

Electroless deposition of Ni–B, Co–B and Ni–Co–B alloys using dimethylamineborane as a reducing agent

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Fundamental aspects of electroless Ni–B, Co–B and Ni–Co–B alloys have been systematically examined. The composition, crystal structure and deposition rate of the alloys were determined as a function of the concentration of reducing agent (dimethylamineborane) and complexing agents (tartrate, citrate, malonate and succinic acid), bath pH and Ni²⁺/Co²⁺ ratio. Changes in the deposition rate and metallurgical features of the alloys induced by the change in plating parameters are discussed, based on electrochemical polarization data and the formation enthalpy of the nickel and cobalt borides.

Keywords: *electroless Ni–Co–B alloy, dimethylamineborane, complexing agent, deposition rate, crystal structure*

1. Introduction

Electroless plating of various metals has been studied extensively since this technique produces coatings on nonconductive substrates [1–3] with good adhesion and uniformity. In the surface finishing industry hypophosphite and borohydride have been mainly employed as reducing agents for electroless nickel and cobalt plating. The former reducing agent, giving Ni–P and Co–P alloys, has been widely employed because of its reasonable cost. The use of borohydride is somewhat restricted because it is more expensive than hypophosphite. However, the hardness and solderability and magnetic properties of Ni–B, Co–B and Ni–Co–B films are different [4] from those of the corresponding alloys containing phosphorus. Therefore, the use of borohydride has received much attention in the surface finishing of electrical devices.

In this study fundamental aspects of electroless Ni–Co–B alloy deposition were studied with attention being paid to the electrocatalytic nature of nickel and cobalt for the oxidation of dimethylamineborane. The kinetics and the alloy composition are influenced by the interaction between the deposited metal and the reducing agent. The effect of complexing agents of different kinds was also examined as the reactivity of nickel and cobalt complex ions is influenced by introducing two kinds of complexing agent [5]. The effect of complexing agent, pH and the Ni²⁺/Co²⁺ ratio on the kinetics of electroless deposition of Ni–B, Co–B and Ni–Co–B alloys and the

stability of the solution have been studied and characterization of the deposits has been carried out.

2. Experimental details

Cold-rolled steel (SPCC) strips (50 mm × 35 mm × 2 mm) were used as substrates for electroless plating after Pd-activation. The bath composition and its operating conditions for electroless Ni–B, Co–B and Ni–Co–B plating are shown in Table 1 and Table 2, respectively. The deposition rate of the film was determined by weight gain after plating for 1 h. The composition of the films was analysed by X-ray fluorescent and atomic absorption spectroscopy. The films were heat-treated at various temperatures in a vacuum of 1×10^{-3} Pa for 1 h after raising the temperature (5°C min^{-1}) to a finite value. The crystal structure of the films was examined by X-ray diffraction.

Partial anodic and cathodic polarization curves were measured in a solution without metal ion or reducing agent from bath B (pH 6.0) shown in Table 1. In each run, SPCC strips were coated with Ni–B or Co–B alloy and these were employed as the working electrode. Potentio-dynamic measurements were carried out at 60 °C by the use of a computer-aided potential scanning unit. The potential was swept at a rate of 1 mV s^{-1} with reference to a calomel electrode (SCE). The deposition rate of nickel and cobalt was determined by the current density at the mixed potential.

Table 1. Bath composition and plating conditions for electroless Ni-B and Co-B alloy films

Chemicals	Concentration/M					
	Bath A		Bath B		Bath C	
	Ni-B	Co-B	Ni-B	Co-B	Ni-B	Co-B
NiSO ₄ ·6H ₂ O	0.10		0.10		0.10	
CoSO ₄ ·7H ₂ O		0.10		0.10		0.10
Na ₂ C ₄ H ₄ O ₆ ·2H ₂ O	*	*				
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O			0.10	0.10	0.10	0.10
Na ₂ C ₃ H ₂ O ₄ ·2H ₂ O			0.10	0.10	0.10	0.10
C ₄ H ₆ O ₄						
(CH ₃) ₂ NH·BH ₃	0.05	0.05	0.05	0.05	0.025~0.10	0.025~0.10
Bath pH	6.0	6.0	4.0~7.5	4.0~7.5	6.0	6.0
Bath temperature	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C
Plating time	1h	1h	1h	1h	1h	1h

