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Thermodynamics of electrodeposited Ni-B-SiC composite coatings①

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[Abstract] The φ-pH diagram of Ni-B-H_2O system was drawn, and the mechanism of electrodepositing Ni-B-SiC composite coatings was discussed. The results show that the deposition of Ni and B occurs prior to that of H_2 because of the over-potential of H_2 evolution on the Fe substrate. Boron can not singly deposit in aqueous solution. Nickel and boron can co-deposit in the form of Ni_4B_3 without evolution of hydrogen when the cathodical potential is kept to be - 1.415~ - 1.700 V.

[Key words] Ni-B-SiC composite coating; φ-pH diagram; electrodeposition
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1 INTRODUCTION

Requirements on the properties of materials have been put forward with the development of science and technology, and the single material can not meet the needs. The composite coatings with unique physical and mechanical properties, however, have been widely used in engineering technologies recently. Solid particles such as SiC, Al_2O_3 and Cr_2C_3 and base metals or alloys such as Ni, Cu, Fe and Ni-P alloy can be co-deposited to form better wear resistant coatings on the parts of machines using composite electrodeposition techniques and it is one of the effective methods to improve the surface properties of materials[1~5].

There have been many reports on Ni-B alloy and its composite coatings[6~8]. Their wear resistance is much better than that of Ni-P alloy and its composite coatings[9], however, it does not meet the needs of modern development of science and technology. The wear resistance of Ni-B alloy is relatively inferior compared with multiple element composite coatings[10~12], such as Ni-W-B-SiC and Ni-W-P-SiC coatings. However, the thermodynamics of electrodeposited Ni-B alloy and its composite coatings has not been studied up to now. In this way, the thermodynamics of electrodeposited Ni-B alloy has been studied in this paper.

2 EXPERIMENTAL

2.1 Bath composition and plating conditions

$NiCl_2 \cdot 6H_2O$	30 g/L
Complex agent(GZ-1)	40~ 120 g/L
Complex agent(GZ-2)	0~ 60 g/L
KBH_4	1.5~ 3.5 g/L
SiC(3.0~ 3.5 μm)	70 g/L
Current density	3~ 9 A/dm^2
pH	13.5
Temperature	30~ 60 ℃

2.2 Measurement of coating components

An EDAX 9100 electron probe X-ray diffraction spectrum (EPXDS) is used to measure the contents of boron, nickel and silicon carbide, and the average value of five points was needed. The components of the Ni-B-SiC composite coating are shown in Table 1.

Table 1 Components of Ni-B-SiC composite coating (mass fraction, %)

Ni	B	SiC
87.8~ 91.3	2.8~ 4.5	5.6~ 7.4

2.3 Analysis of coating structure

The phase structures of the coatings were analyzed by 3015 X-ray diffractometer made in Japanese.

3 RESULTS AND DISCUSSION

3.1 Thermodynamic data of Ni-B-H_2O system

Some thermodynamic data of Ni-B-H_2O system were obtained from Ref. [13], [14] and [15], and listed in Table 2.

3.2 Equilibrium equations of Ni-B-H_2O system

According to Table 2, some equilibrium equations of Ni-B-H_2O system are listed in Table 3.

3.3 φ-pH diagram of Ni-B-H_2O system

KBH_4 is an unstable compound, and it will decomposes in hot water and alkaline solutions. The following is reaction equations:

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Table 2 Thermodynamic data of Ni-B-H_2O system(25 ℃)

Chemical	$\Delta_f G$/(kJ·mol^{-1})	Chemical	$\Delta_f G$/(kJ·mol^{-1})
Ni	0	H_2	0
Ni^{2+}	- 48.195	O_2	0
$Ni(OH)_2$	- 452.694	HBO_3^{2-}	- 837.212
Ni_3O_4	- 711.227	$H_2BO_3^-$	- 909.568
$Ni_2O_3 \cdot H_2O$	- 706.253	$B_4O_7^{2-}$	- 2574.88
NiO_2	- 198.550	$HB_4O_7^-$	- 2626.169
H_2O	- 236.964	H_3BO_3	- 962.403
H^+	0	Ni_4B_3	- 305.002

$$BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2 \quad (1)$$

$$BO_2^- + OH^- \longrightarrow HBO_3^{2-} \quad (2)$$

$$BO_2^- + H_2O \longrightarrow HBO_3^{2-} + H^+ \quad (3)$$

Besides, there is an equilibrum in the solutions:

$$HBO_3^{2-} \rightarrow H_2BO_3^- \rightarrow B_4O_7^{2-} \rightarrow HB_4O_7^-$$

It can be seen from φ-pH diagram of B-H_2O system[13] that HBO_3^{2-} is stable and the electromative force for the equation $HBO_3^{2-} + 5H^+ + 3e \longrightarrow B + 3H_2O$ is $\varphi = -0.437 - 0.098$pH ($[HBO_3^{2-}] = 1$ mol/L) when pH value is equal to 13.5. This is far lower than the hydrogen line. Therefore, boron can not singly be deposited in aqueous solution.

