion source increases the bath lifetime without adversely affecting the deposit qualities. Annealing the Ni–B deposit at 400°C for one hour resulted in an increase in the hardness and thereby the wear resistance. The corrosion resistance of as plated electroless Ni–B deposit is higher than the heat treated deposits. Also, the corrosion resistance is highly enhanced by the incorporation of phosphorous to the nickel–boron alloy coating.

**Keywords:** Electroless deposition, Chemical deposition, Nickel boron alloy deposition, Nickel boron phosphorous alloy deposition, Corrosion resistance, Nickel methane sulphonate

## Introduction

Metal deposition from aqueous solutions can broadly be classified into two categories: electrolytic and electroless plating.<sup>1,2</sup> Electrolytic plating is based on the cathodic discharge of the metal ions. Electroless plating is a chemical reduction process, which depends upon the catalytic reduction of a metal ion in an aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy. The basic chemical reactions for electroless plating are given by the following equations<sup>3</sup>



where ‘R’ indicates the reducing agent and ‘Me’ indicates the metal to be deposited on the substrate.

Among the various types of electroless plating, electroless nickel has gained immense popularity due to its ability to provide a uniform, hard, wear and corrosion resistant surface.<sup>3–5</sup> Hypophosphite reduced electroless nickel plating has received widespread acceptance and attention has now shifted towards borohydride reduced electroless nickel deposits in the recent years. For the electroless plating of Ni–B alloy, sodium borohydride and dimethylamineborane are commonly used as reducing agents. But the reduction efficiency of sodium borohydride is much higher than that of dimethylamineborane and sodium hypophosphite.<sup>6</sup> Also, borohydride reduced baths are preferred

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more than dimethylamineborane based baths in terms of cost effectiveness of operation.<sup>7</sup>

Electroless nickel–boron plating is utilised by the aerospace, automotive, chemical and electrical industries mainly due to its excellent solderability and lubricity, high hardness, high wear and abrasion resistances.<sup>8</sup> The principal advantages of borohydride reduced electroless nickel deposits are its high hardness and superior mechanical wear resistance in the as deposited condition. Electroless Ni–B coatings are more wear resistant than tool steel and hard chromium coatings and it can replace gold in electronic industries.<sup>6</sup> The columnar structure of electroless nickel–boron coatings is useful in retaining lubricants under conditions of adhesive wear. Electroless Ni–B coating possess good solderability compared to electroless Ni–P coating because its oxide layer is thin and thus can be penetrated by the solder.<sup>9</sup> Besides electroless Ni–B coating also received considerable importance in the copper interconnects technology, due to its ability to act as a capping layer to prevent the diffusion of copper.<sup>10–12</sup>

To suit the rapid changing needs of engineering industries and various other industries, it is necessary to develop coatings that possess high hardness, good wear and abrasion resistance and good corrosion resistance, and one such coating which seems promising is the borohydride reduced electroless nickel coating. In this perspective, the present work aims to study the formation and characterisation of borohydride reduced electroless nickel deposits.

Experimental

Sample fabrication process

Copper panels (5 × 5 cm) and mild steel panels (10 × 10 cm) were used as substrates. The copper panels were mechanically polished, degreased, cleaned with washing powder to obtain a wet surface, and then dried using an air drier. The weight of the panel was determined using an electronic balance. The panels were then activated in palladium chloride solution. After activation, the panels were washed well, rinsed and subjected to electroless plating. The weight of the panel was noted after electroless plating. From the difference in the two weights, the coating thickness was calculated. The mild steel panels were subjected to acid dip initially. The same procedure is followed for mild steel panels except for activation in palladium chloride.

The influence of bath constituents, temperature and pH on the rate of deposition was studied. The optimised chemical composition of the plating bath employed and its operating conditions are given in Table 1.

