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Formation and characterization of borohydride reduced electroless nickel deposits

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Abstract

The present work aims to study the formation of electroless Ni-B deposits and evaluation of their characteristic properties. An alkaline bath having nickel chloride as the source of nickel and borohydride as the reducing agent was used to prepare the electroless Ni-B deposits. The influence of variation in bath constituents as well as operating conditions on the plating rate, and, the nickel and boron content, of the resultant Ni-B deposits were studied. Selected deposits were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), evolved gas analysis (EGA), vibrating sample magnetometer (VSM) and transmission electron microscope (TEM), respectively, for assessing the phase content, phase transformation behaviour, liberation of hydrogen during crystallization, saturation magnetic moment and micro-structural features. The corrosion resistance of Ni-B deposits, in 3.5% sodium chloride solution, both in as-plated and heat-treated (450 °C/1 h) conditions, was also evaluated by potentiostatic polarization and electrochemical impedance studies. XRD patterns reveal that Ni-B deposits of the present study are amorphous in as-plated condition and undergo phase transformation to crystalline nickel and nickel borides upon heat-treatment. DSC traces exhibit two exothermic peaks at 306 and 427 °C, corresponding to the phase transformation of amorphous Ni-B to crystalline nickel and Ni_3B phases and the transformation of a higher phase compound to Ni_3B and Ni_2B, respectively. TEM microstructures and EGA strongly support the occurrence of phase transitions at 306 and 427 °C. Electroless Ni-B deposits demonstrate a moderate corrosion resistance in 3.5% sodium chloride solution. The extent of corrosion resistance offered by electroless Ni-B deposits is relatively less compared to electroless Ni-9 wt.% P deposit.

Keywords: Transition metal alloys; Amorphous materials; Electrochemical reactions; Thermal analysis; TEM

1. Introduction

Electroless deposition process has undergone numerous modifications to meet the challenging needs of a variety of industrial applications since Brenner and Riddell invented the process in 1946. Among the various types of electroless plating, electroless nickel has gained immense popularity due to its ability to provide a hard, wear and corrosion resistant surface [1–3]. Hypophosphite-reduced electroless nickel plating has received widespread acceptance and attention has shifted towards borohydride reduced electroless nickel deposits in recent years. As boron is one of the most important amorphous elements, various boron-containing alloys have been prepared in a search for superior characteristics. The formation of an amorphous solid is extremely difficult by liquid quenching method whereas electroless deposition offers a viable alternative. For electroless plating of Ni-B alloy deposits, boron-containing reducing agents such as sodium borohydride or dimethylamine borane are commonly used. The reduction efficiency of sodium borohydride is much higher than that of dimethyl amine borane and sodium hypophosphite. It can provide up to eight electrons for reduction of some metals as opposed to two electrons that can be provided by sodium hypophosphite, for the same reaction [4]. Besides the high reduction efficiency, borohydride reduced baths are preferred to dimethyl amine borane based baths in terms of cost-effectiveness of operation [5]. However, borohydride ions hydrolyze readily in acid or neutral solutions and will spontaneously yield nickel boride in presence of nickel ions in the plating bath [4,5]. Hence control of pH is important to avoid the spontaneous decomposition of

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the bath solution and to decrease the cost of operation. The properties of sodium borohydride reduced electroless nickel coatings are often superior to those of deposits reduced with other boron compounds or with sodium hypophosphite. The principal advantages of borohydride-reduced electroless nickel deposits are its hardness and superior wear resistance in the as-deposited condition [4]. Electroless Ni-B coatings are more wear resistant than tool steel and hard chromium coatings and it can replace gold in electronic industries [4]. The columnar structure of Ni-B coatings is useful in retaining lubricants under conditions of adhesive wear. The rapid changing needs of engineering industries warrant the development of coatings that possess high hardness and good wear and abrasion resistance and in this respect one such coating which seems promising is the borohydride-reduced electroless nickel deposit. Much remains to be explored about borohydride-reduced electroless nickel deposits so that they can be effectively manipulated to suit the needs. In this perspective, the present work aims to study the formation and characterization of borohydride-reduced electroless nickel deposits.

2. Experimental

Medium carbon steel (30 mm diameter and 5 mm thick), copper (electrolytic grade; 4 × 2 × 0.2 cm) and stainless steel (AISI 304 grade) were used as substrate materials for the deposition of Ni-B coatings. Copper substrate was employed to assess the plating rate whereas stainless steel substrate was used to prepare thin films of Ni-B for differential scanning calorimetry (DSC), evolved gas analysis (EGA), vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM) evaluation. Medium carbon steel coupons were used to determine the corrosion resistance of the Ni-B deposits. The substrates were degreased with acetone, electrolytically cleaned in an alkaline solution and washed thoroughly with de-ionized water. A nickel strike using Watt's nickel bath was given to substrates prior to their immersion in electroless plating bath. An alkaline bath having nickel chloride as the source of nickel and sodium borohydride as the reducing agent was used to prepare the electroless Ni-B deposits. Besides nickel salt and borohydride, the plating bath also contained suitable quantities of ethylenediamine and a polyamine complexing agent. Thallium acetate was used as the stabilizer. The temperature of the bath was maintained at 95 ± 1 °C. During plating the bath solution was agitated using a magnetic stirrer at 600 rpm. The chemical composition of the plating bath employed and its operating conditions are given in Table 1. The influence of variation in bath constituents as well as operating conditions on the plating rate and the nickel/boron content of the resultant Ni-B deposits was studied. The boron and thallium content of the electroless Ni-B deposits were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES). The nickel content of the electroless Ni-B deposit was determined gravimetrically after precipitating nickel and Ni-DMG complex. Selected deposits, both in as-plated and heat-treated (325 °C/1 h and 450 °C/1 h) conditions, were characterized by X-ray diffraction (XRD) (Cu and Co Kα radiations), differential scanning calorimetry (DSC), evolved gas analysis (EGA), vibrating sample magnetometer (VSM) and transmission

