# **Characteristics of Nickel Boron Coatings prepared by Direct Current Electrodeposition Technique**

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Received: 12 November 2016 / Accepted: 9 January 2017 / Published: 12 February 2017

In this research, Ni-B coatings with different boron content (1.85 to 18.63 at.%) were produced by direct current electrodeposition technique and from a bath containing trimethylamineborane (TMAB) at 0.06M. The influence of deposition current density on the composition, surface morphology, grain size, hardness, corrosion resistance and wear properties of the coatings was investigated. Our result found that the boron content in the coatings decreases significantly with increasing deposition current density. The further analysis showed the great influence of boron content on the grain size and hardness of the coating. A maximum hardness of about 954 Hv was obtained for a nanocrystalline Ni-B coating with a boron content of 4.38 at.%, while the amorphous-like Ni-B coating at a boron content of 18.63 at.% has a lower hardness as compared to those nanocrystalline Ni-B coatings. The potentiodynamic polarization measurement showed that the Ni-B coatings had higher corrosion resistance than that of pure nickel coating. Grain size is the main factor affecting corrosion resistance of the coatings. Wear test results show that the wear resistance of Ni-B coatings is governed by the microhardness. An increase in the hardness of the Ni-B coating leads to promotion of the wear resistance.

Keywords: Ni-B coatings; Electrodeposition; Corrosion resistance; Wear resistance

## **1. INTRODUCTION**

Surface coatings technology has over the past few years been widely applied in various sectors, including electronics, automobiles, aviation, modes, daily necessities, etc. Hard chromium plating, in

particular, has been applied most extensively. Hexavalent chromium (Cr<sup>6+</sup>) coatings, in spite of their several advantages, such as its high hardness, excellent corrosion resistance and surface smoothness, are hazardous to the human body and environment [1-3]. It is urgent, therefore, to replace hexavalent chromium coatings. Nickel alloy coatings have long been regarded as the best substitute. Traditional nickel coating is characterized by its corrosion resistance, current efficiency and surface smoothness. However, it is inferior to hard chromium plating in hardness and durability. In response to the call for better mechanical properties, Ni-based alloy coatings such as Ni-P, Ni-Mo, Ni-W, Ni-Fe and Ni-Co have been developed [4-9]. So far, most alloy coatings have been fabricated by applying wet process techniques (electroplating and electroless plating), which are characterized by low cost, easy operation and high deposition rate [10-15].

Owing to their high hardness, good corrosion resistance, long durability, and suitable solder ability [16, 17], the Ni-B alloy coating has been developed in several engineering fields in recent years. In addition to work carried out on the preparation of Ni-B deposits by the electroless method [18-20], Ni-B coatings obtained by electrodeposition have been recently reported [21-27]. General speaking, the properties of the Ni-B coating are affected by the electrodeposition conditions. The Ni-B coatings were produced by electroplating from Ni electrolytes in the presence of a reducing agent, such as dimethylamineborane (DMAB) [21-24], triethylamineborane (TMAB) [22, 25] or sodium decahydrodecaborate (Na<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) [26] which acted as the borne source.

Krishnaveni et al. [21] examined the structural characteristics, hardness and wear resistance of the Ni-B coatings electrodeposited from a Watt's nickel bath containing 3 g/L DMAB. Ogihara et al. [22] prepared Ni–B alloy films by electrodeposition using a conventional Ni plating bath containing DMAB or TMAB as boron sources. Their results found that the hardness, boron content, and crystalline structure of electrodeposited Ni-B films were significantly affected by the type of boron sources and other electrodeposition conditions. It is worth to mention that the electroless deposition of Ni-B coating will be occurred along with the electrodeposited Ni-B coating when the concentration of DMAB in the bath is over 3 g/L. This observed phenomenon is in agreement with the report by López et al. [23]. However, electroless deposition of Ni-B was not observed in TMAB containing bath. Liang et al. [24] reported that the as-plated Ni-B coatings are inferior to hard chrome in hardness, however, they have higher wear resistance than that of hard chrome. All the literatures mentioned above believed that the grain size is the main factor determining the hardness of Ni-B coating. However, their results of the grain size effect on hardness of the resulting coating are controversial. Ogihara et al. [22] reported that the X-ray amorphous Ni–B alloy films showed high hardness, while highly crystalline structure showed low hardness. On the other hand, Bekish et al. [26] indicated that the highest hardness was observed for the nanocrystalline Ni-B coating.

