Hydrogen Generation from Ammonia-Borane over Ni-B Amorphous Alloys Prepared from Aqueous Solution Based on Thermodynamic Prediction of Hidden Metastable of State

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Amorphous alloys are advantageous to obtain excellent catalytic activity from a disordered atomic arrangement and more dangling bonds. The compositional range of the Ni-B amorphous alloy was thermodynamically predicted. The function of the Gibbs energy of mixing, $\Delta_{\text{mix}}G_{\text{Ni-B}}^{\text{liquid}}$, and the activities of the Ni and B components, $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$, of the liquid phase was extrapolated to room temperature. The negative $\Delta_{\text{mix}}G_{\text{Ni-B}}^{\text{liquid}}$ was found from $X_{\text{Ni}} = 0.45$ to 0.92, indicating the existence of the liquid phase as metastable state, i.e. formation of amorphous alloy. The small $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$, that is, the strong attractive interaction between the Ni and B components suggested the liquid phase structure was stable. The Ni-B amorphous alloys were prepared from aqueous solution using reducing agent consistent well with the thermodynamic prediction. The preparation method from aqueous solution was useful to prevent from thermal migration of the atoms toward the equilibrium state. The quasi equilibrium oxygen pressures, $p_{\text{O}_2}(\text{Ni in amor.})$, and $p_{\text{O}_2}(\text{B in amor.})$, of Ni and B components in the amorphous alloys were evaluated from $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$. $p_{\text{O}_2}(\text{B in amor.})$ was found to be smaller than $p_{\text{O}_2}(\text{Ni in amor.})$, revealing that B components in amorphous alloy were preferentially oxidized and inhibited Ni oxidation. Not only a characteristic disordered atomic arrangement but also chemical alloying effect of B results in the excellent catalytic activity of the Ni-B alloy. [doi:10.2320/matertrans.MT-M2020284]

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1. Introduction

Amorphous alloys are thermally non-equilibrium materials with a short-range ordered atomic arrangement but no long-range order, and attract attention from academia and industry because of their superior corrosion resistance, mechanical toughness, magnetic, electronic, and catalytic properties compared to crystalline alloys. A. Takeuchi and A. Inoue^{1,2)} proposed the following three empirical rules for the formation of amorphous alloys, which are used as indices for the fabrication of amorphous alloys: (1) The alloy should consist of three or more elements; (2) The respective mixing enthalpies among the constituents should be negative; (3) The atomic size ratio of the constituents should be 12% or more.^{1,2)} It is possible to predict the constituent elements of amorphous alloys according to these rules obtained from extensive research data. However, it is still difficult to theoretically predict the composition range of amorphous alloys. In determining the composition range of amorphous alloys, the thermodynamic prediction on the basis of the accumulation of experimental data is essential, and no alternative method for the accurate prediction of the composition range of amorphous alloys has been found.

In this study, we focus on the prediction of amorphous alloys compositional ranges based on thermodynamic data. In our previous report, the phase diagram of the Ni-W-B³⁾ and Ni-Mo-B⁴⁾ ternary systems were determined from the thermodynamic calculation on the basis of the thermodynamic data of the Ni-Mo⁵⁾ and Ni-W⁶⁾ solid solutions, Ni₃B,⁷⁾ Ni₂B,⁷⁾ Mo₂B,⁸⁾ MoB,⁹⁾ W₂B,¹⁰⁾ WB,¹⁰⁾ NiMo₂B₂,⁵⁾ NiW₂B₂,⁶⁾ and NiMo⁵⁾ measured in our laboratory. In this

process, the interaction parameter, $\Omega_{\text{Ni-B}}^{\text{liquid}}$, of the liquid phase in the Ni-B binary system was optimized.^{3,4,11)} Extrapolating the function of the Gibbs energy of mixing, $\Delta_{\text{mix}}G_{\text{Ni-B}}^{\text{liquid}}$,^{3,4,11)} of the liquid phase calculated from $\Omega_{\text{Ni-B}}^{\text{liquid}}$ ^{3,4,11)} to room temperature, it is possible to predict the metastable compositional range of the liquid phase structure, i.e., the metastable compositional range of the amorphous structure. In the present study, the compositional range of formation of the Ni-B amorphous alloy was predicted from the function of $\Delta_{\text{mix}}G_{\text{Ni-B}}^{\text{liquid}}$,^{3,4,11)} and the Ni-B amorphous alloy was prepared from aqueous solution using reducing agent. A common method for the preparation of amorphous alloys is the liquid quenching method, which requires the mother alloy to be melted at temperatures above 1000 K and then rapidly solidified. In this study, Ni-B amorphous alloys were prepared from aqueous solution with minimal temperature variation during the preparation process.