*0.20 mol dm⁻³ Na₂C₄H₄O₆·2H₂O, Na₃C₆H₅O₇·2H₂O, Na₂C₃H₂O₄·H₂O or C₄H₆O₄

3. Results and discussion

3.1. Effect of complexing agent on deposition rate and boron content of Ni-B and Co-B alloys

The effect of complexing agent on the deposition rate and boron content of Ni-B and Co-B films from bath A shown in Table 1 was studied. Sodium tartrate (Na₂C₄H₄O₆·2H₂O), sodium citrate (Na₃C₆H₅O₇·2H₂O), sodium malonate (Na₂C₃H₂O₄·H₂O) and succinic acid (C₄H₆O₄) were employed as complexing agent. The results are shown in Figs 1 and 2. The deposition rate of Ni-B alloy was different depending on the kind of complexing agent employed. In general, the complexing agents having smaller stability constant to nickel ion resulted in higher deposition rates and deposition rates of nickel films decreased with increasing complexing agent. The acceleration of Ni-B deposition was explained by the buffering action inhibiting the pH change in the reaction layer. The acceleration effect was pronounced in the case of complexing agent having low stability constant. The deposition rate of Ni-B alloys was decreased by the presence of the excess complexing agent, which decreased the free nickel ion. The boron content of

the Ni-B films varied in the range 3 to 6 wt% as a function of complexing agent and of concentration. The boron content decreased with increasing alloy deposition rate.

In the case of Co-B alloys, the same tendency was also observed in the relationship between deposition rate and boron content. However, a characteristic feature was that the deposition rate and boron content of Co-B alloys were significantly smaller than those of Ni-B alloys, because the catalytic activity for the oxidation of dimethylamineborane and the tendency for boride formation were small in the cobalt-boron system. Available thermodynamic data indicated that boron was liable to codeposit with nickel compared to cobalt. The formation enthalpies of Ni₃B and Co₃B were reported to be -132.8 kJ mol⁻¹,

Table 2. Bath composition and plating conditions for electroless Ni-Co-B alloy films

Chemicals	Concentration/M	
	Bath A	Bath B
NiSO ₄ ·6H ₂ O	0~0.10	0.09
CoSO ₄ ·7H ₂ O	0.10~0	0.01
Na ₂ C ₄ H ₄ O ₆ ·2H ₂ O	0.1	0.1
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	0.1	0.1
(CH ₃) ₂ NH·BH ₃	0.05	0.05
Bath pH	6	5.0~7.5
Bath temperature	60 °C	60 °C
Plating time	1h	1h

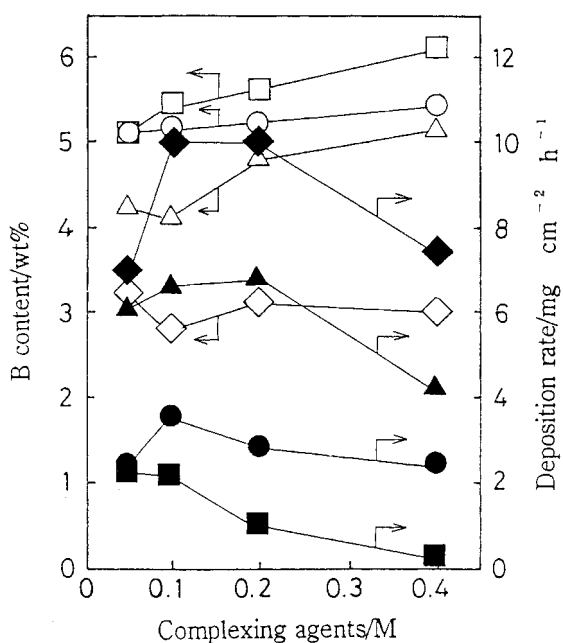


Fig. 1. Effect of complexing agent on deposition rate and boron content of Ni-B alloy films from bath A. Key: (○, ●) Na₂C₄H₄O₆·2H₂O; (□, ■) Na₃C₆H₅O₇·2H₂O; (△, ▲) Na₂C₃H₂O₄·H₂O; (◇, ◆) C₄H₆O₄.

