

Synthesis and Properties of Electrodeposited Ni-B-Zn Ternary Alloy Coatings

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Ni-B coatings have decent properties like high hardness, wear resistance and decent anti-corrosion properties which make them suitable for automotive, aerospace, petrochemical, textile and electronics industries. Despite these promising properties, further improvement in their properties is essential in order to address more challenging requirements and new developments. Taking a note of above consideration, novel Ni-B-Zn coatings have been synthesized. In the present study, a comparison of properties of Ni-B and Ni-B-Zn coatings in their as deposited state is presented to elucidate the effect of zinc addition on structural, thermal, mechanical and electrochemical properties. The coatings were deposited on mild steel substrates through conventional electrodeposition process using dimethylamine borane (DMAB) as reducing agent. The structural analyses (XRD) indicate that Ni-B coatings amorphous in as deposited condition. However, the addition of zinc to Ni-B results in improvement in crystallinity. The study of surface morphology through SEM and AFM reveals the formation of uniform, dense and fine-grained deposits in both the coatings. However, addition of Zinc increases the roughness of the Ni-B matrix. It is also noticed that nanomechanical properties of Ni-B coatings are significantly improved by the addition of zinc due to solid solution strengthening nickel-boron matrix with zinc. The electrochemical polarization tests indicate that incorporation of zinc into Ni-B matrix shifts the E_{corr} and I_{corr} to more positive values and thus demonstrates a decent reduction in the corrosion rate of the coatings.

Keywords: Alloys, coatings, Ni-B-Zn ternary alloy coatings, electrodeposition, hardness, crystalline, amorphous, corrosion

1. INTRODUCTION

The gradual deterioration of metallic components in industrial plants is observed due to corrosion and wear phenomenon. The gradual deterioration of components results in loss of plant

efficiency and sometimes it may cause a plant shutdown. The more alarming fact is that, if corrosion and wear phenomenon are combined, these may cause much higher material loss that can be caused by each of them separately. Corrosion and wear often combine to cause aggressive damage in a number of industries such as mining, mineral processing, chemical processing, pulp and paper production, and energy production [1]. In many applications the surface of the component is subjected to vigorous mechanical forces and solvent attack. Therefore, in such cases, modifying the surface properties has proven to be an efficient and economical way rather than improving the bulk properties [2-4]. The surface properties (hardness, wear, abrasion and corrosion) can be successfully improved by many techniques like carburizing [5, 6] nitriding[7, 8] carbonitriding [9, 10] flame hardening[11], laser hardening[12, 13], induction hardening[14, 15] internal oxidation[16, 17], chemical vapour deposition[18, 19] and physical vapour deposition[20, 21] etc.

Currently, metal deposition processes using aqueous solutions are getting substantial attention owing to their remarkable advantages such as simplicity, economy, high deposition rate, uniformity of the deposit, decent wear and corrosion properties [22-33]. Both electroless and electrodeposition processes have been adopted to deposit different types of coatings including the Ni-B coatings. Ni-B coatings possess very attractive properties like high hardness, high wear resistance (better than hard chromium coatings) and decent anti-corrosion properties (Ni-P coatings). In addition, many other amazing characteristics of Ni-B coating such as cost-effectiveness, thickness uniformity, lubricity, good ductility, excellent solderability, good electrical properties, antibacterial property, low porosity, superior bonding and extraordinary electromagnetic properties have also been recognized[27, 31, 32, 34-46]. Owing to their tempting properties, Ni-B coatings are finding their applications in automotive, aerospace, nuclear, petrochemical, computer, electronics, plastic, optics, textile, paper, food and printing industries [32, 40, 41, 43, 47-52].

Electroless Ni-B coatings (EN) and their invariants have been deposited on a variety of substrates like mild steel [27, 40-42, 47, 50], stainless steel[27], aluminum[32, 33], copper [27], and magnesium alloys [53]. Electroless Ni-B coatings can be deposited either using dimethylamine borane [43, 54, 55] or sodium borohydride[27, 32, 42, 50, 51, 56] as reducing agents. The principal advantages of borohydride-reduced electroless nickel deposits are their superior hardness and wear resistance in the as-deposited condition[49], [27]. In addition, decent anti corrosion properties and columnar structure (typical cauliflower) is also useful for retaining lubricant to reduce the wear action in some wear conditions [44]. However, borohydride baths are operated at high temperature (70-90 °C) and with high pH values (13-14). In addition, a strict control of pH value is essential as nickel ions readily hydrolyze in neutral or acidic environment [27, 32, 35, 42]. Electrodeposition (ED) is a unique technique in which a variety of materials can be processed including metals, ceramics and polymers. The electrochemical deposition, being an atomic deposition process, can be used to synthesize nano composites. The development of nano composites has generated a great deal of interest in recent years. The obvious advantages of electrodeposition includes; low cost, low porosity, high purity, large production rate, no shape limitations, higher deposition rates, use of a range of substrates, ease of control of alloy composition and ability to produce compositions unattainable by other techniques[46, 57]. Electrodeposition of Ni-B coatings have accomplished by use of a different reducing agents such as sodium borohydride[58], dimethylamine borane[31, 45, 59], trimethylamine borane[60], carborane

ion[46] and sodium decahydroclovodecaborate[46, 61]. Instead of apparent advantages, synthesis of Ni-B coatings through electrodeposition process has been reported less as compared to electroless coating process. A few reports are available on deposition mechanism and properties of electrodeposited Ni-B coatings.