In addition to hardness and wear resistance, corrosion resistance is also an important characteristic in practical application of coatings. Due to the hydrogen release from the reduction of hydrogen ions during the electrodeposition process yields the high internal stress, resulting in the crack formation on the surface [21]. It will deteriorate the corrosion property. Krishnaveni et al. [27] compared the corrosion resistance of electroplated Ni-B and Ni-B-Si<sub>3</sub>N<sub>4</sub> composite coatings and reported that the incorporation of Si<sub>3</sub>N<sub>4</sub> particles into Ni-B matrix resulted in marginal improvement in corrosion resistance. Several baths have been used for electrodeposition of Ni and Ni-based alloy

films. Among them, the use of nickel sulfamate bath allows depositing smooth Ni-B coating with a low intrinsic stress [28]. However, it has been reported that the corrosion resistance of Ni-B coating electrodeposited from a sulfamate bath at pH of 3.0-3.5 with DMAB as the boron source was low due to the presence of cracks [23]. With the addition of saccharin into the electrolyte, the cracks were successfully eliminated [24].

In this study, we aimed at preparing the crack-free Ni-B coatings with different boron contents from a TMAB containing sulfamate bath at a high pH value 0f 6.5. The hydrogen evolution will be decreased and eliminate the crack formation at high pH, which favored the corrosion resistance. The effect of deposition current density on deposition efficiency, surface morphology, grain size and hardness was clarified. And their influences on the wear properties and corrosion resistance were also elucidated.

## 2. EXPERIMENTAL DETAILS

## 2.1 Pre-plating treatment

The Ni-B alloy coatings were electrodeposited a low-carbon steel sheet  $(40 \times 30 \times 0.5 \text{ mm})$ . The stainless steel was degreased with a 1 M NaOH solution at 65°C for 30 s, pickled in a 10% hydrochloric acid solution for 2.5 min, and cleaned by deionized water prior to electroplating of Ni-B.

## 2.2 Control of plating bath composition and pre-treatment

Bath composition		Operating conditions	
Ni(SO <sub>3</sub> .NH <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O	0.80 M	Deposition Current density	$1 \cdot 3 \cdot 5 \cdot 10 \text{ A/dm}^2$
NiCl <sub>2</sub> •6H <sub>2</sub> O	0.15 M	Temperature	45°C
$B(OH)_3$	0.52 M	pН	6.5
A-Complexing agent	0.18 M	Stirring speed	450 rpm
TMAB	0.06 M	Time	120 min

Table 1. Composition and operating conditions of the plating bath used to produce Ni-B coatings

The plating baths and operating conditions used in the electroplating process are listed on Table 1. The nickel sulfamate (Ni(SO<sub>3</sub>.NH<sub>2</sub>)<sub>2</sub>.4H<sub>2</sub>O) was used as the main salt of the electrolyte, nickel chrolide (NiCl<sub>2</sub>•6H<sub>2</sub>O) was used to increase the solution conductivity and boric acid (B(OH)<sub>3</sub>) was utilized to stabilize the solution pH value. TMAB (Trimethylamine borane) with a fixed concentration of 0.06 M was the main source of boron ions in the bath. A-complexing agent was added to enhance bath stability and control deposition rate. The plating solution was poured into a 1-litter beaker, which was then stirred by a magnetic stirrer (D-55122 Mainz) with stirring rate of 450 rpm and heated to

 $45^{\circ}$ C with an infrared heat source. The deposition current density was set at 1, 3, 5 and 10 A/dm<sup>2</sup>, respectively.

2.3 Characterizations analyses and mechanical properties tests

The surface and cross-sectional morphologies of the Ni-B coatings were observed by scanning electron microscope (SEM, Jeol model JSM-6500). The thickness of the N-B film was measured at five randomly chosen locations of each sample from the cross-sectional SEM micrograph. The reported value of the thickness was averaged. The composition of the Ni-B coating was measured by an electron probe X-ray micro-analyzer (EPMA, JEOL JXA-8200). Surface roughness (Ra) of the Ni-B coatings was measured using a surface roughness tester (KOSAKA- SURFCORDER SE1700). The roughness measurements for each sample were carried out at four different positions with a scan rate of 0.1mm/s and through length 12.5 mm, and the results were averaged. The texture and grain size of the Ni-B coatings were decided using a Rigaku-RIMT 2000/PC X-ray diffractometer. The hardness of the deposited coatings were determined using a Vicker's microhardness indenter with a load of 100 g for 10 s, and the reported value was taken the average for 10 measurements.

Corrosion characteristic of the Ni-B coatings was tested by potentiodynamic polarization tests in a 3.5 wt.% NaCl aqueous solution at room temperature with a three-electrode cell system, in which the Ni-B coating was set as the working electrode, a platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. A CHI 660 electrochemical analyzer with computer control was used in the electrochemical experiments.

The wear tests were conducted with a high-frequency reciprocating wear testing machine (SENSE-5). The frictional count pairs were adopting the ball-on-disk type, in which the Ni-B coatings deposited on the disk surface and ball material is  $ZrO_2$  with the hardness of 1200 Hv. All the tests were carried out in the dry sliding condition and at ambient temperature  $25\pm3$  °C, relative humidity  $55\%\pm5$ %. The sliding frictional condition was fixed at a normal load of 10 N, a stroke of 1 mm, an average velocity of 0.032 m/s, and the sliding distance was around 57.6 m.