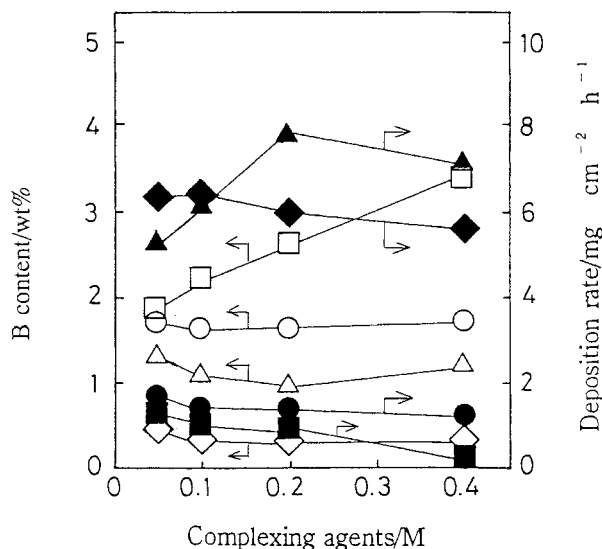


Fig. 2. Effect of complexing agent on deposition rate and boron content of Co-B alloy films from bath A. Key: (○, ●) $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$; (□, ■) $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$; (△, ▲) $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$; (◇, ◆) $\text{C}_4\text{H}_6\text{O}_4$.

and $-66.9 \text{ KJ mol}^{-1}$, respectively [6, 7], which suggests that nickel boride was quite stable and easy to form compared to cobalt boride.

3.2. Effect of pH on deposition rate and boron content of Ni-B and Co-B alloys

The effect of pH on Ni-B and Co-B alloy deposition was examined for bath B, shown in Table 1, in which both sodium citrate and sodium malonate were used as complexing agents. The deposition rate and boron content of the alloys were measured as a function of pH and the results are shown in Fig. 3. The deposition rate of Ni-B and Co-B alloys increased with increasing pH and the oxidation of dimethylamineborane was enhanced. The boron content of Ni-B alloys was

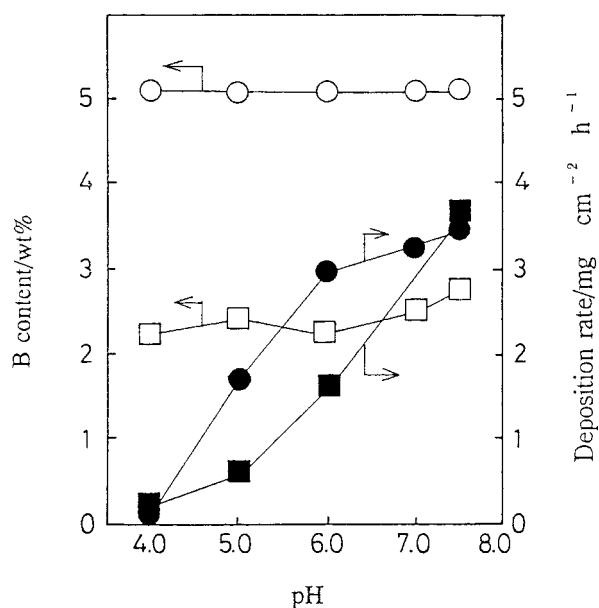


Fig. 3. Effect of pH on deposition rate and boron content of Ni-B and Co-B alloy films from bath B. Key: (○, ●) Ni-B alloy film; (□, ■) Co-B alloy film.

little changed with pH and remained nearly constant at around 5.2 wt%. However, the boron content of Co-B alloys increased slightly from about 2.2 wt% to 2.8 wt% with increasing pH. In this case, a reverse relationship between the boron content and the deposition rate of Ni-B and Co-B alloys was detected.

3.3. Effect of reducing agent concentration on deposition rate and boron content of Ni-B and Co-B alloys

The effect of dimethylamineborane concentration was evaluated for bath C (Table 1). The results of the deposition rate and boron content of Ni-B and Co-B alloys are shown in Fig. 4. The deposition rate and boron content of the alloys increased with increase in the concentration of reducing agent from 0.025 to 0.10 M. The boron content increased as the amount of boron source increased. However, it reached a limiting value at concentrations higher than 0.075 M.