The coating systems are desired to have high hardness, high wear resistance and good anti corrosive properties. Unfortunately, the developed coatings in as their deposited condition may not possess all the above laid down properties. However, the properties of coatings can be further improved by many ways such as addition of soluble metals (alloy formation), addition of insoluble second phase particles (composite formation) and through the process of heat treatment [27, 29, 30, 32, 33, 62-64]. A large number of ternary Ni-X-P alloy coatings (X = Cu, Zn, Co, W, Mo, Sn etc) have been developed to improve the properties of the binary systems (Ni-P) for the different requirements. The addition of copper [65-67], zinc [62, 68-70], cobalt [71-73], tungsten[74-76], molybdenum [77-79] and tin [80] into Ni-P have resulted in improvement of properties such as mechanical, thermal stability, corrosion resistance, solderability, magnetic and electrical properties, are superior to those of electroless Ni-P deposits. Although, Ni-X-P alloy coatings have been studied extensively but Ni-X-B alloy coatings have not yet been studied thoroughly. Some limited reports on Ni-Co-B ternary alloy coatings showing improvement in magnetic properties [28, 39, 71, 81-83] have been published. There is need to study the effect of different alloying elements on properties of Ni-X-B coatings.

The incorporation of second phase particles into nickel coating has resulted in the synthesis of novel composite coatings. Both electrodeposited and electroless Ni-P and Ni-B alloy matrix possess high hardness and superior wear resistance. Hence, they can be considered as an ideal choice for the incorporation of second phase particles [31, 59, 64, 84, 85]. A large number of reports on Ni-X-P composite coatings have been published showing improvement in the properties of binary coating system. The composite coatings such as Ni-P-TiO₂ [86, 87], Ni-P-SiO₂ [88, 89], Ni-P-Al₂O₃[90, 91], Ni-P-ZrO₂[92, 93], Ni-P-CeO₂[94, 95], Ni-P-Fe₃O₄[96], Ni-P-CNTs[97, 98], Ni-P-SiC [99, 100], Ni-P-B₄C [101, 102], Ni-P-BN[103, 104], Ni-P-Si₃N₄[105, 106] and Ni-P-MoS₂[107] composite coatings can be found in the literature. The addition of different second phases has been undertaken to get improvement in hardness, wear, corrosion, high temperature oxidation etc. The presence of hard second phase provides resistance to the movement of dislocations and thus improves the wear and hardness of the composite coatings. Although, extensive literature is available on Ni-P-composite coatings but a limited reports on Ni-B-X composite coatings are available. Only few reports on synthesis and properties of Ni-B-Si₃N₄ [84]and Ni-B-C composite coatings have published so far.

Keeping in view the above literature back ground it is thus evident that there is a plenty of room available to develop Ni-B alloy and composite coatings. The understanding of their coating formation mechanism, optimization of processing parameters controlling properties and microstructures will thus assist to develop cost effective coatings with improved properties well suited to a range of applications.

It has been reported that the addition of zinc into Ni-P matrix has a remarkable influence on its microstructure, mechanical and electrochemical properties. The electrochemical results have confirmed that Ni-Zn-P alloy coatings are more cathodic or noble as compared to other ternary alloys coatings. Owing to their decent properties, Ni-Zn-P coatings have found their use in many

applications such as electro catalysis and under-bump metallization of solder joints. It has also been reported that Ni–Zn–P alloy coatings with high Ni contents (80–90% wt. %) and Zn (around 10 wt. %) are more positive to steel and offer excellent corrosion resistance. However, so developed Ni-P-Zn coatings could not be used as a sacrificial coating to steel. Increasing zinc contents from (10.8 to 17.9 wt. %) has resulted in the development of Ni-P-Zn coatings which are more electronegative (anodic) to steel and thus exhibit the sacrificial behavior. In addition, the incorporation of Zinc causes transformation of the amorphous structure of Ni–P into a crystalline, which has been ascribed to the lowering of phosphorous contents in the Ni-P-Zn coatings[62, 68-70, 108-110].

In the present study, novel Ni-B-Zn ternary alloy coatings have been synthesized through conventional electrodeposition process. A comparison of properties of Ni-B and Ni-B-Zn coatings in their as deposited state has been presented to elucidate the role of zinc addition on structural, thermal, mechanical and electrochemical properties. A significant improvement in the mechanical properties has been noticed due to solid solution strengthening of Ni-B matrix. However, Ni-B-Zn coatings are slightly more anodic to Ni-B but still much more cathodic to steel substrate and hence can be used as protective coatings. The remarkable superior mechanical properties of Ni-B-Zn as compared to Ni-B may be a compensating factor for a slight loss of their cathodic character. We think, this first report on Ni-B-Zn alloy coating will be much useful and motivate the research community for the development of other novel Ni-B alloy coatings.

2. EXPERIMENTAL DETAILS

Ni-B and Ni-B-Zn alloy coatings were electrodeposited on low carbon steel substrates (20 mm diameter and 5 mm thick). The chemical composition of the substrate material is presented in Table 1. All substrates were mechanically cleaned from corrosion products prior to the coating process. During the process of mechanical cleaning, the substrates were gradually cleaned up to 1200 SiC paper. After mechanical cleaning, all the samples were degreased with acetone, cleaned in an alkaline solution and thoroughly washed with distilled water. Finally, the surfaces of all the above prepared substrates were activated with a 20 % solution of HCl for about 1 minute and then rinsed with distilled water. The chemical composition and operating conditions for electrodeposition of Ni-B and Ni-B-Zn coatings are presented in Table 2. The coating bath consists of nickel sulphate-NiSO₄.6H₂O (source of nickel), dimethylamine borane-BH₃NH(CH₃)₂ (reducing agent and source of boron), boric acid-H₃BO₃ (complexing agent) and ZnSO₄ (alloying addition). Hot rolled nickel plate (99.7%) was used as anode and low carbon steel substrate was used as cathode. Anode was placed parallel with substrate in the plating bath. The coatings deposition was conducted at 43±1 °C for a time period of 30 minutes during which the bath was vigorously agitated with magnetic stirrer. The Ni-B-Zn coatings were synthesized by adding ZnSO₄ into the above mentioned Ni-B coating solution. The chemical composition of the synthesized coatings was determined with ICP-AES (Thermo, iCAP 6500, USA) and EDX analyses. The contents of nickel and boron were determined with ICP while cerium oxide contents were determined with EDX analysis. The phase purity and structural analysis of the coatings were carried out using X-Ray diffractometer (Rigaku, Miniflex2 Desktop, Tokyo, Japan) equipped with Cu K α