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

Bath composition	
Nickel chloride	30 g/l
Sodium borohydride	0.8 g/l
Ethylenediamine (98%)	90 g/l
Poly-amine complexing agent	0.4 g/l
Sodium hydroxide	90 g/l
Thallium acetate	16 mg/l
Operating conditions	
pH	14
Temperature	95 ± 1 °C

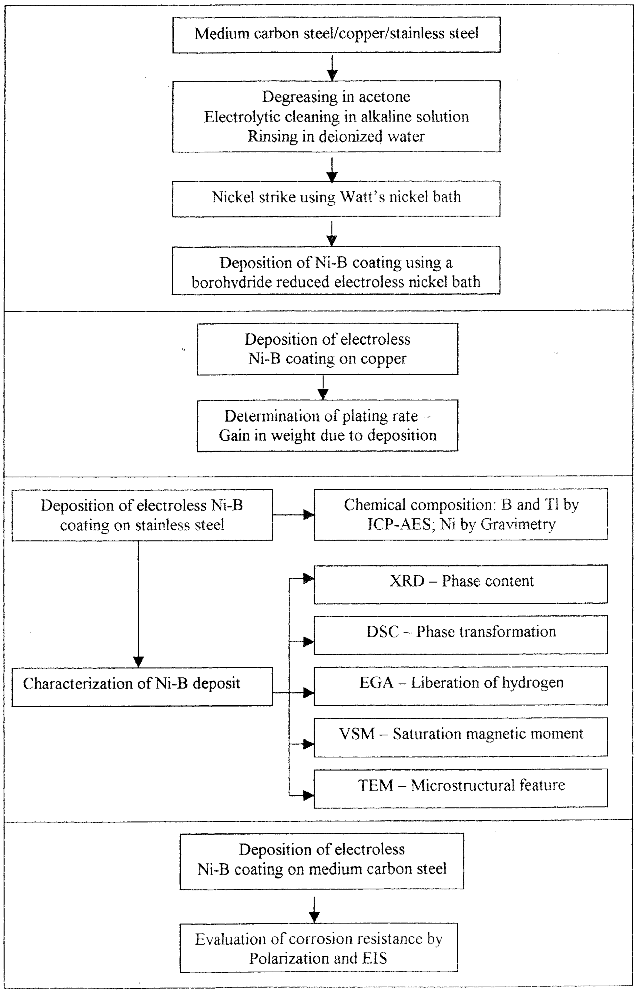

Fig. 1. Flow chart depicting the experimental details on the deposition and characterization of electroless Ni-B coatings on copper, stainless steel and medium carbon steel.

electron microscope (TEM), respectively, for assessing the phase content, phase transformation behaviour, liberation of hydrogen during crystallization, saturation magnetic moment and micro-structural features. The corrosion resistance of electroless Ni-B coatings, both in as-plated and heat-treated (450 °C/1 h) conditions was evaluated by potentiodynamic polarization and electrochemical impedance studies in 3.5% NaCl solution using a Gill AC potentiostat (ACM Instruments, UK). The corrosion cell consists of four electrodes. The electroless Ni-B coated medium carbon steel forms the working electrode, whereas a saturated calomel electrode and a platinum electrode serves as the reference and counter electrodes, respectively. The fourth electrode is a platinum electrode, which is connected to the reference electrode, reduces the noise during the electrochemical measurement. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using Tafel extrapolation method. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from the Nyquist plot by fitting the data as a semicircle using the built-in analysis software of ACM Instruments, UK. The experimental details on the deposition and characterization of electroless Ni-B coatings on copper, stainless steel and medium carbon steel is shown in Fig. 1.

3. Results and discussion

The formulation of sodium borohydride based electroless nickel bath allows only a narrow window of operation. Since sodium borohydride readily hydrolyze in acidic or neutral condition, the bath should be alkaline, preferably the pH should be higher than 12. This warrants the addition of higher concentration of alkali, which in turn necessitates the presence of an effective complexing agent in the bath. Ethylenediamine is the most preferred complexing agent for borohydride-reduced electroless nickel plating bath [6]. In the present work, besides ethylenediamine, a poly-amine complexing agent is also added to the bath. The selection of stabilizer is very critical. Although lead nitrate and mercapto benzothiazole are good in stabilizing the bath, the plating rate is poor in these baths. The only choice to achieve better bath stability and higher deposition rate is the addition of thallium compounds as stabilizers. This is due to the ability of thallium ions, which not only stabilizes the plating bath but also increases the reduction efficiency of borohydride [4]. The rate of deposition of Ni-B coatings is found to be a function of molar ratio of ethylenediamine to nickel. The plating rate increases with increase in temperature whereas it decreases with increase in molar ratio of ethylenediamine to nickel. The plating rate is not linear through out and it decreases with time, following the build up of alkali metal borate in the bath. The plating rate of electroless Ni-B coatings obtained using the bath composition and operating conditions given in Table 1 is 18–20 μm per hour. The Ni-B deposits so produced are matte in appearance and dark gray in colour. Chemical analysis of the deposit reveals that it contains 93.36 wt.% nickel, 6.4 wt.% boron and 0.24 wt.% thallium.