The prepared Ni-B alloy was used as a catalyst in the hydrogen production reaction from ammonia borane. Hydrogen is expected to be a next-generation energy source, but it is difficult to store and transport. As a solution to this problem, hydrogen generation systems using high-hydrogen compounds such as ammonia borane are attracting attention. Qu *et al.*^{12,13)} reported that hydrogen was efficiently produced during hydrolysis of ammonia borane ($\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2$) in the presence of a metal catalyst.^{12,13)} Therefore, converting hydrogen into ammonia borane once enables safe storage and transportation, and also makes it possible to generate hydrogen as needed. The development of low-cost and highly efficient catalysts is important for the practical application of this system.^{12,13)} We reported that skeletal Cu,¹⁴⁾ skeletal Ni,¹⁵⁾ Ru-supported CeO₂,¹⁶⁾ Ru-Fe-supported CeO₂,¹⁷⁾ and Ni-supported

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CeO₂¹⁸⁾ showed excellent catalytic activity in hydrogen generation reactions from ammonia borane. Among these, Ni is a relatively inexpensive and highly active metal in hydrogen generation from ammonia borane. In this study, the properties as the catalyst of the Ni-B amorphous alloy were also investigated. To investigate the effect of the atomic arrangement on the catalytic properties, Ni-B crystalline alloy prepared by heating Ni-B amorphous alloy under vacuum. The catalytic properties were evaluated by the hydrogen generation amount from ammonia borane. Moreover, to investigate the effect of B species on the catalytic properties of Ni species, the quasi equilibrium oxygen pressures, $p_{O_2}(Ni_{in\ amorr.})$, and, $p_{O_2}(B_{in\ amorr.})$, of Ni and B components in the amorphous alloys were determined based on the thermodynamic data.

2. Method

2.1 Thermodynamic prediction of formation of amorphous alloys

We previously optimized Ω_{Ni-B}^{liquid} for calculating the Ni-Mo-B ternary phase diagram, expressed as^{3,4,11)}

$$\begin{aligned} \Omega_{Ni-B}^{liquid}/(J \cdot mol^{-1}) = & -161870 + 4.69 \times 10T \\ & + (-327140 + 1.81 \times 10^2 T)(1 - 2X_B) \\ & + (291380 - 9.78 \times 10T)(1 - 2X_B)^2 \\ & + (85853 - 5.25 \times 10T)(1 - 2X_B)^3 \\ & + (-237160 + 9.70 \times 10T)(1 - 2X_B)^4 \end{aligned} \quad (1)$$

where the standard states for Ω_{Ni-B}^{liquid} are the liquid phases of pure Ni and pure B.^{3,4,11)}

When the pure fcc Ni and rhombohedral B is taken as the standard states, the function of $\Delta_{mix}G_{N-B}^{liquid}(Ni^{fcc}$ and $B^{rhom.})$ was defined as^{3,4,11)}

$$\begin{aligned} \Delta_{mix}G_{N-B}^{liquid}(Ni^{fcc} \text{ and } B^{rhom.}) \\ = \Omega_{Ni-B}^{liquid}X_{Ni}X_B + RT(X_{Ni} \ln X_{Ni} + X_B \ln X_B) \\ + ({}^\circ G_{Ni}^{liquid} - {}^\circ G_{Ni}^{fcc})X_{Ni} + ({}^\circ G_B^{liquid} - {}^\circ G_B^{rhom.})X_B \end{aligned} \quad (2)$$

where $({}^\circ G_{Ni}^{liquid} - {}^\circ G_{Ni}^{fcc})$ ¹⁹⁾ and $({}^\circ G_B^{liquid} - {}^\circ G_B^{rhom.})$ ²⁰⁾ are the standard Gibbs energies of fusion of fcc Ni and rhombohedral B, given by

$$({}^\circ G_{Ni}^{liquid} - {}^\circ G_{Ni}^{fcc})/(J \cdot mol^{-1}) = 17615 - 10.21T \quad (3)$$

$$({}^\circ G_B^{liquid} - {}^\circ G_B^{rhom.})/(J \cdot mol^{-1}) = 50208 - 21.23T \quad (4)$$