Table 1 Chemical composition and operating conditions of borohydride reduced electroless nickel plating bath

Bath composition	
Nickel as methane sulphonate	6 g L <sup>-1</sup>
Sodium borohydride	1.2 g L <sup>-1</sup>
Ethylene diamine	60 mL L <sup>-1</sup>
Sodium hydroxide	90 g L <sup>-1</sup>
Ethylene thiourea	0.2 mg L <sup>-1</sup>
Operating conditions	
pH	13
Temperature, °C	95

The bath was subjected to mechanical agitation. The temperature of the bath was maintained through a heater and relay system. The pH of the solution was frequently monitored using a pH meter and the pH was controlled by suitable addition of sodium hydroxide. The constituents of the bath nickel methane sulphonate and sodium borohydride were properly replenished depending upon the residual nickel content in the solution. Sodium borohydride was analysed by iodometric titration. The nickel content was analysed by EDTA complexometric titration.

The influence of sodium hypophosphite as reducing agent on the Ni–B deposit has also been studied. Sodium hypophosphite was analysed by iodometric titration.

Sample characterisation

The following characterisation methods were employed in order to determine the deposit morphology and the physical properties of the selected electroless deposits:

- (i) the surface morphology of the electroless Ni–B coatings was assessed using scanning electron microscopy (SEM)
- (ii) the precipitated phase of the deposit was analysed by X-ray diffraction (XRD)
- (iii) X-ray fluorescence spectroscopy and atomic absorption spectroscopy techniques were employed to find out the nickel content and boron content in the deposits
- (iv) Vickers microhardness measurements were carried out on selected electroless Ni–B deposits by employing 50 gf load
- (v) wear resistance measurements were made by Taber Abraser with a load of 1 kg for about 2000 cycles on the plated as well as heat treated (400°C for 1 h) surfaces
- (vi) the corrosion resistance characteristics of the selected electroless deposits were evaluated by potentiodynamic polarisation and electrochemical impedance studies in 3.5% NaCl solution. An electrochemical cell comprising of saturated calomel electrode as the reference electrode, platinum foil as the counter electrode and the electroless nickel plated panel as the working electrode was employed. The corrosion current density ( $i_{\text{corr}}$ ) and the corrosion potential ( $E_{\text{corr}}$ ) were determined by Tafel extrapolation method. The charge transfer resistance ( $R_{\text{ct}}$ ) and double layer capacitance ( $C_{\text{dl}}$ ) were determined from the Nyquist plot by fitting the data as a semicircle where the  $x$  axis represents the real part of the impedance.

Results and discussion

Effect of coating bath constituents on rate of deposition

In the electroless deposition of nickel–boron alloy using sodium borohydride as the reducing agent, the bath must be operated at highly alkaline conditions (pH>12), since borohydride hydrolyses readily in acidic or neutral solutions. This requires the addition of higher concentration of alkali, which in turn necessitates the presence of an effective complexing agent in the bath. Ethylene diamine is the most preferred complexing agent for nickel ions in the electroless plating bath.<sup>13–16</sup> McComas<sup>17</sup> suggested a combination of

**Table 2 Effect of ethylenediamine (complexing agent) on rate of deposition**

Concentration of ethylenediamine, mL L <sup>-1</sup>	Rate of deposition, μm h <sup>-1</sup>
40	3.1
60	20.2
80	11.9
100	10.4

ethylenediamine, water soluble salts of tartaric acid and ammonia as the most preferred one for electroless nickel plating bath. Citrate and tartrate based complexing agents have also reported in many electroless plating baths. In the present work, ethylenediamine has been used as the complexing agent. The effect of ethylenediamine on the rate of Ni–B deposition is given in Table 2. At 60 mL L<sup>-1</sup> of ethylenediamine concentration, the rate of Ni–B deposition was maximum. Hence, the concentration of ethylenediamine has been optimised to 60 mL L<sup>-1</sup>.

Borohydride reduced baths are highly susceptible to decomposition in the absence of a suitable stabiliser. Hence, stabilisers are necessary to control the reduction reaction and prevent solution breakdown by shielding catalytically active nuclei. Stabilisers such as thallium nitrate<sup>18</sup> and thallium acetate<sup>14,19</sup> are highly efficient. But due to its toxicity, it can be replaced by ethylene thiourea which has been used as the stabiliser in the present study.