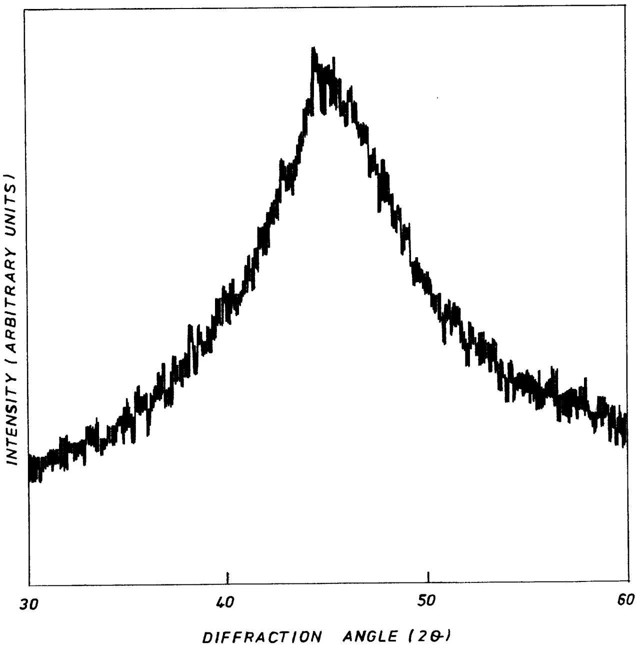

Fig. 2. XRD pattern of electroless Ni-B coating in the as-plated condition (Cu Kα radiation).

X-ray diffraction pattern of the electroless Ni-B coating in the as-plated condition exhibits a single broad peak indicative of the amorphous nature of the coating (Fig. 2). Theoretically, a disorder in arrangement of atoms manifests itself as a broad peak in XRD. In electroless deposition process, the extent of segregation of metalloid alloy in the coating determines its crystallinity. Since the required boron segregation (6.4 wt.%) is relatively large, nucleation of nickel phase is prevented and this has resulted in amorphous structure. TEM microstructure confirms the amorphous nature of Ni-B film in its as-plated condition. The SAD pattern reveals the presence of diffused halo rings, which is a typical characteristic of amorphous structure (Fig. 3). Watanabe et al. [7], Srivastava et al. [8] and Evans and Schlesinger [9] also observed the amorphous nature of electroless Ni-B films in the same composition range. However, TEM analysis carried out at different regions, indicate the presence of micro cracks, which spreads throughout the film and their presence is more pronounced at the edges (Fig. 4). Analysis performed at the cracks/boundary regions reveals the presence of nanometer-sized crystals, which are concentrated in these regions. The dark field image confirms the presence of very small crystallites (white spots), which are nanocrystalline in size (Fig. 5). Hence it can be inferred that electroless Ni-B films in the as-plated condition consist of two phases; the major part is amorphous whereas a small portion of it is nanocrystalline.

Electroless Ni-B coatings undergo phase transformation upon heat-treatment, which is best characterized by

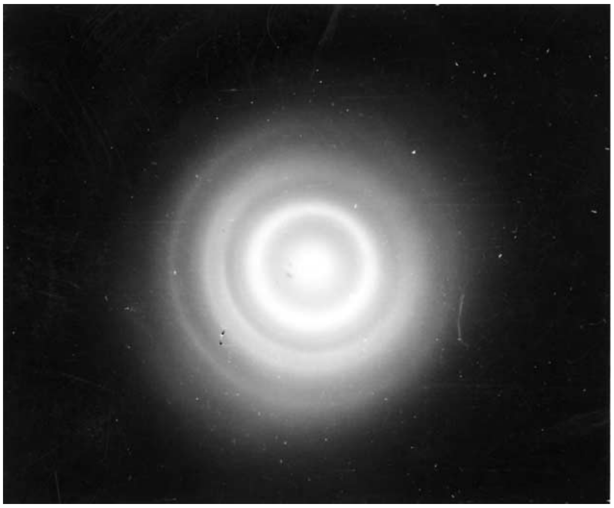

Fig. 3. SAD pattern of electroless Ni-B coating in the as-plated condition.

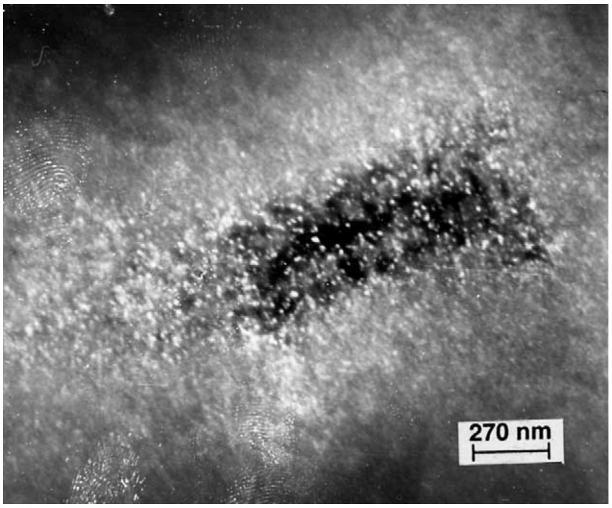

Fig. 5. Dark field image of electroless Ni-B coating in the as-plated condition at the crack/boundary region.