## **3. RESULTS AND DISCUSSION**

## 3.1 Morphology and compositions of Ni-B coatings related to the operating parameters

Dependence of the boron content in the coatings as well as the deposition rate on deposition current density are shown in Fig. 1. The boron content shows a tendency to decrease with the deposition current density. Ogihara and his co-workers [22] investigated the effect of deposition current density on the boron content in Ni-B coating electrodeposited from TMAB containing bath and reported that the boron content was remarkably decreased by increasing deposition current densities, which is in good agreement with our present result. The decrease of boron content with increasing deposition current density can be explained by the amount of boron co-deposited with nickel becomes constant regardless of the applied deposition current density due to the concentration of TMAB is kept

constant in the bath (0.6 g/L), whereas the amount of nickel increases with increase in deposition current density [21], and as a result the boron content decreases.

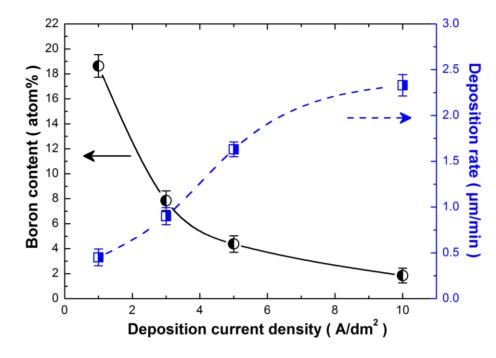
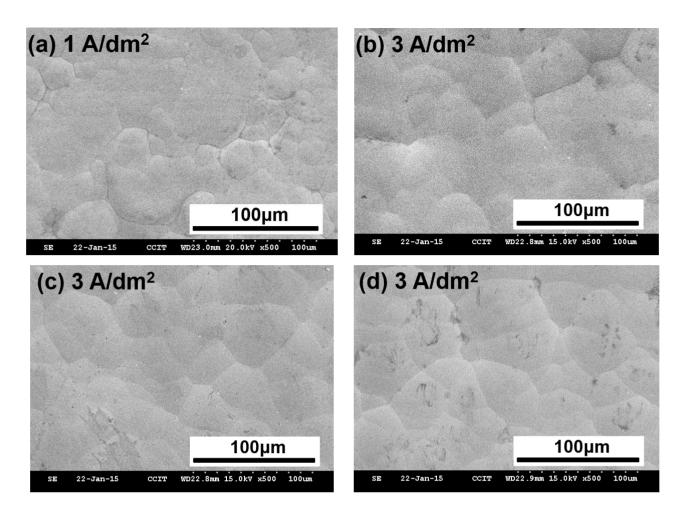


Figure 1. Effect of the deposition current density on deposition rate and boron content in Ni-B coating.

The minimum boron content, about 1.85 at.%, was obtained at the deposition current density of  $10 \text{ A/dm}^2$  and maximum boron content of about 18.63 at.% was obtained at a deposition current density of  $1 \text{ A/dm}^2$ . Since the boron content is low in the Ni-B deposits, it suggests that the deposition rate is mainly governed by the reduction rate of nickel ions.

Hence, the deposition rate of Ni-B alloy coatings increases with the deposition current density, as also shown in Fig. 1. Fig. 2 shows surface morphology of Ni-B coatings obtained at different deposition current densities. It shows from Fig. 2 that the all deposits are crack free and exhibit nodular morphology regardless of the deposition current density at which they were deposited. Fig. 3 displays the averaged surface roughness of the Ni-B coatings as a function of deposition current density. It can be seen from Fig. 3 that the roughness of Ni-B coating decreases with the deposition current density rise.



**Figure 2.** Surface morphology of Ni–B coatings electrodeposited at different current densities: (a) 1, (b) 3, (c) 5, and (d) 10 A/dm<sup>2</sup>.

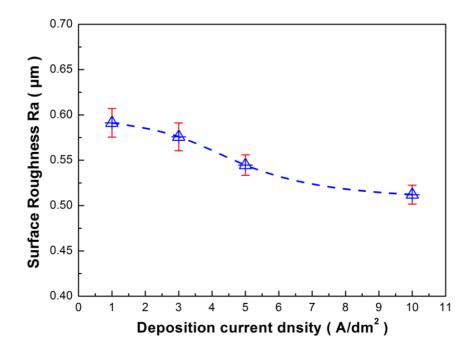


Figure 3. The relationship between surface roughness and deposition current density of Ni-B coatings.