Extrapolating $\Delta_{mix}G_{N-B}^{liquid}$ (eq. (2)) to room temperature, the formation composition range of the Ni-B amorphous alloy at 298 K was predicted.

Omori and Hashimoto⁷⁾ measured the Gibbs energies of mixing of Ni_{0.75}B_{0.25} and Ni_{0.67}B_{0.33}, given by

$$\begin{aligned} \Delta_{mix}G(Ni_{0.75}B_{0.25}, (Ni^{fcc} \text{ and } B^{rhom.}))/ (J \cdot mol^{-1}) \\ = -33201 + 11.05T \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta_{mix}G(Ni_{0.67}B_{0.33}, (Ni^{fcc} \text{ and } B^{rhom.}))/ (J \cdot mol^{-1}) \\ = -35733 + 10.10T \end{aligned} \quad (6)$$

where they⁷⁾ measured them, taking fcc Ni and rhombohedral B as the standard states. The phase stability of the amorphous alloys was discussed, compared with these equilibrium phases of Ni_{0.75}B_{0.25} and Ni_{0.67}B_{0.33}.

In our previous study,^{3,4,11)} the crystal structure of B was described as orthorhombic. However, strictly speaking, its symmetry is rhombohedral being further lower than orthorhombic. In the present study, the description of crystal structure of B is corrected.

2.2 Experimental

2.2.1 Preparation of the catalyst

Although the chemical reduction method is the most frequently used for the preparation of metal-boron alloy particles, the intense exothermic reaction between metal ions and boron hydride (BH₄⁻) induces aggregation of particles and makes it difficult to prepare amorphous alloys stably.²¹⁾ S. J. Chiang *et al.*²²⁾ succeeded the synthesis of Ni-B amorphous alloys in a water-in-oil microemulsion. However, this system makes it difficult to separate the solvent from the alloy particles and leads to environmental pollution. M. P. Pileni *et al.*²³⁾ and M. J. Schwuger *et al.*²⁴⁾ reported nanoparticle synthesis in reverse microemulsion. Hexing Li *et al.*²⁵⁾ reported Co-B amorphous alloy by controlling the size of amorphous nanoparticles using the inverse microemulsion method. Following the literature,²⁵⁾ uniform Ni-B amorphous alloys were prepared by chemical reduction of Ni²⁺ using the oil-in-water microemulsion method. To obtain Ni-B alloys with different atomic ratios, samples with various NiCl₂ addition amount (*i* mmol, *i* = 1, 2, 3, 4, 5, 6, 7) were prepared. NiCl₂·6H₂O (*i* mmol) and polyethylene glycol (Mw = 20,000, 5.0 g) were dissolved in distilled water (40 ml). Then 10 mL of cyclohexane was added to this solution. The mixture was treated under ultrasonic radiation at room temperature for 30 mi to form oil-in-water microemulsion. 10 mL of 2.0 M KBH₄ solution was dropped into the solution with vigorous stirring. After 2 h, the precipitate was washed with distilled water until pH 7 was achieved, then it was washed with ethanol and stored in ethanol until used. The prepared Ni-B alloys were denoted as a-Ni-B(*i*) (*i* = 1, 2, 3, 4, 5, 6, 7; NiCl₂ addition amount (mmol)). To obtain Ni-B particles with the desired composition, an excess amount of B source (KBH₄(aq), 20 mmol) was used. The standard electrochemical potentials, E° , of elemental B(cr) from BH₄⁻(aq) was calculated as -1.185 [V] from the standard Gibbs energy of formation, $\Delta_f G_m^\circ$, of BH₄⁻(aq)²⁶⁾ at 298.15 K (See Appendix). E° of elemental Ni from Ni²⁺(aq) was generally known as -0.237 [V].²⁷⁾ Therefore, to preparation of the Ni-B particle from eutectic precipitation of BH₄⁻(aq) and Ni²⁺(aq), activity of BH₄⁻(aq) should be increased to compensate such a large precipitation potential difference between -1.185 and -0.237 [V]. Therefore, an excess much amount of KBH₄ was used.