differential scanning calorimetry. Fig. 6 depicts the DSC trace of Ni-B coating in the temperature range from 50 to 550 °C at heating rate of 20 °C per minute. Two distinct exothermic peaks are evident; the first one is seen at 306 °C whereas the second one is noticed at 427 °C. Literature reports on the DSC traces obtained for electroless Ni-B deposits indicate that the number of exothermic peaks and the temperature range at which they occur is a function of the boron content of the film [10,11]. Accordingly, for electroless Ni-B films with less than 6 at.% of boron, DSC curves hardly exhibit any thermal effects corresponding to phase formation. For films having 6–20 at.% boron a single exothermic peak around 300–350 °C is prevalent. The exact position of this exothermic peak in this temperature range depends on the boron content of the film, the higher the boron content, the earlier the occurrence of the peak. For films having higher than 20 at.% boron, besides the crystallization of nickel and Ni_3B, the formation of Ni_2B phase is evident at higher temperatures above 400 °C. Thermograms of Ni-B films having a boron content higher than 30 at.%, exhibit a single broad exothermic peak at 410–415 °C. The chemical composition of the Ni-B film of the present study reveals that the boron content is 6.4 wt.%, which falls in the range of 20–30 at.%. Hence the exothermic peak which occurs at 306 °C can be attributed to the precipitation of metallic nickel phase and formation of orthorhombic Ni_3B phase. Similarly the exothermic peak that occurs at 427 °C would corroborate the formation of Ni_2B phase. XRD patterns of Ni-B coatings heat-treated at 325 and 450 °C for 1 h ascertain the formation of Ni_3B and Ni_2B phases, respectively (Figs. 7 and 8).

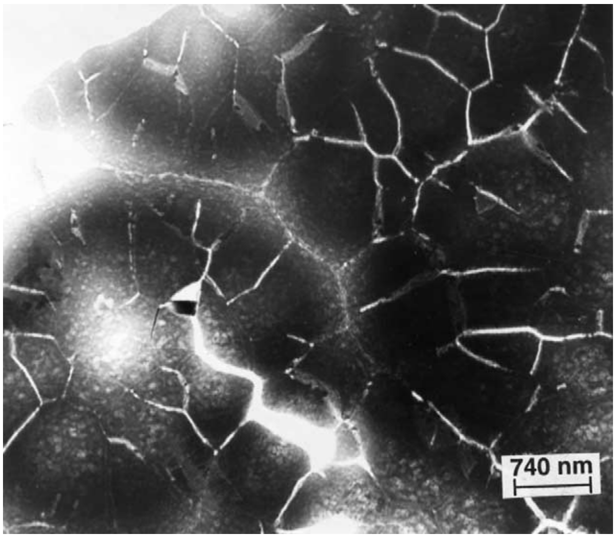

Fig. 4. TEM microstructure of electroless Ni-B coating in the as-plated condition.

The estimation of rate of liberation of hydrogen from the Ni-B deposit during annealing is of great significance. Evolved gas analysis (EGA) performed using Ni-B deposits of the present study clearly reveals the liberation of hydrogen upon annealing (Fig. 9). It is obvious that the hydrogen occluded during plating should be liberated before the

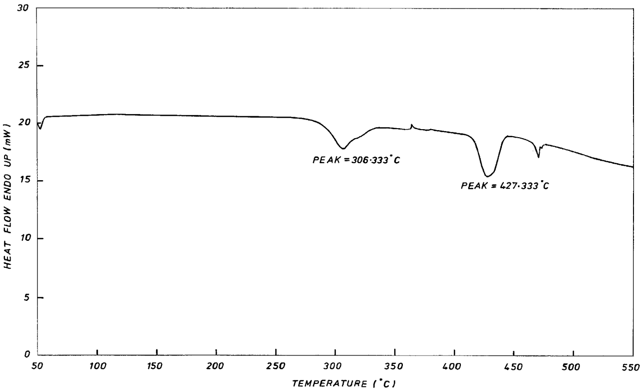

Fig. 6. DSC trace of electroless Ni-B coating at a heating rate of 20 °C/min.

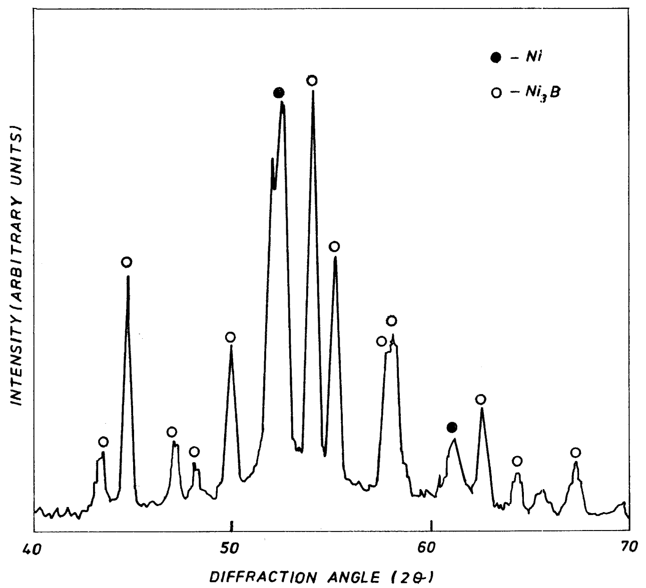

Fig. 7. XRD pattern of electroless Ni-B coating heat-treated at 325 °C for 1 h (Co Kα radiation).