The roughness of electrodeposited Ni-B decreased slightly from 0.59 to 0.51  $\mu$ m as the deposition current density rose from 1 to 10 A/dm<sup>2</sup>. The results of deposition current density effect on surface roughness at different studies with different baths and deposition conditions were distinct. Abdel-Karim et al. [29] has investigated the effect of deposition current density effect on surface roughness of Ni-Mo composite coating, their results showed that increasing deposition current density increased the surface roughness. Kang and Hwang [30], in this regard, reported that the surface roughness of electrodeposited Ni-W coatings decreased as the deposition current density increased.

#### 3.2 Analysis of grain size and micro construction

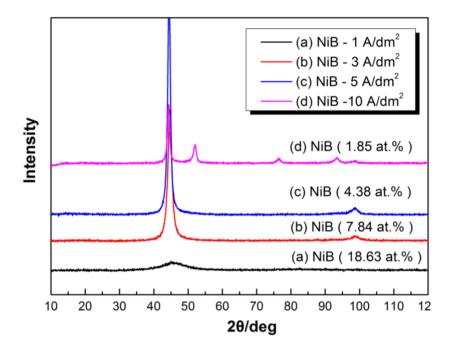
Deposition		Coatings properties			Polarization data			
cases de	current density (A/dm <sup>2</sup> )	Surface roughness Ra (µm)	Hardness (Hv)	Boron content (at.%)	$I_{\rm corr} (A/cm^2)$	Ba (mV)	Bc (mV)	$\begin{array}{c} Rp\\ (\Omega cm^2) \end{array}$
1 3 5 10	1	0.5912	802	18.63	5.84×10 <sup>-6</sup>	103.43	133.46	4,338
	3	0.5784	939	7.84	6.13×10 <sup>-7</sup>	155.21	105.12	44,545
	5	0.54466	954	4.38	3.22×10 <sup>-7</sup>	73.02	79.48	51,349
	10	0.5120	927	1.85	4.15×10 <sup>-7</sup>	75.65	57.82	34,310
Pure Ni	5	0.3559	245	Full	1.43×10 <sup>-5</sup>	123.14	298.05	2,640

**Table 2.** The properties and corrosion parameters of pure Ni and Ni-B coatings electrodeposited at different deposition current densities.

Table 2 compares the characteristics such as boron content, surface roughness, micro hardness and corrosion current density of the Ni-B coatings electrodeposited at different deposition current densities. Although it was reported that the hardness of Ni-B coating electrodeposited from a TMAB Watt bath increased linearly until 3 at.% of boron content and the hardness was stable at 730–880 Hv when boron content was higher than 3 at.% [22]. However, it can be clearly seen from Table 2 that the hardness of electrodeposited Ni–B coating is 802 Hv at 18.63 at.% boron. As the boron content decreases to 4.38 at.%, the hardness of electrodeposited Ni–B coating increases to 954 Hv. When the boron content further reduces to 1.85 at.%, however, the hardness decreases slightly to 927 Hv. Both results suggested that the variation of hardness is not directly related to boron content in the coatings. The effect of other factors such as microstructure and grain size on the hardness should be investigated.

The structures of the Ni-B deposits were characterized by X-ray diffraction (XRD) in this research. The XRD patterns of the Ni-B coatings are displayed in Fig. 4. It can be clearly observed that the microstructure of Ni-B coating is dependent on the boron content. Two diffraction peaks located at 45° and 52° were detected for Ni-B coating with boron content of 1.85 at.%, which were assigned as the Ni (1 1 1) and Ni (2 2 2) reflection planes. Due to no peak corresponding to B or Ni-B was seen, it

implies that boron atoms are finely deposited in the crystalline lattice of Ni. Similar results were reported by Ogihara et al. [22] and López et al. [23], respectively. The width at half height of diffraction line assigned to Ni (1 1 1) increases and its intensity decreases with increasing boron content, which might be attributed to a decrease in the nickel crystallite size caused by the co-deposition of the boron. It indicates that the structure of the Ni–B coating changes from crystal state to amorphous-like.



**Figure 4.** XRD patterns of the Ni-B coatings deposited at different deposition current densities, and the resultant Ni-B coatings having different boron contents: (a) 1 A/dm<sup>2</sup>; 18.63 at.%, (b) 3 A/dm<sup>2</sup>; 7.84 at.%, (c) 5 A/dm<sup>2</sup>; 4.38 at.%, and (d) 10 A/dm<sup>2</sup>; 1.85 at.%.