Table 3 gives the effect of concentration of sodium borohydride (reducing agent) on the rate of deposition. From the table, it can be seen that the rate of deposition increased with an increase in the concentration of reducing agent. However, at a concentration of 2.0 g L<sup>-1</sup> of sodium borohydride (NaBH<sub>4</sub>), the electroless bath decomposed. The concentration of sodium borohydride in the bath has been optimised to 1.2 g L<sup>-1</sup>.

Table 4 shows the effect of temperature on the rate of deposition. No deposit has been observed up to 50°C. Upto 80°C, there was no marked variation in the rate of deposition. Above this temperature, the rate of deposition increased significantly upto 100°C. The bath was operated at an optimum temperature of 95°C.

Table 5 gives the effect of pH on the rate of deposition. Borohydride ions hydrolyse readily in acid or neutral solutions. Hence borohydride reduced baths must be operated at highly alkaline conditions. A good rate of deposition of 20 μm h<sup>-1</sup> and above is observed at a pH equal to 13 and 14. Hence increasing the bath

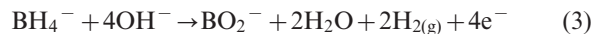
**Table 3 Effect of reducing agent (NaBH<sub>4</sub>) on rate of deposition**

Concentration of sodium borohydride, g L <sup>-1</sup>	Rate of deposition, μm h <sup>-1</sup>
0.4	2.3
0.6	10.8
0.8	11.9
1.0	16.5
1.2	20.2
1.4	22.1
1.6	23.7
1.8	25.1
2.0	Bath decomposed

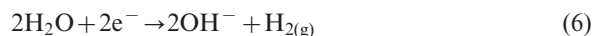
pH increases the rate of deposition. An optimum pH of 13 has been used for the present study.

pH of the solution has a great effect on the rate of deposition. To obtain a uniform deposit, it is necessary to keep the pH constant throughout the deposition process. In the electroless deposition of nickel–boron alloy using sodium borohydride as the reducing agent,<sup>3,5</sup> two simultaneous reactions i.e. oxidation and reduction are taking place on the catalytic surface.

Borohydride oxidises as given in the following reactions during electroless deposition



In the reduction process, two competing reactions occur, i.e. nickel ion reduction and hydrogen ion reduction. Reduction of nickel ion occurs through electrons produced by the interaction of borohydride with hydroxide ions. The reactions involved are as follows



For the optimised chemical composition and operating conditions of the electroless bath, the rate of nickel–boron deposition was 20.2 μm h<sup>-1</sup>.

Table 6 gives the effect of sodium hypophosphite as reducing agent on the rate of Ni–B deposition. It can be seen from the table that there is no marked variation in the rate of deposition from 8 to 12 g L<sup>-1</sup> of sodium hypophosphite concentration. Hence, the concentration of sodium hypophosphite in the bath has been optimised