3.4. Effect of $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio on deposition rate and composition of Ni-Co-B alloys

The effect of $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio on the deposition rate and alloy composition was investigated for bath A (Table 2). The results shown in Fig. 5 indicate that the Ni/Co ratio of the alloys was greater than the $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio in the solution, indicating preferential deposition of cobalt. For example, the alloy composition was found to be 3.4 at % Ni : 94 at % Co : 2.6 at % B when the $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio was adjusted to 1. Therefore, a nickel-rich composition was obtained by increasing the $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio above 9. Consequently, the electroless deposition of Ni-Co-B alloys was classified as anomalous in which the electrochemically less noble metal was preferentially deposited.

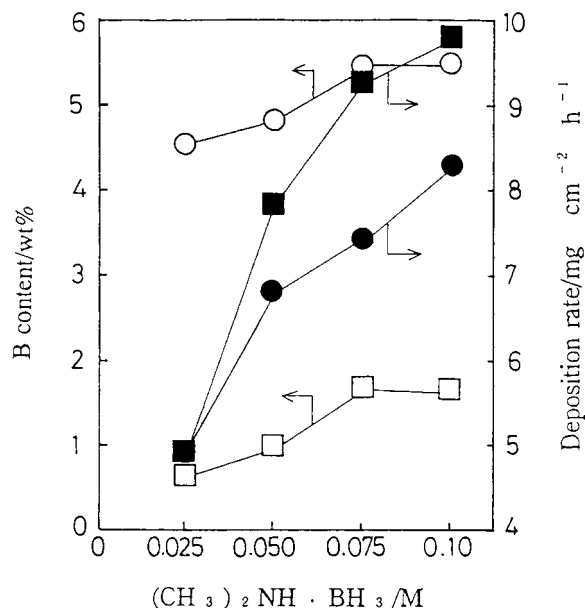


Fig. 4. Effect of DMAB concentration on deposition rate and boron content of Ni-B and Co-B alloy films from bath C. Key: (○, ●) Ni-B alloy film; (□, ■) Co-B alloy film.

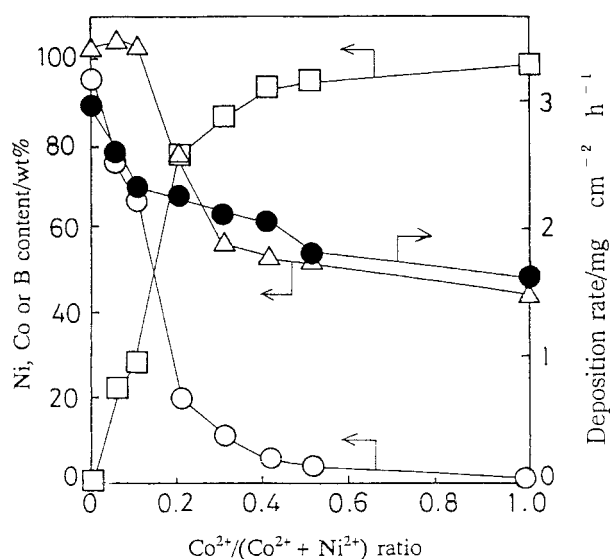


Fig. 5. Effect of $\text{Co}^{2+}/(\text{Co}^{2+} + \text{Ni}^{2+})$ ratio on composition and deposition rate of Ni-Co-B alloy films from bath D. Key: (○) Ni content, (□) Co content, (Δ) B content ($\times 1/10$) and (●) deposition rate of Ni-Co-B alloy.

The deposition rate of Ni-Co-B alloys increased with increasing nickel content of the alloy. To elucidate this phenomenon, the electroless deposition of the alloys was electrochemically analysed based on mixed potential theory. The anodic oxidation curves of dimethylamineborane and the cathodic reduction of nickel and cobalt ions were examined at the Ni-B or Co-B electrode and the results are shown in Fig. 6. The mixed potentials at Ni-B and Co-B electrodes were found to be -0.88 and -0.81 V vs SCE, respectively. The current densities at the mixed potential that directly correlated with the deposition rate of Ni-B and Co-B films were found to be 1.3 and 1.2 mA cm^{-2} , respectively. These values are much smaller than the deposition rates determined by weight gain. Consequently, interaction between the partial anodic and