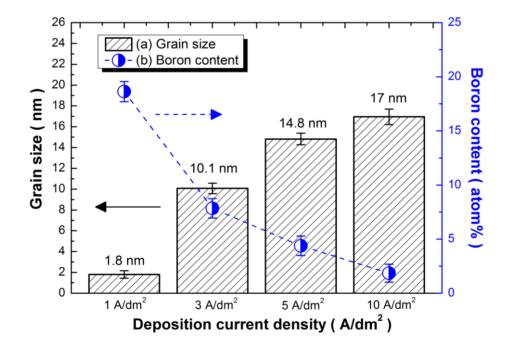
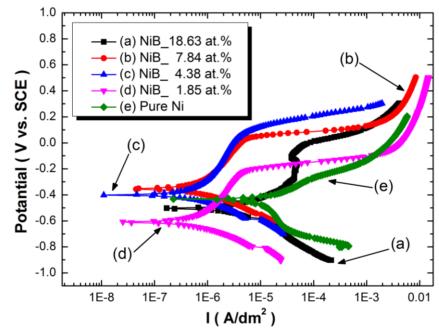


Figure 5. Deposition current density effects on the grain size and boron content of Ni-B alloy coating electrodeposited.

On the other hand, the peak assigned to Ni (2 2 2) disappears with the boron content in the Ni-B coating increasing boron content from 1.85 to 4.83 at.%. The grain size of the Ni-B coatings was calculated from the width of the Ni (111) peak observed in the X-ray diffractograms using Scherrer's equation. The variation of grain size with boron content for Ni-B coating is displayed in Fig. 5. It shows that the grain size of Ni reduces with increasing boron content in the Ni-B coatings. The Ni-B coating electrodeposited at 1 A/dm<sup>2</sup> having the highest boron content 18.63 at.% exhibits the finest grain size at approximately 1.8 nm, which is very close to amorphous-like. This result is consistent with that reported by Onoda et al. [31] that the deposition current density will affect boron content in Ni-B coating, a decrease in the deposition current density of co-deposited boron induces the formation of more amorphous structure.

#### 3.4 Evaluation of corrosion resistance



**Figure 6.** Polarization curves of Ni and Ni–B coatings that obtained with scan rate of  $0.5 \text{ mVs}^{-1}$  in 3.5% aqueous NaCl solution: Ni–B coatings with different boron contents: (a) 18.63 at.%, (b) 7.84 at.%, (c) 4.38 at.%, (d) 1.85 at.%, and (e) Ni coating.

The polarization curves obtained for the pure Ni coating and Ni-B coatings related to the boron contents in coatings are shown in Fig. 6. The values of electrochemical corrosion parameters, such as corrosion current density ( $I_{corr}$ ) and polarization resistance Rp, are also show in Table 2, in which are derived from the polarization curves following the method described in Ref. [32]. In contrast with the pure Ni coating, the polarization curves of all Ni-B coatings exhibit the formation of a passive film on the surface of specimen in the beginning of corrosion process. The corrosion current density ( $I_{corr}$ ) of these Ni-B coatings is at least one order of magnitude lower than that of pure Ni coating. Moreover,

the corrosion current density of Ni-B electrodeposited at 5  $A/dm^2$  is the lowest among all tested specimens. Concerning the boron content effect on the corrosion resistance of Ni-B coating, it reveals that the corrosion current density decreases with the boron content in the coating from 18.63 at.% to 4.38 at.%, while below 4.38 at.%, the corrosion current density slightly increases.

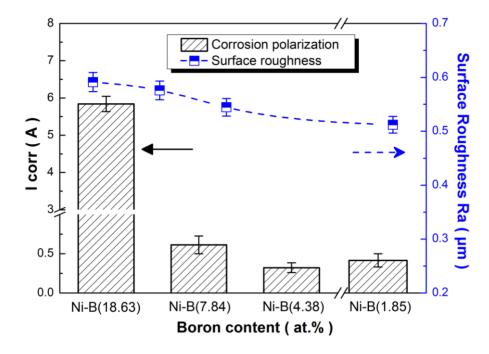


Figure 7. (a) Corrosion current and surface roughness of Ni-B coatings with different boron contents.

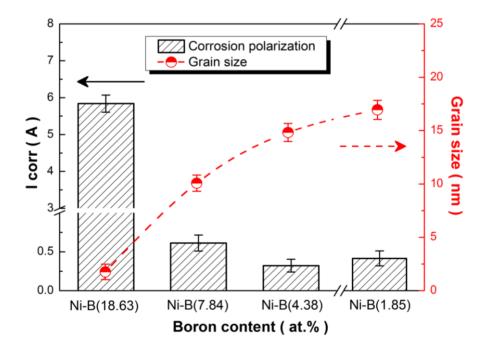
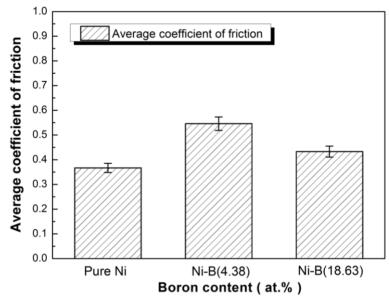


Figure 7.(b) Corrosion current and grain size for Ni-B coatings with different boron contents.