As a comparison, a-Ni-B(5) was annealed at 773 K under vacuum for 2 h to obtain a Ni-B crystalline alloy. Heat-treated samples are denoted as c-Ni-B(5).

2.2.2 Catalyst characterization

X-ray diffraction (XRD) measurements were performed to analyze the crystallinity of the samples (Ultima IV, Rigaku). In addition, the surface areas of the samples were estimated by the Brunauer-Emmett-Teller method using nitrogen physisorption isotherms obtained at 77 K (MicrotracBEL Corp. BEL-SORP mini). The X-ray photoelectron spectroscopy (XPS) analyses were conducted employing a

photoelectron spectrometer (ULVAC-PHI Inc., PHI5000) using monochromatic X-rays (Al K α , 1486.6 eV) to evaluate the atomic ratio. A charge neutralizer (low energy electrons and Ar⁺ ions) was used to compensate for the charging effect. Field emission-scanning electron microscopy (FE-SEM; JEOL, JSM-7001) was used to determine the surface morphology of the samples.

2.2.3 Catalytic reaction

The prepared catalysts (20 mg) were placed in a quartz reaction vessel equipped with a gas burette. An aqueous solution of ammonia borane (1 mmol) was injected into the vessel to initiate the reaction. The aqueous solution of ammonia borane was stirred magnetically at 308 K and the progress of the reaction was monitored periodically by reading the scale of the gas burette.

3. Results and Discussions

3.1 Prediction of the composition range of amorphous alloys

Figure 1 shows the calculated $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$ at 298.15 K from eq. (2) as dashed line, compared with the $\Delta_{\text{mix}}G(\text{Ni}_{0.75}\text{B}_{0.25})$ and $\Delta_{\text{mix}}G(\text{Ni}_{0.67}\text{B}_{0.33})$ from eqs. (5) and (6) as solid line. The negative $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$ (Ni^{fcc} and $\text{B}^{\text{rhomb.}}$) was found from $X_{\text{Ni}} = 0.45$ to 0.92, indicating that the existence of the liquid phase as metastable state, i.e. formation of amorphous alloy. $\Delta_{\text{mix}}G(\text{Ni}_{0.75}\text{B}_{0.25})$ and $\Delta_{\text{mix}}G(\text{Ni}_{0.67}\text{B}_{0.33})$ of the equilibrium solid phases were found to be more negative than $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$ of the metastable liquid phase.

Ni-B amorphous alloy particles were prepared from aqueous solution using reducing agent, which allows the alloy synthesis at room temperature. The synthesis at room temperature suppresses the migration of Ni and B atoms, preventing them from reaching an equilibrium crystalline state and preserving the amorphous atomic arrangement.

The crystallinity of Ni-B alloys prepared from aqueous solution using reducing agent was investigated by XRD

Fig. 1 The extrapolated Gibbs energy of mixing of the liquid phase, $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$ of the Ni-B binary system into 298.15 K, compared with those of $\text{Ni}_{0.75}\text{B}_{0.25}$ and $\text{Ni}_{0.67}\text{B}_{0.33}$.

Fig. 2 XRD patterns of a-Ni-B alloys.

Fig. 3 SEM images of Ni-B amorphous alloy ((a): a-Ni-B(1), (b): a-Ni-B(2), (c): a-Ni-B(3), (d): a-Ni-B(4), (e): a-Ni-B(5), (f): a-Ni-B(6), (g): a-Ni-B(7)).

measurements as shown in Fig. 2. No sharp peaks were observed in a-Ni-B (2, 3, 4, 5, 6), but a broad pattern typical of amorphous alloys was observed around 40°–55°, suggesting that a-Ni-B(2, 3, 4, 5, 6) were found to be mainly composed of amorphous structure. On the other hand, the peaks in a-Ni-B(1, 7) were observed at 33°–34° and 59°–61°, suggesting partial crystallization of Ni-B alloy.