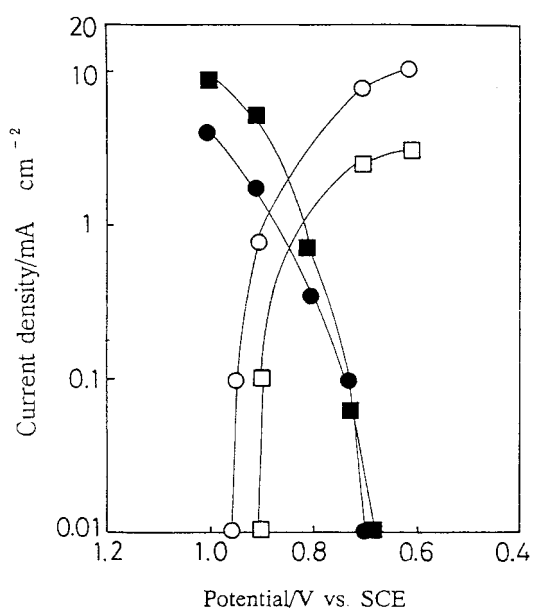


Fig. 6. Anodic oxidation curves of DMAB and cathodic reduction curves of Ni^{2+} and Co^{2+} at Ni-B and Co-B electrodes. Key: (○, ●) Ni-B electrode; (□, ■) Co-B electrode.

cathodic reactions is suggested. However, important information may be derived from Fig. 6. The partial polarization curves are characterized by low overvoltage for the reduction of cobalt ions in the mixed potential region and also by high catalytic activity of the Ni-B electrode for the oxidation of dimethylamineborane. This low overvoltage for cobalt deposition is a major factor in preferential cobalt deposition. The boron content of the Ni-Co-B alloys increased with increase in nickel content. This fact is reasonably explained by taking into account the difference in formation enthalpy of the nickel and cobalt borides. An increase in nickel content results in higher boron content in the alloys because of the strong affinity of nickel for boride formation.

3.5. Effect of pH on deposition rate and composition of Ni-Co-B alloys

The pH dependence was investigated for bath B, (Table 2). The deposition rate of Ni-Co-B alloys and their composition are shown in Fig. 7. The deposition rate increased linearly with pH. The deposition rate at pH 7.5 was ten times that at pH 5.0. In addition, both boron and nickel contents also increased with increasing pH, which is consistent with the thermodynamic data for boride formation.

3.6. Changes in crystal structure of Ni-B and Co-B alloys with heat-treatment

Typical X-ray diffraction patterns of Ni-B and Co-B alloys containing 5.6 wt % B (25 at % B) measured before and after heat-treatment are shown in Fig. 8. Ni-B and Co-B films with high boron content are characterized by the amorphous structure as indicated by the broadening of the diffraction line. The X-ray diffraction pattern greatly depended on boron

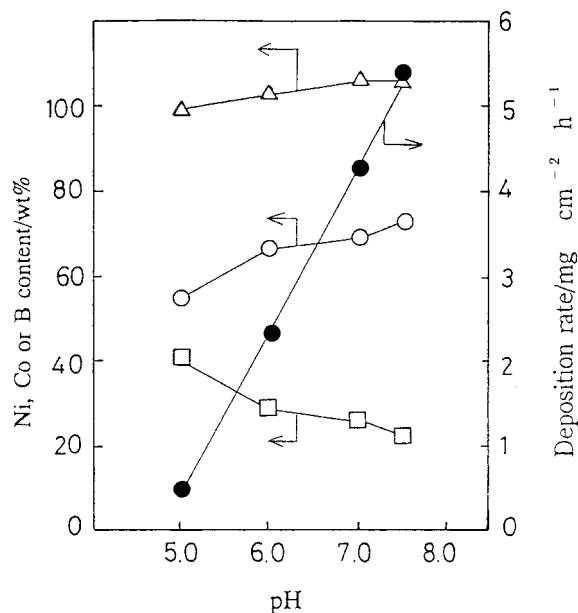


Fig. 7. Effect of pH on composition and deposition rate of Ni-Co-B alloy films from bath E. Key: (○) Ni content, (□) Co content, (Δ) B content and (●) deposition rate of Ni-Co-B alloy.