In general, coating corrosion resistance is influenced by coating property that including coating materials, thickness, micro structure (grain size) and surface morphology (roughness). In this research, the Ni-B and nickel coatings fabricated were controlled at the same thickness ( $60 \mu m$ ). Therefore, we can assumption that the grain size and surface roughness are regarded as the two factors affecting corrosion resistance of the coating. The variation of corrosion current density with the surface roughness, and the variation of corrosion current density with the grain size are presented in Fig. 7(a) and Fig. 7(b) respectively. From Fig. 7(a), it can be seen that the surface roughness of all tested samples is between 0.51 and 0.59  $\mu m$ , whereas the corrosion current density of Ni-B coatings varies tremendously. We can inference that the effect of surface roughness on corrosion resistance is insignificantly. On the other hand, as shown in Fig. 7(b), a trend that corrosion current density of Ni-B coating the grain size is the dominant factor for the corrosion resistance.

The increase of corrosion resistance with increasing grain size can be explained by the more grain boundaries existence for small grain compared to large grain. Hence, due to the corrosion solution can penetrate into Ni-B coatings through these boundaries and reach the substrate, resulting in weakening the corrosion resistance. The effect of the boron content on corrosion resistance of the resulting coating was investigated by Bekish et al. [26], they study Ni-B alloy coatings with different boron contents ranging from 4 to approximately 28 at.% by electrodeposition in a nickel-plating bath containing sodium decahydroclovodecaborate (Na<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) as a boron source and investigated the influence of the boron content in the coatings on their structure, morphology, corrosion behavior, and physico-mechanical properties. Their results found that the corrosion resistance of the nanocrystalline Ni-B coatings (boron content  $\leq 8$  at.%) was higher than that of the amorphous ones (boron content  $\geq 20$ at.%) and the Ni-B coating with a relatively low boron content (4 at.%) had the best corrosion resistance. Similarly, our present result found that the maximal corrosion resistance was obtained for Ni-B coating having a boron content of 4.38 at.%, which is in good agreement with their result. The better corrosion resistance of the Ni-B coatings obtained in present study as compared to those reported by other investigator [23] might be ascribed to the fact that the elimination of cracks in the surface of coatings which prevents the penetration of chloride solutions into the coating and as a result, the corrosion resistance increases.

## 3.5 Wear characteristics



**Figure 8.** (a) Average coefficient of friction of different coatings: (a) Pure Ni, (b) Ni-B-4.38 at.%, and (c) Ni-B-18.63 at.% .

Fig. 8 demonstrates that the hardness of sample has a substantial effect on the friction coefficient and wear resistance. Fig. 8(a) shows the relationship between the average coefficient of friction and the boron content of electrodeposited Ni and Ni-B coatings. Two Ni-B coatings were chosen for wear test. One sample is the Ni-B coating having the highest hardness, and the other one is the coating having the least hardness. It can be clearly from this figure that the coefficient of friction is less for pure Ni coating compared to those obtained for Ni-B coatings. Owing to it having an extremely low hardness (245 Hv), a serious plastic deformation occurs during the wear test for pure Ni coating. As a consequence, the coefficient of friction of pure Ni coating is low (0.367).

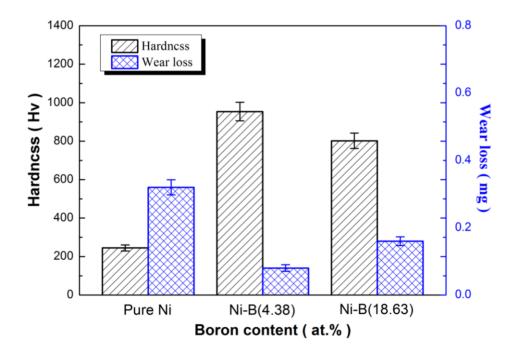


Figure 8. (b) The hardness and the wear loss for different coatings: (a) Pure Ni (b) Ni-B-4.38 at.% (c) Ni-B-18.63 at.%.

The wear loss of the tested samples is given in Fig. 8(b). As seen, the wear loss decreases with increasing hardness of the coatings, in the following order: pure Ni (0.32 mg), Ni-B-18.63 at.% (0.16 mg), Ni-B-4.38 at.% (0.08 mg). The wear loss of Ni-B-4.38 at.% is 4 times less than that of pure Ni. This result agrees with Archard's equation that the wear of a material is inversely proportional to its hardness. Hence it can be concluded that tailoring the boron content in the coating by adjusting the electrodeposition current density allows for precise control of hardness.