radiations. The surface morphology of the coatings was determined with the help of field emission scanning electron microscope (FE-SEM-Nova Nano-450, Netherland) and atomic force microscopy (AFM-USA). The AFM device MFP-3D Asylum research (USA) equipped with a Silicon probe (Al reflex coated Veeco model– OLTESPA, Olympus; spring constant: 2 N m^{-1} , resonant frequency: 70 kHz) was used in our experiments. Measurements were performed under ambient conditions using the Standard Topography AC air (tapping mode in air). An AFM head scanner applied with Si cantilever adjacent vertically in the sample resonant frequency of the free-oscillating cantilever set as the driving frequency. The phase transformation in the coatings was studied with differential scanning calorimetry (DSC, JADE, Perkin Elmer) in the temperature range of 25-450 °C using argon as protective medium. The information about nano-mechanical properties of Ni-B and Ni-B-Zn coatings, such as hardness and Young's modulus, were obtained using MFP-3D NanoIndener with Standard tip indenter (with typical spring constant equals 4000 N/m). The Berkovich diamond indenter tip composed of an industrial diamond brazed to a screw-threaded hex tooled metallic chuck was used. The indentation measurement was carried out using 1 mN of the indentation force. The contact depth was estimated from the unloading curve using Oliver and Pharr method. Results about nano-mechanical properties were evaluated from five different indentations zones on each sample.

The corrosion resistance of electrodeposited Ni-B and Ni-B-Zn alloy coatings in their as deposited state was evaluated at room temperature by linear polarization using a Potentiostat/Galvanostat (Autolab, AUT85308, Netherlands). A platinum rod and an Ag/AgCl/KCl (sat.) electrode (0.199 Vs the SHE) with Luggin probe were used as counter and reference electrodes respectively. The substrate material with an exposed area of 1 cm^2 was used as working electrode used in these measurements. The sweep rate was 1.0 mVs^{-1} . All measurements were performed in non deaerated 3.5 % NaCl aqueous solution.

Table 1. Chemical composition of the steel substrate.

C (Wt.%)	Si (Wt.%)	Mn (Wt.%)	P (Wt.%)	S (Wt.%)
0.186	0.214	0.418	0.029	0.019

Table 2. Solution composition and operating conditions of electrodeposited coating bath.

Sr.#	Chemicals	Composition
1	Nickel sulphate hexa hydrate	240g/l
2	Nickel chloride hexa hydrate	45g/l
3	Boric acid	30g/l
4	Dimethylamine borane complex	3g/l
5	Zinc sulphate	0 and10 g/l
Operating conditions		
1	pH	4
2	Temperature	$43 \pm ^\circ \text{C}$
3	Deposition time	30 minutes
4	Current density	50 mA/cm^2
5	Bath agitation	300 rpm

3. RESULTS AND DISCUSSION

The incorporation of dimethylamine borane complex ($\text{BH}_3\text{NH}(\text{CH}_3)_2$) and zinc sulphate into a nickel plating electrolyte results in co-deposition of boron (B) and zinc (Zn). Table 3 presents the chemical composition of Ni-B and Ni-B-Zn alloy coatings. It can be noticed from Table 3 that both boron (B) and Zinc (Zn) have been successfully co-deposited with nickel forming Ni-B and Ni-B-Zn alloy coatings on the surface of the steel substrate. The addition of zinc into Ni-B matrix results in change in metallic luster and chemical composition. These findings are consistent with previous studies [31, 45, 59]. The mechanism of co-deposition of boron in Ni-B coatings prepared by electrodeposition technique is not yet fully understood. It is assumed that boron is incorporated into Ni-B coating due to the adsorption of DMAB (used as a source of boron content) on the surface of already formed nickel which is then decomposed to elemental boron. Therefore, the amount of boron co-deposited with nickel can be determined by the distribution of DMAB, and, the thickness of the diffusion layer at the cathode surface, regardless of the electrode potential. Since the concentration of DMAB is kept constant in the bath (3 g l^{-1}), the amount of boron co-deposited with nickel becomes constant regardless of the applied current density [31]. The incorporation of mechanism of zinc into electrodeposited Ni-B matrix can be explained on the basis of formation and subsequent reduction of $\text{ZnNi}^+_{\text{ad}}$ species at the surface of the steel substrate. Miranda et al. have observed that the formation of Ni-rich phase in Zn-Ni alloy occurs at low potentials through the formation and subsequent reduction of $\text{ZnNi}^+_{\text{ad}}$ species. This observation tends to suggest that a similar phenomenon occurs in the electrodeposition of Ni-Zn-B which is very much similar to Ni-Zn-P coatings[111].

Table 3. Chemical compositions of Ni-B and Ni-B-Zn coatings.