**Table 4 Effect of temperature on rate of deposition**

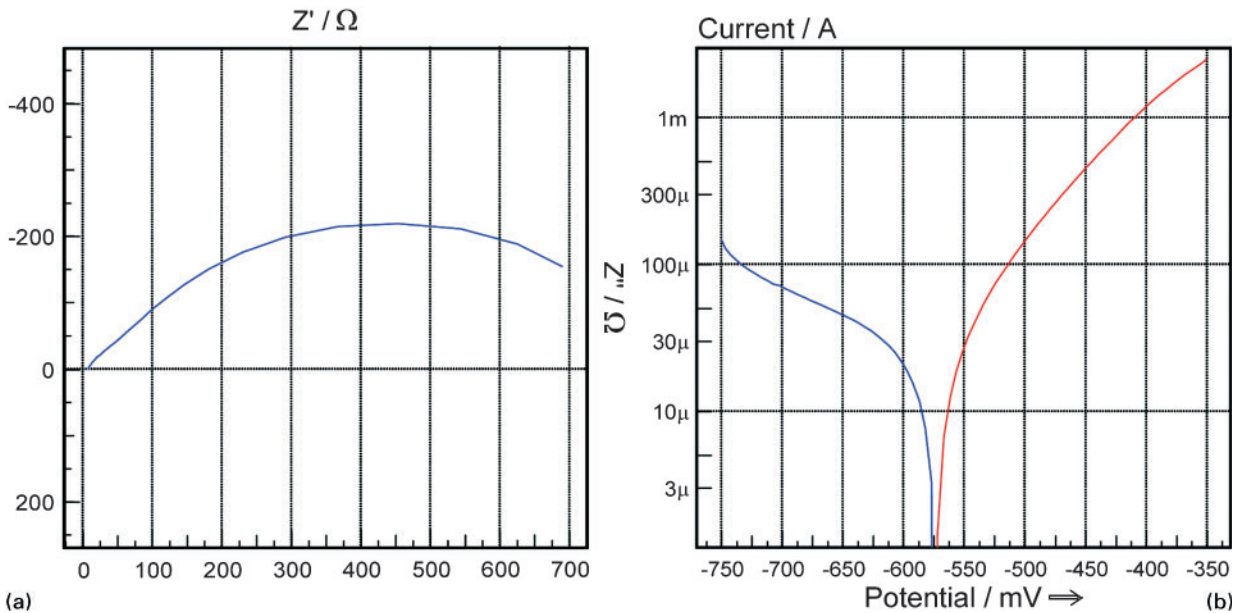
Temperature, °C	Rate of deposition, μm h <sup>-1</sup>
35	Nil
40	Nil
50	Nil
60	1.9
70	2.5
80	2.6
90	12.4
95	20.2
100	22

**Table 5 Effect of pH on rate of deposition**

pH	Rate of deposition, μm h <sup>-1</sup>
12	0.4
13	20.2
14	25.1

**Table 6 Effect of sodium hypophosphite on rate of deposition**

Concentration of sodium hypophosphite, g L <sup>-1</sup>	Rate of deposition, μm h <sup>-1</sup>
4	19.4
8	20.1
10	20.1
12	20.2
16	22.2
20	23.1



1 Nyquist plot for as plated Ni–B deposit and *b* polarisation curve for as plated Ni–B deposit

to 10 g L<sup>-1</sup> and the rate of Ni–B–P deposition was 20.1 μm h<sup>-1</sup>.

Hardness and wear resistance characteristics

Table 7 gives the values of hardness and wear resistance of the plated as well as heat treated Ni–B coatings. The hardness of the as deposited Ni–B coating is 682 VHN under a load of 50 gf. Very high hardness values can be attained by applying appropriate heat treatments to the Ni–B deposit.<sup>3,5,20</sup> Thus, the heat treatment of the Ni–B deposit at 400°C for one hour hardened the deposit to a value of 1102 VHN. The increase in hardness is due to the precipitation of the Ni<sub>3</sub>B phase leading to the phenomenon of precipitation hardening. The values of wear resistance were taken by a Taber Abraser with a load of 1 kg for about 2000 cycles. The wear resistance is expressed in terms of weight loss in grams. It can be noted from the table that the wear resistance of the heat treated Ni–B deposit is greater than the as plated Ni–B deposit. Hence, optimum values of hardness and wear resistance can be obtained after annealing the coatings at 400°C for one hour.