The surface morphologies of a-Ni-B were observed by SEM. The SEM images of a-Ni-B(*i*) (*i* = 1, 2, 3, 4, 5, 6, 7) are shown in Fig. 3. Spherical particles were observed in all the samples, and their average diameter was about 40–60 nm.

Table 1 shows the surface areas and atomic ratios of the Ni-B amorphous alloys. The surface area of a-Ni-B(1) was hardly measured by the nitrogen absorption/desorption

Table 1 Surface area and atomic ratio of Ni-B amorphous alloy.

Sample	Surface area /m ² · g ⁻¹	Atomic ratio		XRD results amorphous ○ crystalline △
		Ni	B	
a-Ni-B(1)	—	56	44	○ + △
a-Ni-B(2)	53	61	39	○
a-Ni-B(3)	53	65	35	○
a-Ni-B(4)	39	67	33	○
a-Ni-B(5)	66	69	31	○
a-Ni-B(6)	31	71	29	○
a-Ni-B(7)	50	74	26	○ + △

measurement due to the small amount of sample. The surface area of the samples ranged from 30 to 70 m²g⁻¹, and a-Ni-B(5) showed the largest surface area among the samples. The atomic ratios of Ni and B in the prepared Ni-B alloys were investigated by XPS measurements (Table 1). The Ni atomic ratio increased with increasing the amount of NiCl₂. Ni-B alloys were prepared in the range of 56–74 mol% Ni. Excess much amount of KBH₄ (20 mmol) was required to prepare Ni-B alloys with high Ni ratio (56–74 mol% Ni). To prepare Ni-B particles from eutectic precipitation of BH₄⁻(aq) and Ni²⁺(aq), it is necessary to increase the activity of BH₄⁻(aq) to compensate for such a large precipitation potential difference between -1.185 and -0.237 [V] (See Appendix).

The results of XRD measurement (Fig. 2) and XPS measurement (Table 1) showed that the composition range of the amorphous alloy was 61–71 mol%Ni. It was found that Ni-B amorphous alloys can be formed in a narrower range (61–71 mol%Ni) than in the predicted range (Fig. 1, 45–92 mol%Ni). There are two reasons that caused the differences between the predicted range (45–92 mol%Ni) and experimental results (61–71 mol%Ni). Firstly, the Ni-B interaction parameters³⁾ determined in our previous study were optimized at high temperatures, and the application of the parameter to room temperature cause discrepancies between the prediction and experimental results. At room temperature, the accumulation of strain energy due to the difference in atomic radii between Ni and B atoms cause a positive shift in ΔG , which make the amorphous structure unstable. Secondly, the reaction heat between KBH₄ and metal ions affect the thermal activation process to the equilibrium crystal state. When the heat of the reaction is greater than the activation energy to crystallize the amorphous structure, the Ni and B atoms migrate toward the equilibrium crystalline state. The thermodynamic equilibrium theory hardly deals with the kinetic process of crystallization of amorphous structures.

3.2 Hydrogen generation over Ni-B amorphous alloys

To investigate the effect of the composition ratio of Ni-B alloys on the catalytic activity, the hydrogen generation from ammonia borane was carried out over a-Ni-B(*i*) (*i* = 1, 2, 3, 4, 5, 6, 7). Figure 4 showed the hydrogen generation amount per surface area over a-Ni-B(*i*) (*i* = 1, 2, 3, 4, 5, 6, 7)

Fig. 4 Amount of evolved hydrogen per sample surface area over prepared Ni-B alloy.

Fig. 5 Ni2p XPS spectra of Ni-B alloys.

at 10 min. a-Ni-B(5) showed the highest catalytic activity per surface area (Table 1), despite its higher surface area than the other samples. The catalytic activity increased with the increase in the amount of Ni, suggesting that Ni is the active site in this reaction. However, the activity of a-Ni-B(6) and a-Ni-B(7) decreased with increasing Ni ratio.