Coatings	Ni (Wt.%)	B (Wt.%)	Zn (Wt.%)
Ni-B	92.339	7.661	-
Ni-B-Zn	82.032	6.542	11.426

Fig. 1(a) shows the comparison of XRD spectra of substrate, Ni-B and Ni-B-Zn coatings deposited on steel substrate in their as deposited states. The same XRD pattern on small 2θ range (40-60) is also presented for clarity purpose in Fig. 1(b). It can be observed that X-ray diffraction pattern of electrodeposited Ni-B coating exhibits a single broad peak as clearly shown in Fig. 1(b). The presence of single broad Ni (111) peak is an indicative of amorphous nature of the coating in its as deposited state. It is reported well that the structure of Ni-B coatings is highly influenced by the coating composition and thermal history. Usually, in their as deposited state the coatings are nanocrystalline or quasi amorphous depending upon the boron content, the smaller the grain size the more amorphous character of the coatings is prevalent. Generally, coatings containing 4.0 wt.% or more boron contents are considered as amorphous[50]. The presence of single broad peak in our Ni-B XRD pattern is well consistent with our ICP analysis and the previous studies [35, 42, 43, 51]. The presence of single broaden peak in as plated Ni-B coating can be further explained by considering the fact that Ni-B

coatings are solid solution of boron in f.c.c Ni lattice having a mixed substituted interstitial sites type. The formation of substituted solid solution can be indicative the co-deposition of boron in elementary form. By increasing boron content beyond 8 at. % , the peak (111) is strongly broadened and the other peaks disappear [46].

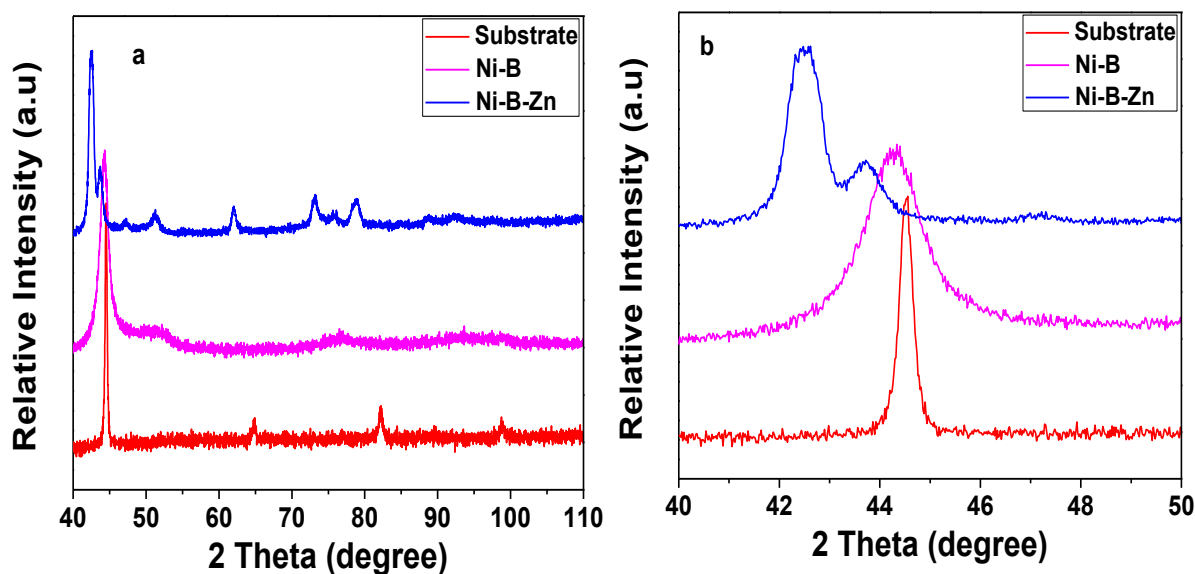


Figure 1. Comparison of XRD spectra of Ni-B and Ni-B-Zn alloy coatings in their as deposited states.

However, unlike Ni-B coating, the XRD pattern of Ni-B-Zn alloy coating exhibits sharp peaks which explain the crystalline nature of the composite coating. This result suggests that the addition of zinc has resulted in transformation of amorphous structure to crystalline structure. It is evident the incorporation of zinc has caused significant changes in the structure of Ni-B coatings. The addition of second phase particles into Ni-B coatings usually result in alteration of metallic luster, surface roughness and composition which effect their structural, mechanical and electrochemical properties[59]. Therefore, by comparing our results with Ni-B coatings, it can be noticed that the addition of zinc into Ni-B matrix has resulted in structural transformation and thus significant increase in the relative intensities of reflections of Ni (111), Ni (200), Ni (220) and Ni (311) in Ni-B coatings. It can be further noticed from Fig. 1(b) that the main peak (111) shifts towards low 2θ values upon addition of Zinc into Ni-B matrix which suggests the expansion of the unit cell by the addition of zinc.

The surface morphology of Ni-B and Ni-B-Zn alloy coatings in their as deposited states is presented in Fig. 2. The comparison of SEM images indicates that Ni-B coatings consist of uniform, fine grained and dense deposits (Fig. 2 (a)). A typical cauliflower structure is obtained which is very useful for wear application. This is due to the reason that these small pockets retain the lubricants and hence reduces the wear of the component. The SEM images of Ni-B-Zn alloy coatings reveal the formation of uniform, well crystallized, uniform and dense structure.