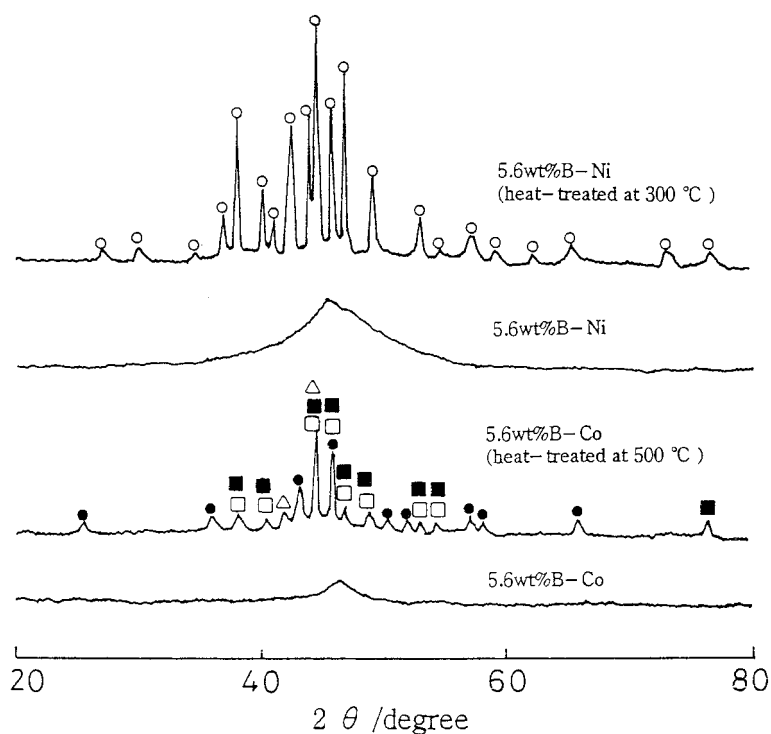


Fig. 8. X-ray diffraction patterns of electroless Ni-B and Co-B alloy films before and after heat treatment. Key: (○) Ni₃B; (●) Co₂B; (□) Co₃B; (■) Co₄B; (△) h.c.p. Co.

content, but was independent of the Ni/Co ratio of the alloys. The diffraction lines corresponded to Co(0 0 2) and Ni(1 1 1) and were recognized with decreasing boron content to values less than 1 wt %, which indicated that structural change from amorphous to crystalline may occur depending on boron content. A fine crystal structure was detected for as-plated Ni-B and Co-B films with boron content of 0.5 wt % (2.66 at %).

Crystallization induced by heating was confirmed by the appearance of diffraction lines corresponding to borides. The crystallization temperature of Co-B alloys was higher than that of Ni-B alloys at the same boron content, but increased with increasing boron content. For example, Ni-B alloys crystallized at 300 °C and Ni₃B was precipitated in the nickel matrix [8]. Further increase in annealing temperature gave no appreciable change in X-ray diffraction pattern. On the other hand, the crystallization of Co-B alloys commenced at 500 °C, resulting in hcp Co and metal borides (Co₂B, Co₃B and Co₄B). The precipitation of nickel boride at lower temperature compared to cobalt boride is consistent with the fact that the absolute value of the formation enthalpy (ΔH) of nickel borides is greater than that of cobalt borides.

4. Conclusions

This study on the kinetic aspects of electroless deposition of Ni-B, Co-B and Ni-Co-B alloys and their metallurgical characterization has led to the following results:

- (i) The boron content of the alloys was greatly influenced by the complexing agent employed. A

strong complexing agent decreased the deposition rate of the films and gave rise to higher boron content, leading to amorphous structures.

- (ii) The deposition rate of Ni-B, Co-B and Ni-Co-B alloys increased with increasing solution pH as a result of the enhanced oxidation of dimethylamineborane. The high catalytic activity of the Ni-B electrode for dimethylamineborane oxidation also explained the higher deposition rate of Ni-B alloys compared to Co-B alloys. In the Ni-Co-B alloy system, preferential deposition of cobalt was induced by the low overvoltage for the reduction of cobalt.
- (iii) The strong affinity of nickel for boron gave rise to higher boron content of Ni-B alloys compared to Co-B alloys. The higher the boron content of the films, the higher the crystallization temperature. The crystallization temperature of nickel boride was higher than that of cobalt boride, as the nickel boride was thermodynamically easy to form.

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