The oxidation state of Ni was measured by XPS to investigate the reason for the decrease in the catalytic activity of a-Ni-B(6) and a-Ni-B(7). Figure 5 and Table 2 shows the Ni2p3/2 XPS spectra and the area ratios of Ni and Ni²⁺, respectively. Table 2 also shows the area ratios of Ni and Ni²⁺ for the Ni supported porous CeO₂, as reported previously.¹⁸⁾ The Ni particles without B species were easily oxidized by exposure to air and showed no catalytic activity.¹⁸⁾ The XPS area ratio of Ni²⁺ increased with the decrease in B content. The decrease in the catalytic activity of a-Ni-B(6) and a-Ni-B(7) was attributed to a decrease in the ratio of Ni⁰ as the B content decreased. Ellingham diagram determined by B. Thomas²⁸⁾ showed that B species were more easily oxidized than Ni species, suggesting that the oxidation of Ni species was suppressed by the preferential oxidation of B. We subsequently evaluated the quasi equilibrium oxygen pressures, $p_{O_2}(Ni_{in\ amor.})$, and, $p_{O_2}(B_{in\ amor.})$, of Ni and B components in the amorphous alloys to confirm the oxidation state of Ni-B amorphous alloy. The relative partial molar Gibbs energies of the Ni and B components in amorphous alloys, $\Delta \tilde{G}_{Ni}^{liquid}$ and $\Delta \tilde{G}_B^{liquid}$, are defined as

Table 2 XPS area ratio (Ni^0 and Ni^{2+}).

Sample	XPS area ratio	
	/ area %	
	Ni^0	Ni^{2+}
a-Ni-B(5)	44	56
a-Ni-B(6)	18	82
a-Ni-B(7)	12	88
Ni/a-CeO ₂ (18)	9	91

$$\begin{aligned}\Delta \bar{G}_{\text{Ni}}^{\text{liquid}} &= \Delta_{\text{mix}} G^{\text{liquid}} - X_{\text{B}}^{\text{liquid}} \frac{\partial \Delta_{\text{mix}} G^{\text{liquid}}}{\partial X_{\text{B}}^{\text{liquid}}} \\ &= RT \ln(1 - X_{\text{B}}^{\text{liquid}}) \\ &\quad + \left(\Omega_{\text{Ni-B}}^{\text{liquid}} - (1 - X_{\text{B}}^{\text{liquid}}) \frac{\partial \Omega_{\text{Ni-B}}^{\text{liquid}}}{\partial X_{\text{B}}^{\text{liquid}}} \right) (X_{\text{B}}^{\text{liquid}})^2 \\ &\quad + ({}^{\circ}G_{\text{Ni}}^{\text{liquid}} - {}^{\circ}G_{\text{Ni}}^{\text{fcc}}) \quad (7)\end{aligned}$$

$$\begin{aligned}\Delta \bar{G}_{\text{B}}^{\text{liquid}} &= \Delta_{\text{mix}} G^{\text{liquid}} + (1 - X_{\text{B}}^{\text{liquid}}) \frac{\partial \Delta_{\text{mix}} G^{\text{liquid}}}{\partial X_{\text{B}}^{\text{liquid}}} \\ &= RT \ln X_{\text{B}}^{\text{liquid}} \\ &\quad + \left(\Omega_{\text{Ni-B}}^{\text{liquid}} + X_{\text{B}}^{\text{liquid}} \frac{\partial \Omega_{\text{Ni-B}}^{\text{liquid}}}{\partial X_{\text{B}}^{\text{liquid}}} \right) (1 - X_{\text{B}}^{\text{liquid}})^2 \\ &\quad + ({}^{\circ}G_{\text{B}}^{\text{liquid}} - {}^{\circ}G_{\text{B}}^{\text{rhomb.}}) \quad (8)\end{aligned}$$

The activities of Ni and B components in the amorphous alloys, $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$, are given by eqs. (9) and (10).

$$a_{\text{Ni in amor.}} = \exp \left(\frac{\Delta \bar{G}_{\text{Ni}}^{\text{liquid}}}{RT} \right) \quad (9)$$

$$a_{\text{B in amor.}} = \exp \left(\frac{\Delta \bar{G}_{\text{B}}^{\text{liquid}}}{RT} \right) \quad (10)$$