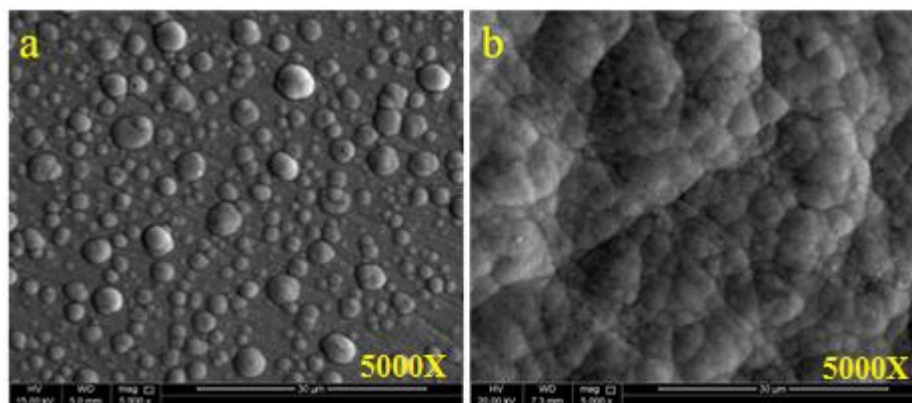


Figure 2. SEM images of synthesized coatings in their as plated conditions; (a) Ni-B and (b) Ni-B-Zn alloy coatings.

The EDX patterns of Ni-B and Ni-B-Zn alloy coatings are presented in Fig. 3 (a, b). The presence of Ni, B can be clearly noticed in Fig. 3 (a). It can also be noticed from Fig. 3 (b) that in addition to Ni and B peaks, peaks of zinc also appeared in the EDX pattern which also confirms the co-deposition of zinc into the Ni-B matrix. This result suggests that zinc atoms can be successfully co-deposited in Ni-B matrix using dimethylamine borane under acidic solution bath conditions.

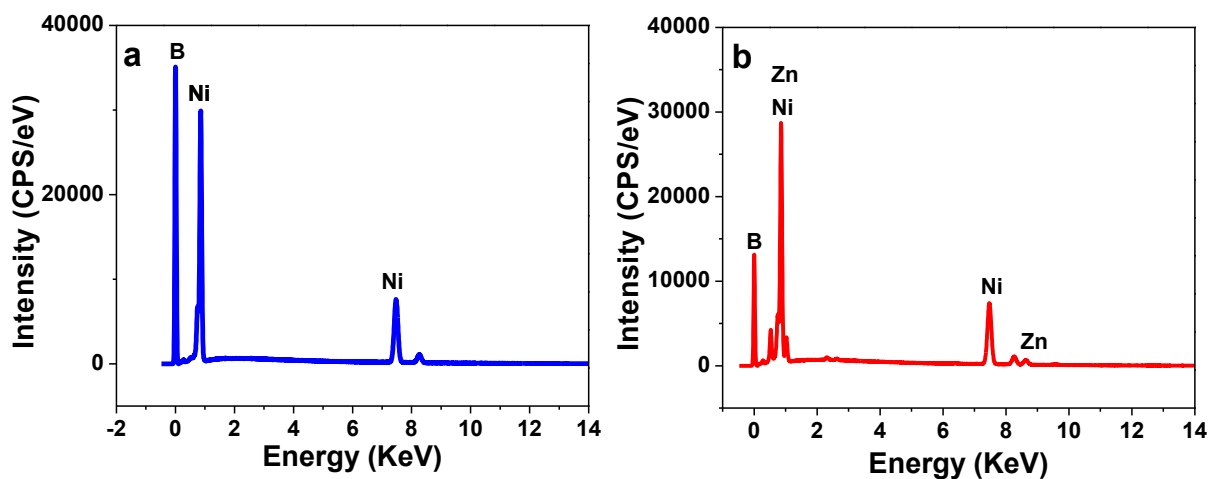


Figure 3. EDX analysis of electrodeposited coatings on steel substrate; (a) Ni-B and (b) Ni-B-Zn.

In order to have deep insight of the surface morphology of the synthesized coatings, the atomic force microscopy (AFM) of the coatings was carried out. The AFM images of Ni-B and Ni-B-Zn alloy coatings with their corresponding surface roughness profiles are presented in Fig. 4 (a, b, c, d). By comparing the surface roughness profiles of both the coatings, it can be noticed that the surface of Ni-B coatings is quite smooth. The surface roughness varies between (0-40 nm) and plain. However, the surface of Ni-B-Zn alloy coatings is rough and the surface roughness varies (-30-30 nm) which is high when compared with Ni-B coatings. This result indicates that incorporation of zinc into Ni-B matrix has resulted in relatively high surface roughness. The 3-D AFM images of Ni-B and Ni-B-Zn alloy

coatings presented in Fig. 5 (a, b) clearly reveal that Ni-B coatings have a smooth surface but Ni-B-Zn alloy coatings are not smooth as compared with Ni-B coatings.