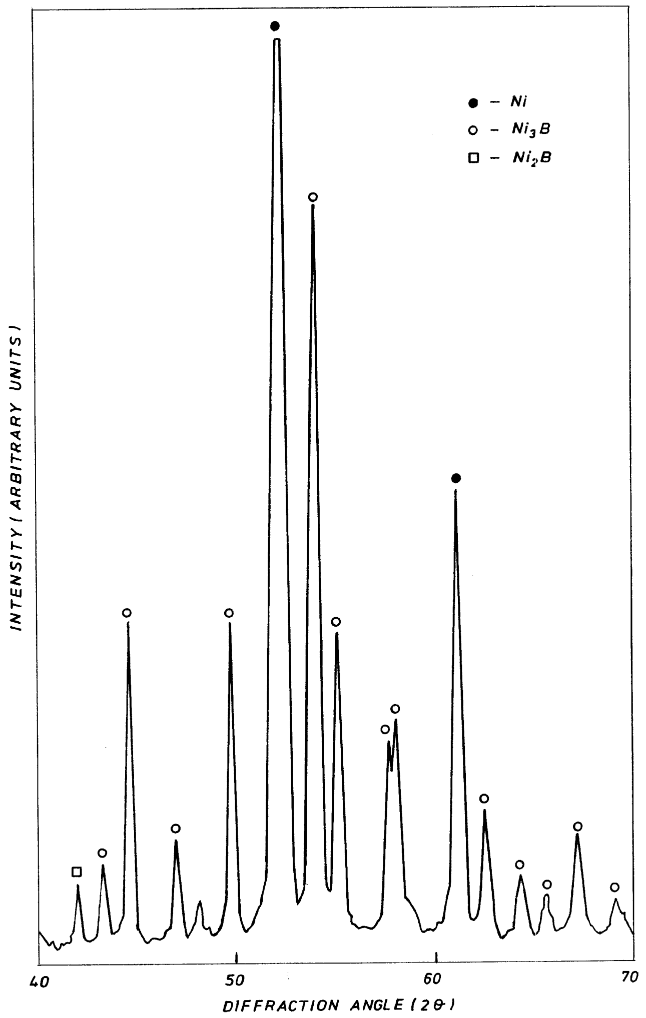

Fig. 8. XRD pattern of electroless Ni-B coating heat-treated at 450 °C for 1 h (Co Kα radiation).

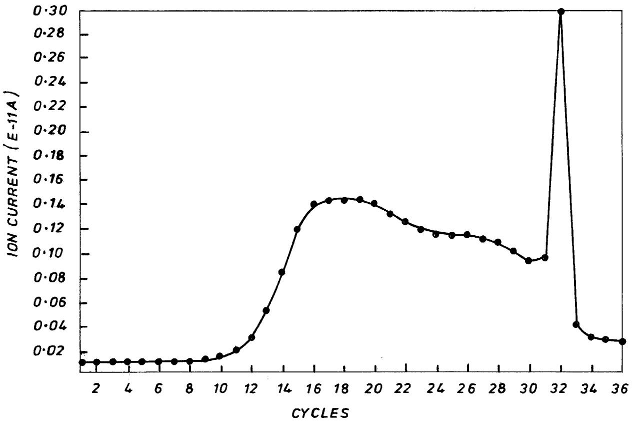

Fig. 9. EGA of electroless Ni-B coatings.

formation of new phases. It is evident from the EGA curve that the rate of liberation of hydrogen is higher at two distinct regions at temperatures just below the point at which Ni_3B and Ni_2B phase formation occurs, complementing the results obtained using DSC and XRD.

The bright field image of Ni-B coating heat-treated at 325 °C for 1 h indicates the formation of well-developed crystallites (Fig. 10). The regions, which appear white in colour, are due to the precipitation of crystalline nickel. The corresponding SAD pattern exhibits the characteristic features of crystalline nickel (Fig. 11). TEM micrograph of electroless Ni-B deposits heat-treated at 450 °C for 1 h reveals an increase in size of the nickel particles (Fig. 12). The SAD patterns taken at different regions reveal the presence of nickel and Ni+Ni_3B phases (Figs. 13 and 14).

VSM studies performed on electroless Ni-B films reveal that they are non-magnetic in as-plated condition and started to exhibit magnetic activity consequent to the formation of crystalline nickel phase in the deposit following heat-treatment (325 and 450 °C/1 h).

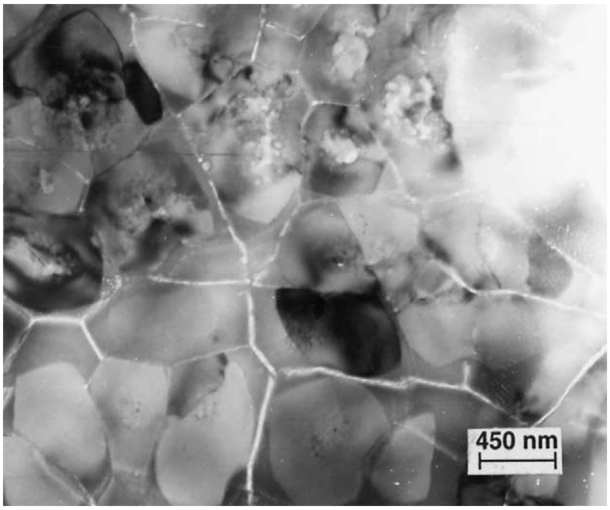

Fig. 10. Bright field image of electroless Ni-B coating heat-treated at 325 °C for 1 h.

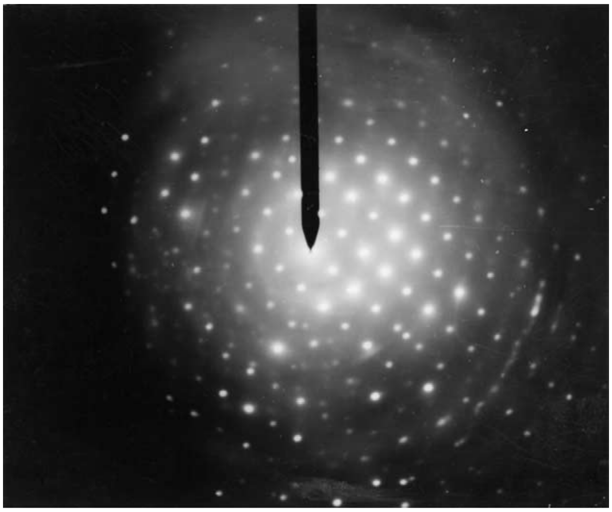

Fig. 11. SAD pattern obtained from white regions of Fig. 10.