The φ-pH diagram of Ni-B-H_2O system shown in Fig. 1 is drawn on the basis of Table 3.

It is known from Fig. 1 that lines (1), (2), (3), (4) and (5) are higher than that of boron in the B-H_2O system[13], but they are still lower than that of hydrogen. It is shown that if boron will be deposited in cathodical coating in the form of Ni_4B_3 when pH value of the bath is 13.5, the current potential must be controlled below - 1.415 V. However, the equilibrium line of Ni_4B_3 is lower than that of hydrogen. In this case, the dissociation reaction of H_2O will take place and produce hydrogen gas. Fortunately, there is an existence of over-potential when hydrogen evolutes on ferrous matrix. It complies with the equation of Tafel[13]:

$$\eta = a + b\lg J$$

where $a = 1.02$; $b = 0.113$; J is current density, A/dm^2.

The potential of evolution of hydrogen on the ferrous matrix must be within - 1.646 ~ - 1.700 V.

Table 3 Equilibrium equations of Ni-B-H_2O system (25 ℃)

No.	Equation	Relationship between φ or pH and concentrations
1	$4Ni + 3H_3BO_3 + 9H^+ + 9e = Ni_4B_3 + 9H_2O$	$\varphi = -0.518 + 0.0197\lg[H_3BO_3] - 0.0591$ pH
2	$16Ni + 3HB_4O_7^- + 39H^+ + 36e = 4Ni_4B_3 + 21H_2O$	$\varphi = -0.484 + 0.00493\lg[HB_4O_7^-] - 0.0640$ pH
3	$16Ni + 3B_4O_7^{2-} + 42H^+ + 36e = 4Ni_4B_3 + 21H_2O$	$\varphi = -0.440 + 0.00493\lg[B_4O_7^{2-}] - 0.0690$ pH
4	$4Ni + 3H_2BO_3^- + 12H^+ + 9e = Ni_4B_3 + 9H_2O$	$\varphi = -0.335 + 0.00493\lg[H_2BO_3^-] - 0.0788$ pH
5	$4Ni + 3HBO_3^{2-} + 15H^+ + 9e = Ni_4B_3 + 9H_2O$	$\varphi = -0.0852 + 0.00493\lg[HBO_3^{2-}] - 0.0985$ pH
6	$HBO_3^{2-} + H^+ = H_2BO_3^-$	$pH = 12.95 - \lg\{[H_2BO_3^-]/[HBO_3^{2-}]\}$
7	$4H_2BO_3^- + 2H^+ = B_4O_7^{2-} + 5H_2O$	$pH = 10.82 - 0.5\lg\{[B_4O_7^{2-}]/[H_2BO_3^-]^4\}$
8	$B_4O_7^{2-} + H^+ = HB_4O_7^-$	$pH = 8.8 - \lg\{[HB_4O_7^-]/[B_4O_7^{2-}]\}$
9	$HB_4O_7^- + H^+ + 5H_2O = 4H_3BO_3$	$pH = 6.8 - \lg\{[H_3BO_3]^4/[HB_4O_7^-]\}$
10	$Ni^{2+} + 2e = Ni$	$\varphi = -0.250 + 0.0295\lg[Ni^{2+}]$
11	$Ni(OH)_2 + 2H^+ = Ni^{2+} + 2H_2O$	$pH = 6.08 - 0.5\lg[Ni^{2+}]$
12	$Ni(OH)_2 + 2H^+ + 2e = Ni + 2H_2O$	$\varphi = 0.110 - 0.0591$ pH
13	$Ni_3O_4 + 2H_2O + 2H^+ + 2e = 3Ni(OH)_2$	$\varphi = 1.305 - 0.0591$ pH
14	$Ni_3O_4 + 8H^+ + 2e = 3Ni^{2+} + 4H_2O$	$\varphi = 1.977 - 0.2364$ pH $- 0.0887\lg[Ni^{2+}]$
15	$3Ni_2O_3 \cdot H_2O + 2H^+ + 2e = 2Ni_3O_4 + 4H_2O$	$\varphi = 1.305 - 0.0591$ pH
16	$2(NiO_2 \cdot 2H_2O) + 2H^+ + 2e = Ni_2O_3 \cdot H_2O + 4H_2O$	$\varphi = 1.434 - 0.0591$ pH
17	$Ni_2O_3 \cdot H_2O + 6H^+ + 2e = 2Ni^{2+} + 4H_2O$	$\varphi = 1.753 - 0.1773$ pH $- 0.0591\lg[Ni^{2+}]$
18	$NiO_2 + 4H^+ + 2e = Ni^{2+} + 2H_2O$	$\varphi = 1.593 - 0.1182$ pH $- 0.0295\lg[Ni^{2+}]$
a	$2H^+ + 2e = H_2(g)$	$\varphi = 0.0295\lg p(H_2) - 0.0591$ pH
b	$O_2(g) + 4H^+ + 4e = 2H_2O$	$\varphi = 1.230 + 0.0148\lg p(O_2) - 0.0591$ pH