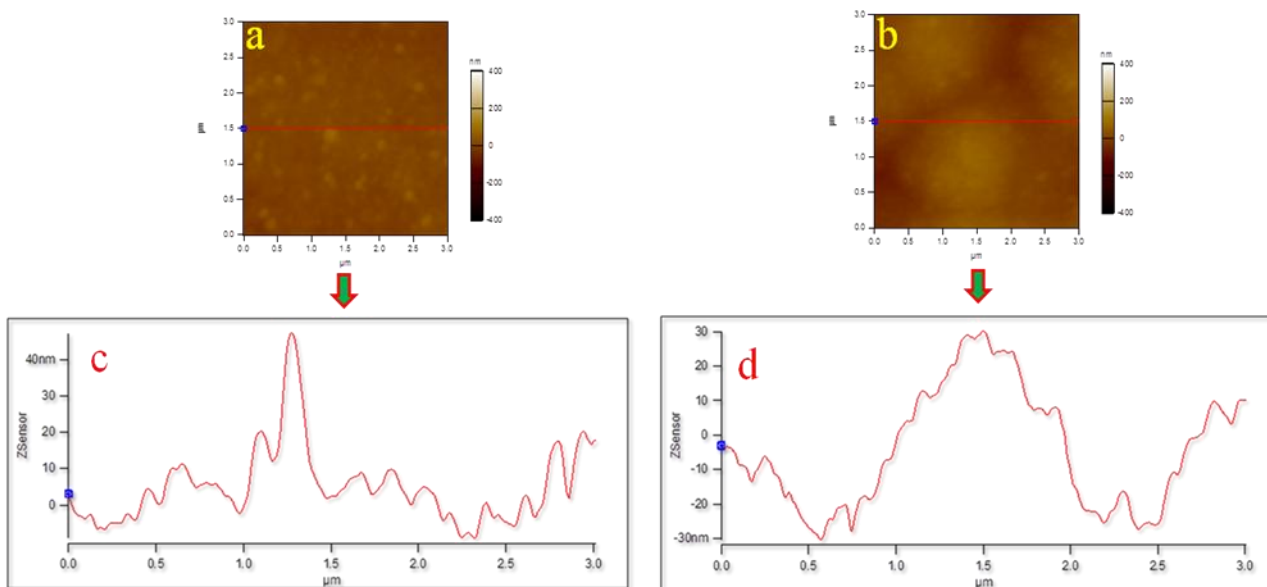


Figure 4. AFM images and corresponding surface profiles of synthesized coatings in as electrodeposited state; (a) Ni-B coatings (b) Ni-B-Zn alloy coatings (c) surface roughness profile.

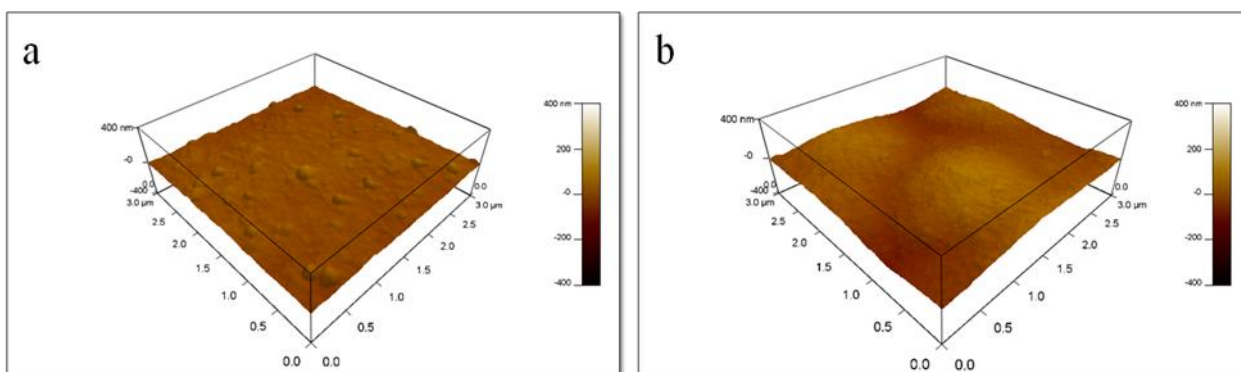


Figure 5. 3-D AFM images of synthesized coatings; (a) Ni-B and Ni-B-Zn alloy coatings in as electrodeposited state.

Ni-B coatings undergo phase transformation with the increase in temperature. The phase transformation can best studied with differential scanning calorimetry (DSC). The DSC results of Ni-B and Ni-B-Zn alloy coatings are presented in Fig. 6. For a clear comparison, the DSC scan of steel substrate is also shown.

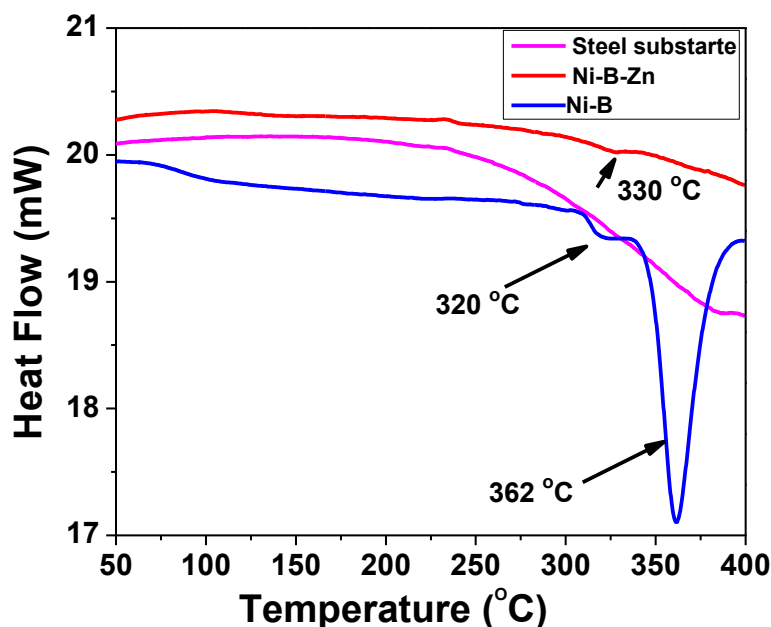


Figure 6. DSC scan of electrodeposited coatings on steel substrate.