Corrosion characteristics

Table 8 gives the values of corrosion current density (*i*<sub>corr</sub>) and the corrosion potential (*E*<sub>corr</sub>) of the electroless coatings, in 3.5% NaCl solution, calculated using Tafel extrapolation method. Nyquist plots are also

obtained for the electroless deposits. From the Nyquist plot, the values of charge transfer resistance (*R*<sub>ct</sub>) and double layer capacitance (*C*<sub>dl</sub>) are obtained as given in Table 8. From the table, it is evident that the corrosion resistance of as plated electroless Ni–B deposit is higher than the heat treated deposits. The amorphous nature of the Ni–B deposit imparts higher corrosion resistance in the as plated condition. As evidenced by XRD, heat treatment induces the crystallinity of deposits, which in turn increases the grain boundaries, which are active sites for corrosion attack. It can also be noted that the higher the concentration of sodium hypophosphite in the bath, the higher the corrosion resistance. The Nyquist plot and Tafel polarisation curve of the as plated Ni–B deposit are given in Fig. 1*a* and *b* respectively. The Nyquist plot and polarisation curve of Ni–B–P deposit for 20 g L<sup>-1</sup> of sodium hypophosphite in the bath are given in Fig. 2*a* and *b* respectively.

Surface topography

Scanning electron microscopy photomicrographs (Figs. 3 and 4) were taken at a magnification of 500 × and 1000 × for the as plated and heat treated samples. The as plated Ni–B coatings appear semibright, whereas the heat treated Ni–B coatings are matte in appearance and dark grey in colour. The morphology resembles a relatively uniform Ni–B deposit with a typical

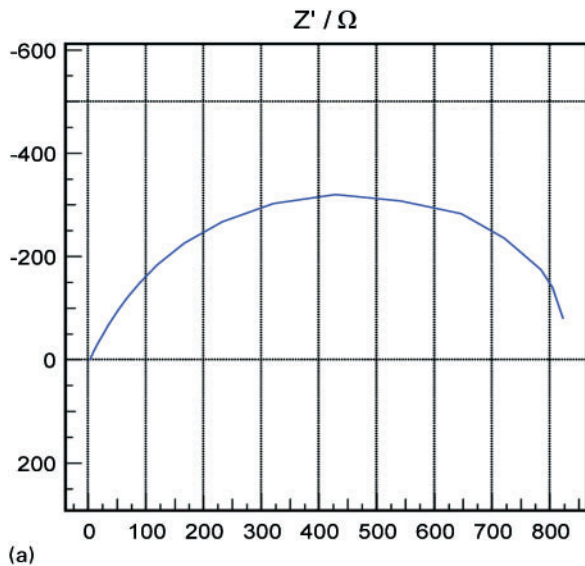
Table 7 Studies on hardness and wear resistance of coating

System studied	Vickers hardness (load 50 g), VHN	Weight loss (load 1 kg), g
Ni–B (As plated)	682	0.0109
Ni–B (Heat treated to 400°C for 1 h)	1102	0.0062

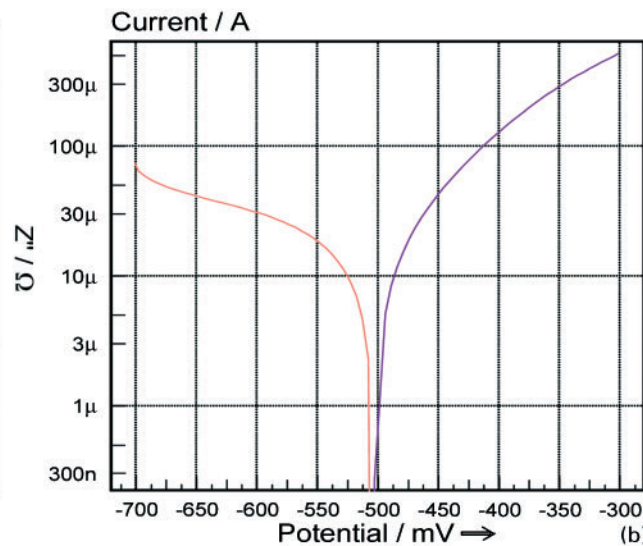
Table 8 Corrosion characteristics

System studied	<i>i</i> <sub>corr</sub> , μA cm <sup>-2</sup>	<i>E</i> <sub>corr</sub> , mV	<i>R</i> <sub>ct</sub> , Ω cm <sup>2</sup>	<i>C</i> <sub>dl</sub> , × 10 <sup>-4</sup> F cm <sup>-2</sup>
Ni–B (as plated)	13.2	–568.4	866.7	6.81
Ni–B (heat treated)	14.7	–576.1	793.8	7.435
Ni–B–P (4 g hypophosphite in the bath)	10	–570.6	831.7	1.628
Ni–B–P (20 g hypophosphite in the bath)	9.22	–503.7	883.3	1.533