The oxidation reactions of the nickel and boron components in the amorphous alloys, $\text{Ni}_{\text{in amor.}}$ and $\text{B}_{\text{in amor.}}$, to form NiO and B_2O_3 are expressed as eq. (11) and (12), respectively

where $\Delta_{\text{f}}G^{\circ}$ is expressed as eq. (13) and (14), and K is the equilibrium constant namely

$$\begin{aligned}\Delta_{\text{f}}G^{\circ} &= -RT \ln K \\ &= -RT \ln \frac{a_{\text{NiO}}^2}{a_{\text{Ni in amor.}}^2 \left(\frac{p_{\text{O}_2}}{p^{\circ}} \right)} \\ &= RT \ln a_{\text{Ni in amor.}}^2 + RT \ln \left(\frac{p_{\text{O}_2}}{p^{\circ}} \right) \\ &= 2\Delta_{\text{f}}G^{\circ}(\text{NiO}) \quad (13)\end{aligned}$$

Fig. 6 Activities of Ni and B components in the amorphous alloys, $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$, at 298.15 K.

$$\begin{aligned}\Delta_{\text{f}}G^{\circ} &= -RT \ln K \\ &= -RT \ln \frac{a_{\text{B}_2\text{O}_3}^{\frac{2}{3}}}{a_{\text{B in amor.}}^{\frac{4}{3}} \left(\frac{p_{\text{O}_2}}{p^{\circ}} \right)} \\ &= RT \ln a_{\text{B in amor.}}^{\frac{4}{3}} + RT \ln \left(\frac{p_{\text{O}_2}}{p^{\circ}} \right) \\ &= 2/3 \Delta_{\text{f}}G^{\circ}(\text{B}_2\text{O}_3) \quad (14)\end{aligned}$$

The quasi equilibrium oxygen pressures, $p_{\text{O}_2}(\text{Ni}_{\text{in amor.}})$, and, $p_{\text{O}_2}(\text{B}_{\text{in amor.}})$, of Ni and B components in the amorphous alloys are expressed as eq. (15) and (16),

$$\frac{p_{\text{O}_2}}{p^{\circ}} = \exp \left\{ -\ln a_{\text{Ni in amor.}}^2 + (2/RT) \Delta_{\text{f}}G^{\circ}(\text{NiO}) \right\} \quad (15)$$

$$\frac{p_{\text{O}_2}}{p^{\circ}} = \exp \left\{ -\ln a_{\text{B in amor.}}^{\frac{4}{3}} + (2/3RT) \Delta_{\text{f}}G^{\circ}(\text{B}_2\text{O}_3) \right\} \quad (16)$$

where $\Delta_{\text{f}}G^{\circ}$ values for NiO and B_2O_3 were referenced from relevant data for NiO ($= -211.660$ [kJ (mol of compound⁻¹)²⁶]; B_2O_3 , ($= -1194.324$ [kJ (mol of compound⁻¹)²⁶]).

Figure 6 shows $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$. $a_{\text{B in amor.}}$ was found to be increased with increasing $X_{\text{B}}^{\text{liquid}}$, while $a_{\text{Ni in amor.}}$ was found to be decreased with increasing $X_{\text{B}}^{\text{liquid}}$ following the Gibbs-Duhem relationship. The obtained small $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$ means that the attractive interaction act between the Ni and B atoms. The amorphous structure is concluded to be resulted from the attractive interaction.

Figure 7 shows $p_{\text{O}_2}(\text{Ni}_{\text{in amor.}})$ and $p_{\text{O}_2}(\text{B}_{\text{in amor.}})$. The $p_{\text{O}_2}(\text{B}_{\text{in amor.}})$ data were found to be smaller than $p_{\text{O}_2}(\text{Ni}_{\text{in amor.}})$, indicating that the component of B was preferentially oxidized, that is, the component of B prevented the component of Ni from oxidation. This is reason for the excellent catalytic activity of the obtained amorphous alloys.

Table 3 summarized the relative partial molar Gibbs energies, $\Delta \bar{G}_{\text{Ni}}^{\text{liquid}}$, and, $\Delta \bar{G}_{\text{B}}^{\text{liquid}}$, activities, $a_{\text{Ni in amor.}}$, and, $a_{\text{B in amor.}}$, and quasi equilibrium oxygen pressures, $p_{\text{O}_2}(\text{Ni}_{\text{in amor.}})$, and, $p_{\text{O}_2}(\text{B}_{\text{in amor.}})$, of Ni and B components in the amorphous alloys. $\Delta \bar{G}_{\text{B}}^{\text{liquid}}$ of a-Ni-B(1) and a-Ni-

Fig. 7 Quasi equilibrium oxygen pressures, $p_{O_2}(Ni_{in\ amor.})$, and, $p_{O_2}(B_{in\ amor.})$, of Ni and B components in the amorphous alloys.