It can be noticed that the substrate material (steel) does not show any phase transformation in the entire studied range of temperature. However, Ni-B and Ni-B-Zn alloy coatings show phase transformation with the increase in temperature. The Ni-B coatings exhibit first exothermic peaks located at 320 °C and the second phase transformation is observed at 362 °C with high amount of heat evolution. These two exothermic peaks correspond to the nucleation of two different phases into the microstructure. However, Ni-B-Zn alloy coatings shows a single exothermic peak at a temperature of 330 °C. The number and positions of exothermic peaks in the DSC scans is remarkably influenced by the composition of the Ni-B coatings. It has been reported that the phase transformation temperature and thus the position of exothermic peaks is sensitive to the boron contents of the coatings. The DSC curves of electroless Ni-B coatings with less than 6 at. % boron hardly exhibits any evidence of phase formation. However, Ni-B coatings with 6–20 at. % boron usually shows a single exothermic peak in the temperature range of 300–350 °C. The exact position of this exothermic peak in this temperature range depends on the boron content of the coating, the higher the boron content, the earlier the occurrence of the peak. Similarly, Ni-B coatings with 20–30 at. % boron, besides the crystallization of nickel and Ni₃B, the formation of Ni₂B phase is also evident at temperatures higher than 400 °C. However, DSC scan of electroless Ni-B coatings having boron contents higher than 30 at. %, exhibit a single broad exothermic peak at 410–415 °C [27, 49]. By considering the above stated strong observations of electroless Ni-B coatings and compositional analysis of our coatings, the exothermic peaks at 320 °C in our Ni-B coatings may be attributed to the re-crystallization of nickel and the nucleation of Ni₃B phases into the nickel matrix whereas the exothermic peak located at 362 °C may be ascribed to the formation of Ni₃B₄ into the structure. Similarly, the existence of an exothermic peak at 330 °C in Ni-B-Zn alloy coatings may also be attributed to re-crystallization of nickel and nucleation of Ni₃B into the structure. These findings are also consistent with some other results of electroless Ni-

B coatings[34]. The detailed analysis of properties of Ni-B and Ni-B-Zn alloy coatings is under heat treated condition is on the way and will be discussed somewhere else at [112].

The nanomechanical properties of Ni-B and Ni-B-Zn alloy coatings were determined to elucidate the useful role of zinc addition into Ni-B matrix. Fig. 7 (a,b) compares the typical results of loading/ unloading profiles versus penetration depth of both types of coatings. The nanoindentation results of Ni-B coatings are comparable with the results of nanoindentation results of Ni-B electroless coatings [55]. The comparison of loading and unloading profiles indicates high hardness of Ni-B-Zn alloy coatings.

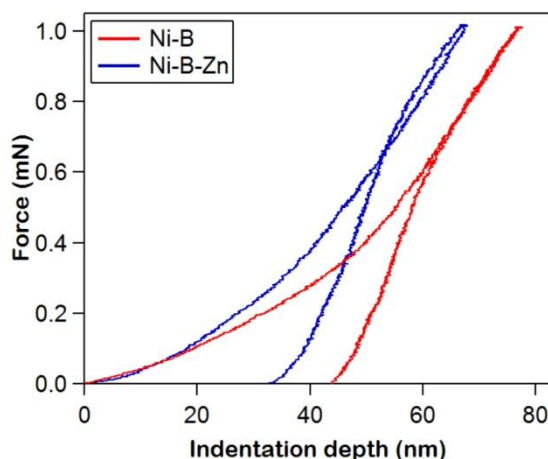


Figure 7. A comparison of load versus penetration depth profiles of coatings in their as electrodeposited states.

The coating hardness was determined by using the Oliver Pharr method described by the following equation.

$$H = F_{max} / Area \dots \dots \dots (1)$$

The area is = $24.5 \cdot h_c^2$ which is default behavior for Berkovich tip.

On the other hand, the elastic modulus was determined by applying the below equation.

$$1/E_r = (1-\nu^2)/E + (1-\nu_i^2)/E_i \dots \dots \dots (2)$$

Where “ E_r ” is reduced modulus, “ ν ” Poisson’s ratio of specimen, “ E ” Young’s modulus of specimen, “ ν_i ” Poisson’s ratio of indenter and “ E_i ” Young’s modulus of indenter.

Fig. 8 (a,b) compares the hardness and elastic modulus of steel substrate, Ni-B and Ni-B-Zn alloy coatings in their as plated conditions. It can be noticed from Fig. 8 (a) that the Ni-B coatings have an average hardness of 11.0 GPa. However, the addition of zinc into Ni-B matrix has resulted in decent improvement in hardness. The value of hardness has increased from 11.00 GPa to about 15 GPa. An improvement of about 36 % in hardness is observed. This improvement in hardness may be attributed to the well known solid solution strengthening of Ni-B matrix with the zinc. The improvement in mechanical properties by alloying addition has been well reported earlier [113-115]. Similarly, an

improvement in modulus of elasticity (18%) has also been noticed by the addition zinc into Ni-B matrix. This improvement in elastic modulus is also consistent with the previous results [55].