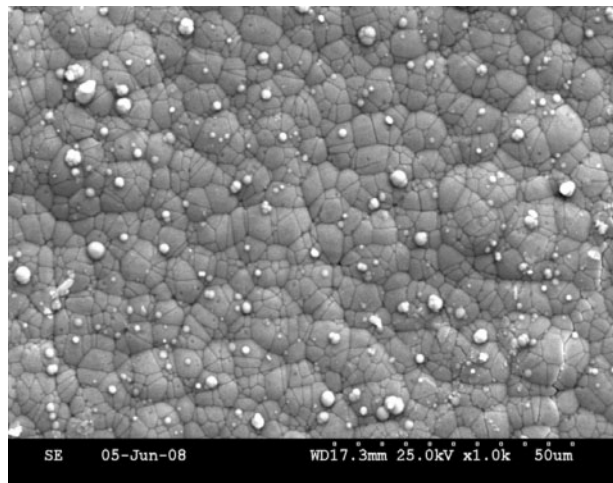


(a)



(b)

- 2 Nyquist plot for Ni-B-P deposit ( $20 \text{ g L}^{-1}$  of sodium hypophosphite) and *b* polarisation curve for Ni-B-P deposit ( $20 \text{ g L}^{-1}$  of sodium hypophosphite)

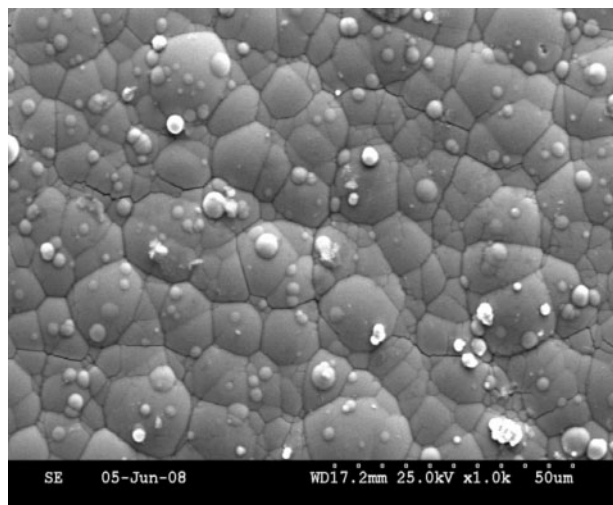


- 3 Photograph (SEM) of as plated electroless Ni-B at  $1000\times$

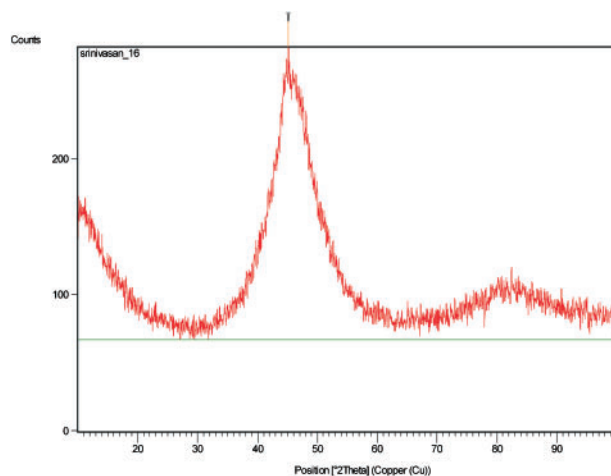
cauliflower like structure, characteristic of electroless plated nickel coatings. This kind of surface morphology is responsible for the lubricious characteristics of Ni-B coatings.<sup>15,21</sup>