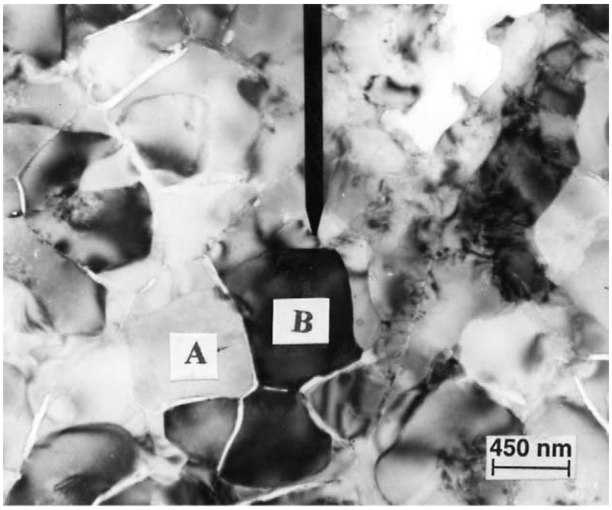

Fig. 12. TEM micrograph of electroless Ni-B coating heat-treated at 450 °C for 1 h.

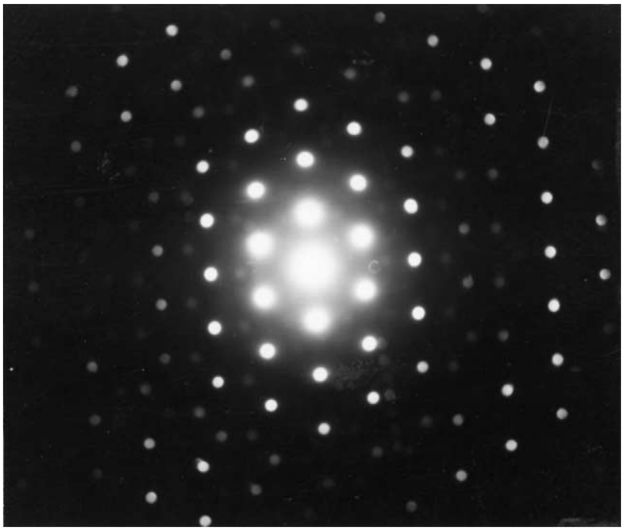

Fig. 13. SAD pattern obtained at region ‘A’ of Fig. 12.

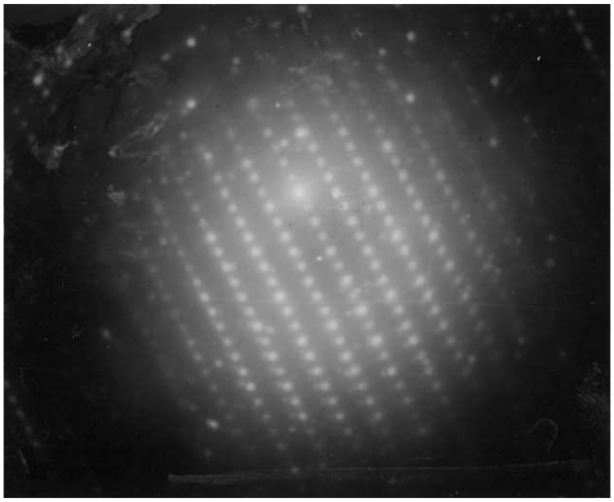

Fig. 14. SAD pattern obtained at region ‘B’ of Fig. 12.

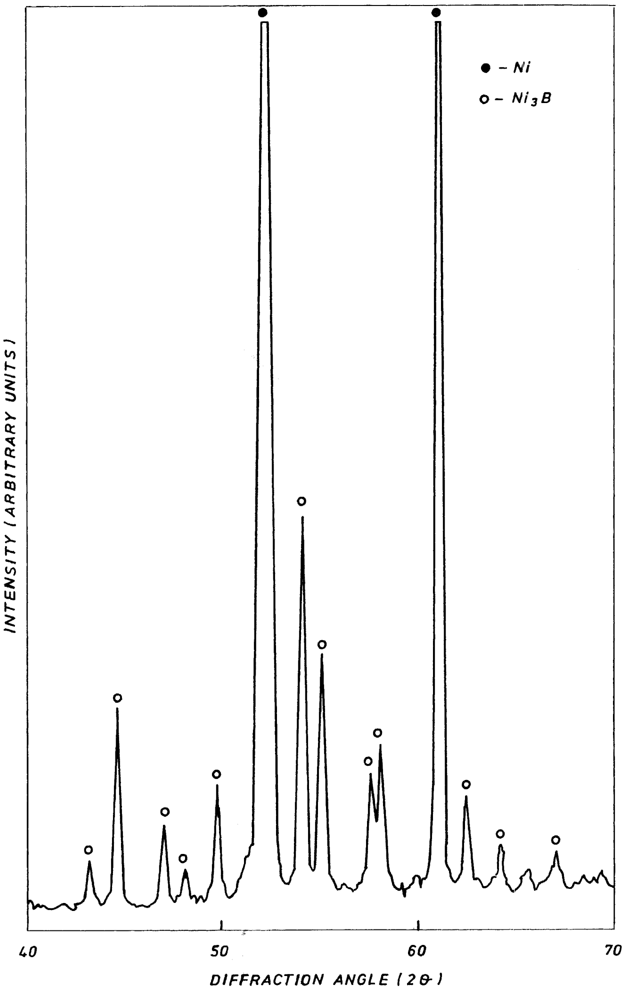

Fig. 15. XRD pattern of electroless Ni-B coating heat-treated at 600 °C for 1 h (Co Kα radiation).