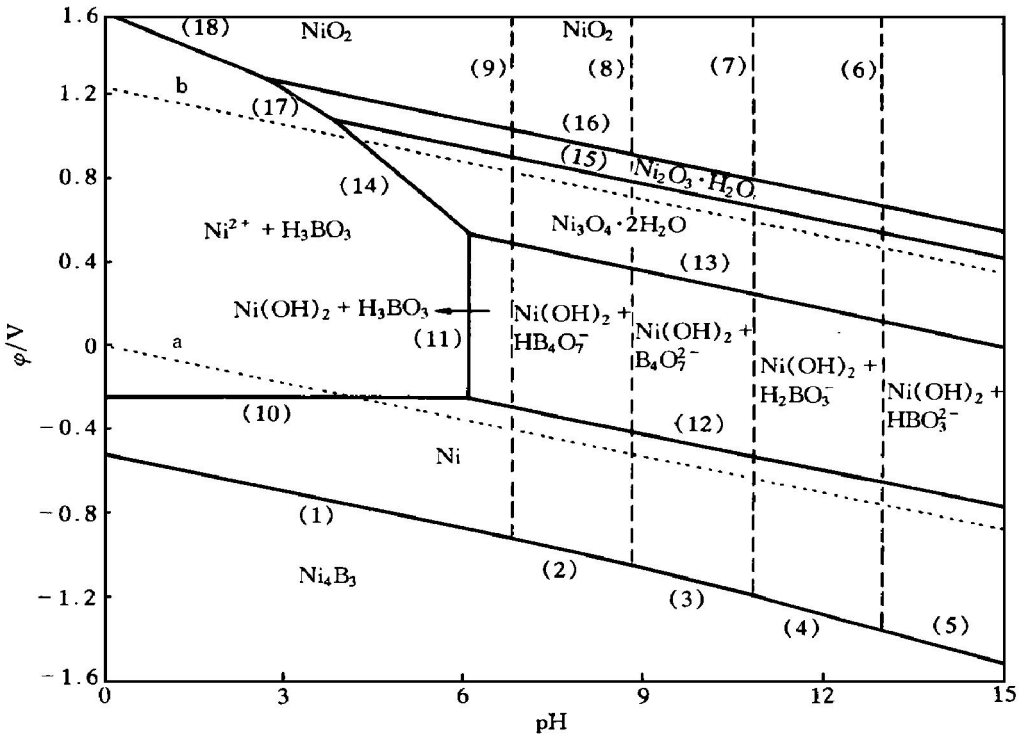

Fig. 1 φ-pH diagram of Ni-B-H_2O system
($[Ni^{2+}]$ = 1 mol/L, $[H_3BO_3]$ = $[H_2BO_3^-]$ = $[HBO_3^{2-}]$ = $[HB_4O_7^-]$ = 1 mol/L, 25 ℃)

There is an over-potential of hydrogen evolution on the nickel matrix as well, and its values are J_k = 1 A/dm^2, η = 0.747 V; J_k = 5 A/dm^2, η = 0.890 V; J_k = 10 A/dm^2, η = 1.048 V respectively. Therefore, nickel and boron can co-deposit in the form of Ni_4B_3 without evolution of hydrogen gas if the cathodical potential is kept to be − 1.415~ − 1.700 V.

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