The hardness, corrosion resistance and friction coefficient of the Ni-B coatings prepared in this work are summarized in Table 3. For comparison, these properties of some electroplated Ni-B coatings reported in literatures are also presented in Table 3. The maximum hardness obtained in the present study (954 Hv) is comparable to that reported in literature (968 Hv, see Table 3). Moreover, the I<sub>corr</sub> of Ni-B obtained in present study ( $3.22 \times 10^{-7} \sim 5.84 \times 10^{-6}$  A•cm<sup>-2</sup>) is about at least one order magnitude lower than that for Ni-B coatings reported in the literatures. It shows from the polarization test results that Ni-B coatings prepared in present study are more resistant to corrosion than those reported in literatures. The above results indicate that the Ni-B coating with high hardness and good corrosion resistance can be successfully fabricated by our method.

Direct current electrodeposition							
	Electroly	yte	Coatings properties and tests performed				
Reference	Nickel bath (pH)	Boron reducing agent	Boron content in the coating	Hardness of the as- deposited coating	$I_{corr}$ (A/cm <sup>2</sup> )	Wear rate Average coefficient of frictiona(C.O.F) Normal Load	
Krishnaveni [21]	Nickel sulfate (3.5)	DMAB	0.6~3 wt.%	600 Hv		$\begin{array}{c} 0.52 \sim 2.46 \\ (\times 10^{-10} \text{ kgN}^{-1} \text{ m}^{-1}) \\ 0.724 \sim 0.784 \text{ /C.O.F} \end{array}$	
						(8 N × 10 N × 12 N)	
Ogihara [22]	Nickel sulfate (1.0-5.5)	DMAB TMAB	5 at.% <sub>(DMAB)</sub> 19 at.% <sub>(TMAB)</sub>	300~968 Hv <sub>(DMAB )</sub> 730~880 Hv <sub>(TMAB)</sub>			
López [23]	Nickel sulfamate (3.0-3.5)	DMAB	0.6~3.4 wt.%	200~716 Hv	1.036×10 <sup>-5</sup> ~1.197×10 <sup>-5</sup>		
Liang [24]	Nickel sulfamate (3.5)	DMAB	Not mentioned	700~800 Hv		4.101×10 <sup>-6</sup> mm <sup>3</sup> / Nm 0.10~0.12 /C.O.F /Lubricated sliding (10 N ≤ 15 N ≤ 20 N)	
Lee [25]	Nickel sulfate (3)	TMAB	2~11 at.%	700~850 Hv		0.2~0.45 /C.O.F (30N)	
Bekish [26]	Nickel sulfate (4.5)	$Na_2B_{10}H_{10}$	4~26 at.%	7600~8500 MPa (775~867Hv)	Not shown	0.2~1.4 ×10 <sup>-2</sup> mm <sup>-1</sup> / Nm 0.9~0.11 /C.O.F	

**Table 3.** The comparison of the electrodeposition parameters and the resultant properties of some electroplated Ni-B coatings reported in literatures with our results from this study.

						(1 MPa)
Krishnaveni [27]	Nickel sulfate (3.5)	DMAB	3 wt.%		1.231×10 <sup>-5</sup>	
Our work	Nickel sulfamate (6.5)	TMAB	1.85~18.63 at.%	802~954 Hv	3.22×10 <sup>-7</sup> ~5.84×10 <sup>-6</sup>	0.43~0.55 /C.O.F.

## 4. CONCLUSIONS

This study investigated the influence of the plating conditions on the properties and corrosion resistance of the resultant Ni-B alloy coatings. The conclusions drawn from our results are provided below:

1. In the electrodeposition process, current density is influencing boron content in the coating and deposition rate. Both the boron content in the coatings and deposition rate decreased with increasing the deposition current density.

2. The crack-free Ni-B coatings with different boron content ranging from 1.85 to 18.63 at.% were prepared by electrodeposition at different current densities in a sulfamate bath containing 0.06 M TMAB. The surface roughness and microhardness for these coatings was in the range of 0.5-0.6  $\mu$ m and 802-954 Hv, respectively.

3. The grain size of the Ni-B alloy coatings decreased from 17 to 1.8 nm with increasing boron content in the coatings, resulting in the micro-structure of the coatings transforms from crystal state to amorphous-like.

4. The Ni-B coatings prepared in present study were crack-free, therefore, they had higher corrosion resistance in 3.5% NaCl solution as compared to pure Ni coating and those reported by other investigator [23]. Grain size, which is negatively correlated to boron content in the coatings, is the main factor affecting corrosion resistance of the coatings. Corrosion resistance decreased with the decrease in grain size for nanocrystalline Ni-B coatings.

5. The nanocrystalline Ni-B coating with boron content of 4.38 at% had a maximal hardness (954 Hv). On the contrary, the Ni-B coating with a high boron content (18.63 at.%) exhibited an amorphous-like structure and had a lowest hardness (802 Hv). The hardness strongly affected wear resistance and friction coefficient of Ni-B coatings.

## ACKNOWLEDGEMENT

The authors express their thanks for the finical support by Ministry of Science and Technology of Taiwan according the contract of MOST 104-2221-E-606-017.