### XRD studies

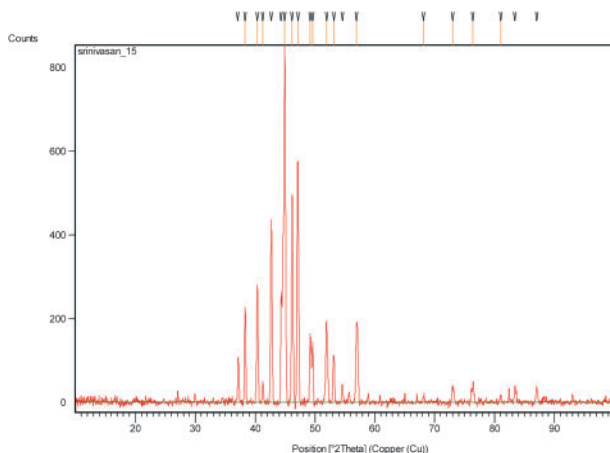
The XRD pattern studies of as plated and heat treated electroless Ni-B deposits is well reported in literature.<sup>14,16,21,22</sup> From the XRD pattern (Fig. 5), it has been noted that the electroless Ni-B coating in the as plated condition is amorphous in nature except for a fine crystallite of nickel. A curve corresponding to boron is observed along with the peak for nickel, which confirms the presence of boron in the alloy coating. The appearance of various sharp peaks in the XRD pattern of heat treated electroless Ni-B coatings (Fig. 6) indicated a rapid crystallisation of the Ni-B alloy coating. On annealing, prominent peaks of  $\text{Ni}_3\text{B}$  phase appeared along with Ni peaks for Ni-B coatings.



- 4 Photograph (SEM) of heat treated ( $400^\circ\text{C}$  for 1 h) electroless Ni-B at  $1000\times$



- 5 X-ray diffraction pattern for as plated electroless Ni-B coating



6 X-ray diffraction pattern for heat treated (400°C for 1 h) electroless Ni–B coating

## Conclusion

A new biodegradable bath has been developed for getting Ni–B alloy coating by electroless deposition and the bath composition and operating conditions have been optimised. The characteristic properties of the selected deposits were evaluated and the following conclusions were drawn.

1. At the optimum concentration, the Ni–B deposit was found to contain 95.06% Ni and 4.94% B.

2. For the optimised concentration of sodium hypophosphite at  $10 \text{ g L}^{-1}$ , the Ni–B–P deposit was found to contain 91.02% Ni, 4.88% B and 4.1% P.

3. Scanning electron microscopy photograph of the as plated Ni–B coatings appear semibright, whereas the heat treated Ni–B coatings are matte in appearance and dark grey in colour. The morphology resembles a relatively uniform Ni–B deposit with a typical cauliflower such as structure, characteristic of electroless plated nickel coatings.

4. X-ray diffraction pattern of the as plated Ni–B deposit exhibits a single broad peak indicative of the amorphous nature of the coating. X-ray diffraction pattern of the heat treated Ni–B deposit to 400°C for 1 h revealed the presence of various sharp peaks of  $\text{Ni}_3\text{B}$  phase along with peaks for nickel.

5. Exceptional values of hardness (682 VHN) and wear resistance (0.0109 g) are obtained for nickel–boron deposit in the as plated condition. Heat treatment of the nickel–boron coating to 400°C for 1 h resulted in an increase in the hardness of the deposits (1102 VHN) and thereby the wear resistance (0.0062 g).

6. The corrosion resistance of as plated electroless Ni–B deposit is higher than the heat treated deposits. Also, the higher the concentration of sodium hypophosphite in the bath, the higher the corrosion resistance. Hence, the corrosion resistance is highly enhanced by the incorporation of phosphorous to the nickel–boron alloy coating.

7. The use of nickel methane sulphonate as a metal ion source helps in extending the bath lifetime without adversely affecting the deposit qualities. Also, the throwing power of the bath is infinite.

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