Table 2
Corrosion characteristics of electroless Ni-B deposits

System studied	E_{corr} (mV vs. SCE)	i_{corr} ($\mu A/cm^2$)	R_{ct} ($Ohms \cdot cm^2$)	C_{dl} (F) $\times 10^{-4}$	Reference
Ni-B as-plated	−516	9.15	3835	3.41	Present study
Ni-B heat-treated	−520	14.60	1203	4.22	Present study
Ni-P as-plated	−354	3.62	7960	1.85	[14]
Ni-P heat-treated	−492	6.89	6498	2.36	[14]

Annealing of electroless Ni-B deposits at temperatures higher than 450 °C results in growth of crystalline nickel and conversion of Ni_2B phase to the more stable Ni_3B phase. XRD pattern of Ni-B deposits heat treated at 600 °C for 1 h indicate the absence of Ni_2B phase and predominance of nickel and Ni_3B phases in the coating (Fig. 15).

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of electroless Ni-B coatings, both in as-plated and

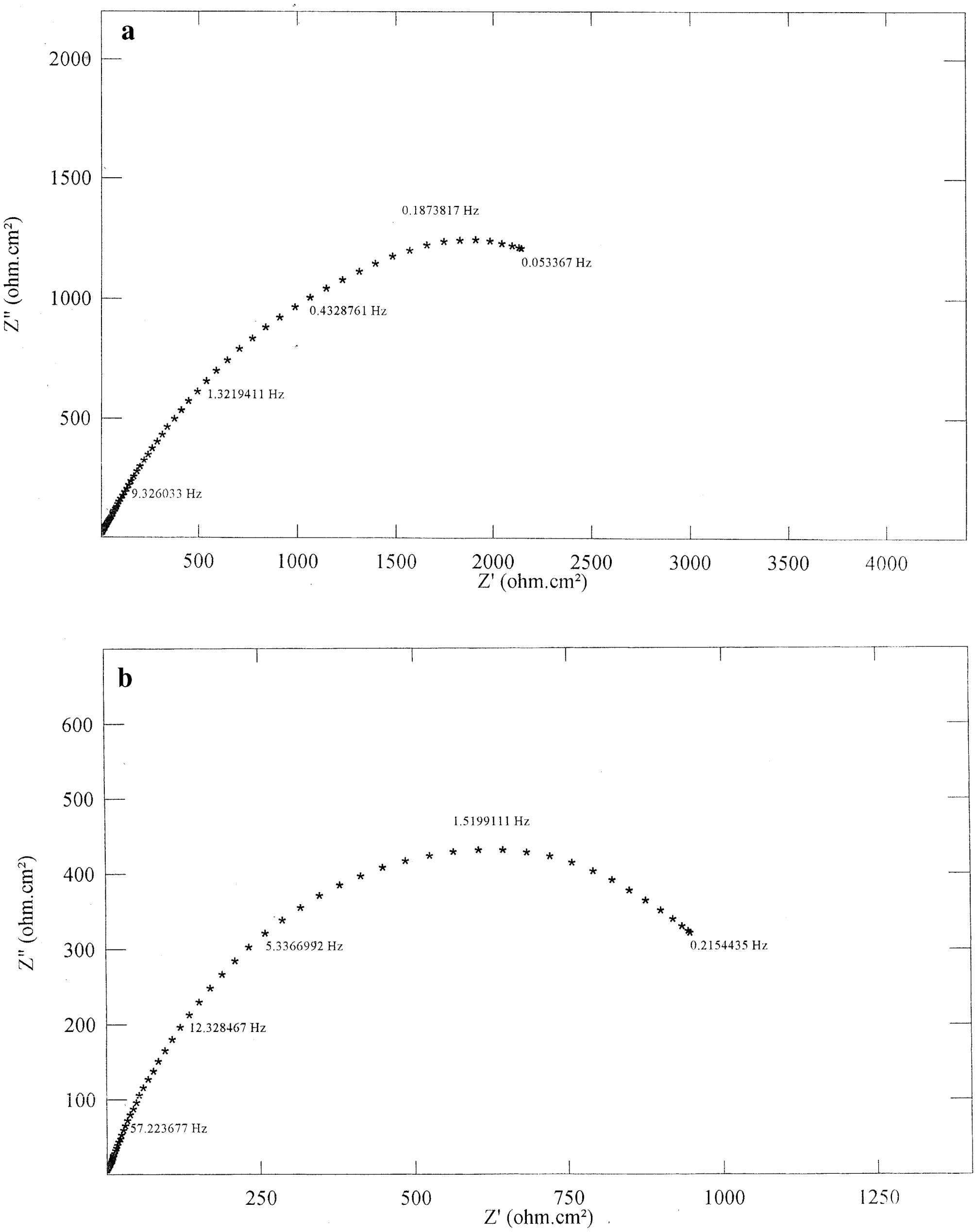

Fig. 16. Nyquist plots of electroless Ni-B coatings in 3.5% sodium chloride solution (a) as-plated condition; and (b) heat-treated condition.