## References

- 1. Y. C. Sharma, Colloids Surf. A Physicochem. Eng. Asp., 215 (2003) 155.
- 2. S. Hena, J. Hazard. Mater., 181 (2010) 474.
- 3. J. L. Gardea-Torresdey, K. J. Tiemann, V. Armendariz, L. Bess-Oberto, R. R. Chianelli, J. Rios, J. G.

Parsons and G. Gamez, J. Hazard. Mater., B80 (2000) 175.

- 4. K. H. Hou, M. C. Jeng and M. D. Ger, *Wear.*, 262 (2007) 833.
- 5. W. T. Tsai and S. T. Chung, J. Supercrit. Fluids., 95 (2014) 292.
- 6. P. C. Huang, K. H. Hou, G. L. Wang, M. L. Chen and J. R. Wang, Int. J. Electrochem. Sci., 10 (2015) 4972.
- 7. K. H. Houa, H. T. Wang, H. H. Sheuc and M. D. Gerca, Appl. Surf. Sci., 308 (2014) 372.
- 8. V. Torabinejad, A. Sabour Rouhaghdam, M. Aliofkhazraei and M. H. Allahyarzadeh, J. Alloys Compd., 657 (2016) 526.
- 9. M. Srivastava, V. K. William Grips and K. S. Rajam, Appl. Surf. Sci., 253 (2007) 3814.
- 10. P. Peeters, G. v. d. Hoorn, T. Daenen, A. Kurowski and G. Staikov, *Electrochim. Acta.*, 47 (2001) 161.
- 11. Z. Liu and W. Gao, Appl. Surf. Sci., 253 (2006) 2988.
- 12. T. S. N. Sankara Narayanan and S. K. Seshadri, J. Alloys. Compd., 365 (2004) 197.
- B. Campillo, P. J. Sebastian, S. A. Gamboa, J. L. Albarran and L. X. Caballero, *Mater. Sci. Eng.* C-Mater., 19 (2002) 115.
- 14. F. Delaunois, J. P. Petitjean, P. Lienard and M. Jacob Duliere, Surf. Coat. Technol., 124 (2000) 201.
- 15. F. Delaunois and P. Lienard, Surf. Coat. Technol., 160 (2002) 239.
- 16. Z. Abdel Hamid, H. B. Hassan and A. M. Attyia, Surf. Coat. Technol., 205 (2010) 2348.
- 17. V. Vitrya, A. Sensa, A. F. Kantab and F. Delaunoisa, Appl. Surf. Sci., 263 (2012) 640.
- A. R. Di Giampaolo, J. G. Ordofiez, J. M. Gugliemacci and J. Lira, Surf. Coat. Technol., 89 (1997) 127.
- 19. M. Anik, E. Körpe and E. Şen, Surf. Coat. Technol., 202 (2008) 1718.
- 20. B. Oraon a, G. Majumdar and B. Ghosh, Mater. Des., 29 (2008) 1412.
- 21. K. Krishnaveni, T. S. N. Sankara Narayanan, S. K. Seshadri, Mater. Chem. Phys., 99 (2006) 300.
- 22. H. Ogihara, K. Udagawa and T. Saji, Sur. Coat. Technol., 206 (2012) 2933.
- 23. J. R. López, P. F. Méndez, J. J. Pérez-Bueno, G. Trejo, G. Stremsdoerfer and Y. Meas, *Int. J. Electrochem. Sci.*, 11 (2016) 4231.
- 24. Y. Liang, Y. S. Li, Q. Y. Yu, Y. X. Zhang, W. J. Zhao and Z. X. Zeng, Surf. Coat. Technol., 264 (2015) 80.
- 25. K. H. Lee, D. Chang and S. C. Kwon, *Electrochim. Acta.*, 50 (2005) 4538.
- 26. Y. N. Bekish, S. K. Poznyak, L. S. Tsybulskaya and T. V. Gaevskaya, *Electrochim. Acta.*, 55 (2010) 2223.
- 27. K. Krishnaveni, T. S. N. Sankara Narayanan and S. K. Seshadri, J. Alloys Compd., 480 (2009) 765.
- 28. I. Mizushima, P. T. Tang, H. N. Hansen and M. A. J. Somers, *Electrochim. Acta.*, 51 (2006) 6128.
- 29. R. Abdel-Karim, J. Halim, S. El-Raghy, M. Nabil and A. Waheed, J. Alloys Compd., 530 (2012) 85.
- 30. S. Y. Kang and W. S. Hwang, Indian J. Sci. Technol., 8(2015) 1.
- 31. M. ONODA, T. TSUCHIYA, K. OGAWA and T. WATANABE, J. Surf. Finish. Society. Jp., 41 (1990) No. 4, 388.
- 32. Y. Wang and D. O. Northwood, Int. J. Hydrogen. Energy., 32 (2007) 895.

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