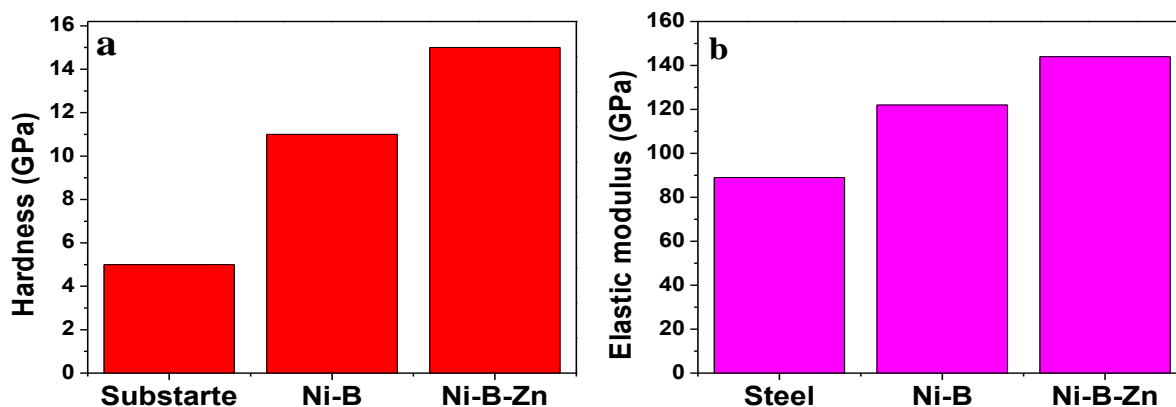


Figure 8. A comparison of nanomechanical properties of Ni-B and Ni-B-Zn composite coatings; (a) hardness and (b) elastic modulus

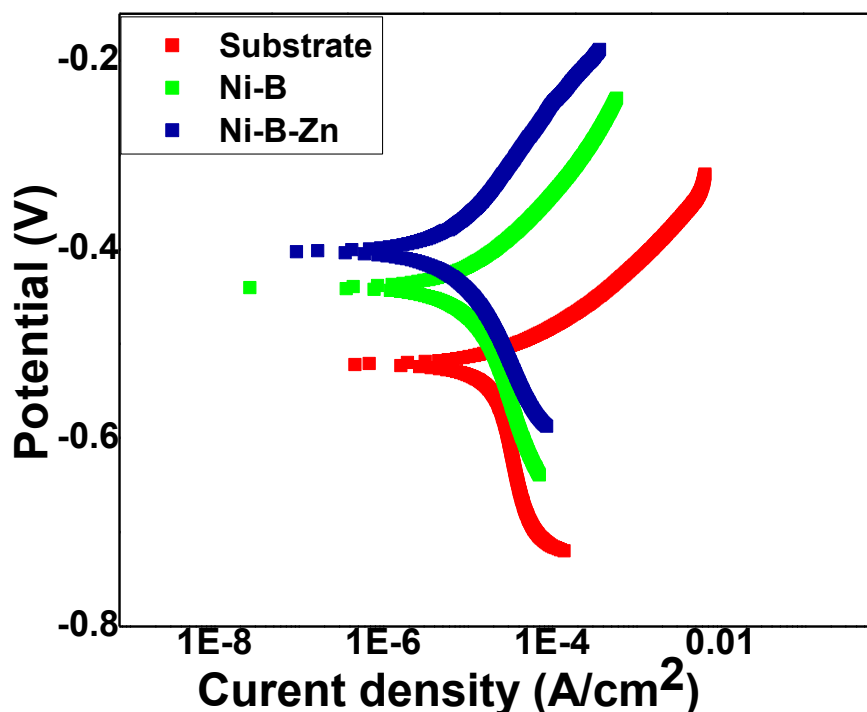


Figure 9. Potentiodynamic Linear polarization curves of steel substrate, Ni-B coatings and Ni-B-Zn alloy coatings in 3.5 % NaCl aqueous solution.

Potentiodynamic polarization curves for steel substrate, Ni-B and Ni-B-Zn alloy coatings are shown in Fig. 9. The values of different corrosion parameters calculated from Fig. 9 are also presented in Table 4 for a clear comparison. Interestingly, it can be noticed the addition of zinc shifts the

corrosion potential towards more positive value as compared to Ni-B coatings. This is so as the value of E_{corr} is less negative and the corrosion rate is lower on the Ni-B-Zn as compared to Ni-B alloy coatings. The cathodic behavior of Ni-B-Zn alloy coatings as compared with Ni-B coatings is although not yet clear and needs further investigation. At this initial stage, it may be attributed to the formation of solid solution of zinc with nickel and born at this composition which is more cathodic to steel and Ni-B coatings. However, it can be further noticed that the value of E_{corr} is much less negative and the corrosion rate I_{corr} is lower on the Ni-B-Zn alloy coatings as compared to steel substrate. These findings are consistent with previous studies carried out on Ni-Zn-P coatings [68, 110]. It has been reported that the α -Ni-Zn solid solution is more cathodic to β -Ni-Zn. Anyhow, decent improvement in mechanical properties and cathodic nature of Ni-B-Zn alloy coatings as compared to Ni-B coatings suggest that these Ni-B-Zn coatings may be attractive for high wear and corrosive applications.

Table 4. Corrosion parameters of steel substarte, Ni-B and Ni-B-Zn alloy coatings.

Sample	I _{corr} (μ A)	E _{corr} (mV)	Corrosion rate (mm/year)
Steel	53.47	-521.88	0.247
Ni-B	15.44	-444.59	0.072
Ni-B-Zn	1.47	-345.71	0.016

4. CONCLUSIONS

It can be concluded that Ni-B-Zn alloy coatings can be synthesized by using acidic coating bath solution. The addition of zinc into Ni-B matrix results in alteraion of chemical composition, metallic luster, structure and surafce roughness. It is noticed that the incorporation of zinc into Ni-B matrix results in improvement in mechanical properties due to solid solution hardening of Ni-B matrix. Finally, it is also noticed that Ni-B-Zn alloy coatings are more cathodic to Ni-B coatings and thus can be successfully employed as protective coatings.

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