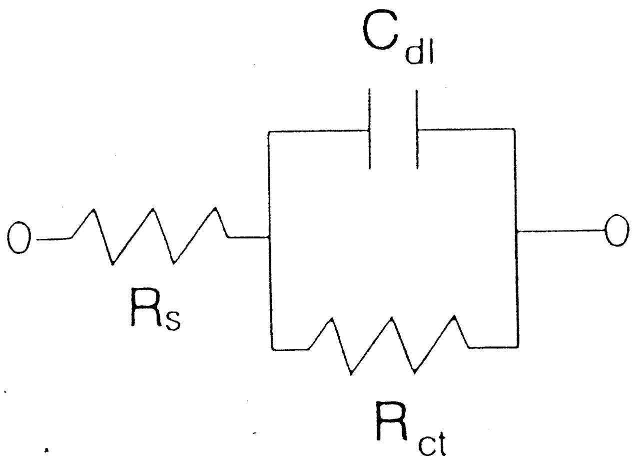

Fig. 17. Equivalent electrical circuit model proposed for the corrosion behaviour of electroless Ni-B deposit.

heat-treated (450 °C/1 h) conditions, in 3.5% sodium chloride solution, calculated using Tafel extrapolation method, are given in Table 2. The Nyquist plots obtained for electroless Ni-B deposits, in as-plated and heat-treated (450 °C/1 h) conditions, in 3.5% sodium chloride solution, at their respective open circuit potentials, are shown in Fig. 16(a,b), respectively. The Nyquist plots exhibit a single semicircle in the high frequency region. However, these curves differ considerably in their size. This indicates that the same fundamental process is occurring on Ni-B coatings, both in as-plated and heat-treated (450 °C/1 h) conditions, but over a different effective area in each case. To account for the corrosion behavior of electroless Ni-B coatings in 3.5% sodium chloride solution, both in as-plated and heat-treated (450 °C/1 h) conditions, at their respective open circuit potentials, an equivalent electrical circuit model (Fig. 17) has been utilized to simulate the metal/solution interface and to analyze the Nyquist plots. Lo et al. [12] and Balaraju et al. [13] have also used a similar model to study the electrochemical impedance behaviour of electroless Ni-P coatings in 1 M NaOH at −1.2 V and in 3.5% NaCl solution at −0.32 V, respectively. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) obtained for electroless Ni-B coatings both in as-plated and heat-treated conditions are also compiled in Table 2. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of electroless Ni-B coatings involves a single time constant. The appearance of a single inflection point in the plot of Log f versus Log Z and a single phase angle maximum in the plot of Log f versus Phase angle (figure not shown), further confirm that the process involves only a single time constant. Hence it is evident that the electroless Ni-B deposit-solution interface exhibit charge transfer behavior.

The corrosion resistance offered by electroless Ni-B coatings, both in as-plated and heat-treated (450 °C/1 h) conditions is compared with data of electroless Ni-9 wt.%P coating (Table 2) [14]. It is evident that the corrosion resistance of as-plated electroless Ni-P and Ni-B coatings is higher than the heat-treated ones. In as-plated condition, the amorphous nature of the Ni-P and Ni-B deposits imparts a higher corrosion resistance. On the other hand, as evidenced by XRD, DSC and TEM characteristics, heat-treatment induces the crystallinity of the deposits, which in turn increases the grain boundaries, which are the active sites for corrosion attack. The corrosion resistance of electroless Ni-B coating is relatively inferior to that of high phosphorous electroless nickel deposit. The difference in corrosion resistance between electroless Ni-P and Ni-B coatings is mainly due to the difference in their structure. It is believed that the passivation films that form on Ni-B coated surfaces are not as glassy or protective enough as those that form on high phosphorous electroless nickel coatings [4]. The phase boundaries present in Ni-B deposits might also be responsible for causing discontinuity of the passivation film, which are the preferred sites for the initiation of corrosion process. Besides, the inhomogeneous distribution of boron and thallium throughout the coating provides areas of different corrosion potential on the surface, which would lead to the formation of minute active/passive corrosion cells and accelerated the corrosion attack.

4. Conclusions

The present work aims to study the formation and characterization of borohydride-reduced electroless nickel deposits. The formulation of sodium borohydride based electroless nickel bath allows only a narrow window of operation. To achieve better bath stability and higher deposition rate, addition of thallium compounds as stabilizers is essential. The rate of deposition of Ni-B coatings is found to be a function of bath temperature and molar ratio of ethylenediamine to nickel. The Ni-B deposits are matte in appearance and dark gray in colour. X-ray diffraction pattern of the electroless Ni-B coating in the as-plated condition exhibits a single broad peak indicative of the amorphous nature of the coating. TEM microstructure and SAD pattern confirms the amorphous nature of Ni-B film in its as-plated condition. The presence of very small crystallites, which are nanocrystalline in size, is noticed in cracks/boundary regions. Hence it can be inferred that electroless Ni-B films in the as-plated condition consist of two phases; the major portion is amorphous whereas a small portion of it is nanocrystalline. DSC traces exhibit two distinct exothermic peaks; the peak at 306 °C can be attributed to the precipitation of metallic nickel phase and formation of orthorhombic Ni_3B phase whereas the peak at 427 °C can be corroborated to the formation of Ni_2B phase. The rate of liberation of hydrogen estimated by EGA is higher at two distinct regions at temperatures just below the point at which Ni_3B and Ni_2B phase formation occurs, complementing the results obtained using DSC and XRD. The bright field images of Ni-B coating heat-treated at 325 and 450 °C for 1 h indicate the formation of well-developed crystallites. The SAD patterns taken at different regions reveal the presence of nickel and $Ni+Ni_3B$ phases. VSM studies performed on electroless Ni-B films reveal that they are non-magnetic in as-plated condition and started to exhibit magnetic activity consequent to the formation of crystalline nickel phase in the deposit. XRD pattern of Ni-B deposits heat treated at 600 °C for 1 h indicate the absence of Ni_2B phase and predominance of nickel and Ni_3B phases in the coating. Electroless Ni-B deposits demonstrate a moderate corrosion resistance in 3.5% sodium chloride solution. The extent of corrosion resistance offered by electroless Ni-B deposits is relatively less compared to electroless Ni-9 wt.% P deposit.

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