B(2) were positive, indicating B is difficult to dissolve into the liquid-like structure. As a result, Ni₂B crystals were precipitated in a-Ni–B(1) consistent with its positive value of $\Delta\bar{G}_{\text{B}}^{\text{liquid}}$. However, no crystalline precipitates were observed in a-Ni–B(2) despite the positive value of $\Delta\bar{G}_{\text{B}}^{\text{liquid}}$. It is likely that the negative value of $\Delta\bar{G}_{\text{Ni}}^{\text{liquid}}$ had a large stabilizing

Ni-B crystalline alloy (c-Ni-B(5)) was prepared by heated a-Ni-B(5) to compare the catalytic properties of amorphous and crystalline alloys. N₂ adsorption and desorption measurements were performed and found that the surface area of c-Ni-B(5) (3 m²g⁻¹) was much smaller than that of a-Ni-B(5) (66 m²g⁻¹), indicating that the particles were agglomerated by the heat treatment. Figure 8 shows the hydrogen production at 10 min per unit surface area of a-Ni-B(5) and c-Ni-B(5). The catalytic activity per surface area of a-Ni-B(5) was found to be higher than that of the c-Ni-B(5), suggesting that the amorphous structure was effective in improving the catalytic activity. Amorphous alloys have a disordered atomic arrangement and more dangling bonds than crystalline alloys. It is assumed that the dangling bonds positively effect on the catalytic activity. The preparation of crystalline transition metal borides requires high temperatures and energy. The crystalline transition metal borides are generally prepared by sintering transition metal and boron powders at temperatures above 1400 K.²⁹⁾ Ni-B amorphous

Table 3 Relative partial molar Gibbs energies, $\bar{G}_{\text{Ni}}^{\text{liquid}}$, and, $\bar{G}_{\text{B}}^{\text{liquid}}$, activities, $a_{\text{Ni}_{\text{in am.}}}$, and, $a_{\text{B}_{\text{in am.}}}$, and quasi equilibrium oxygen pressures, $p_{\text{O}_2}(\text{Ni}_{\text{in am.}})$, and, $p_{\text{O}_2}(\text{B}_{\text{in am.}})$, of Ni and B components in the amorphous alloys. $E \pm kI$ indicates the power of 10.

S a m p l e	A t o m i c r a t i o / %		$\Delta \bar{G}_{\text{Ni}}^{\text{L}}$	$\Delta \bar{G}_{\text{B}}^{\text{L}}$	$a_{\text{Ni in amor.}}$	$a_{\text{B in amor.}}$	p_{O_2} (Ni in amor.)	p_{O_2} (B in amor.)	Struct ure
	Ni	B	k J m o l ⁻¹	k J m o l ⁻¹			b a r	b a r	
a - N i - B (1)	56	44	-66.34	43.97	2.387 E-12	-	1.208 E-57	-	amor. +Ni ₂ B
a - N i - B (2)	61	39	-45.35	14.39	1.133 E-08	-	5.363 E-65	-	amor.
a - N i - B (3)	65	35	-30.75	-10.47	4.106 E-06	1.467 E-02	4.083 E-70	9.003 E-144	amor.
a - N i - B (4)	67	33	-24.41	-22.76	5.290 E-05	1.029 E-04	2.461 E-72	6.703 E-141	amor.
a - N i - B (5)	69	31	-18.77	-34.74	5.144 E-04	8.210 E-07	2.602 E-74	4.206 E-138	amor.
a - N i - B (6)	71	29	-13.83	-46.25	3.771 E-03	7.885 E-09	4.842 E-76	2.060 E-135	amor.
a - N i - B (7)	74	26	-7.68	-62.45	4.510 E-02	1.148 E-11	3.388 E-78	1.248 E-131	amor. + Ni ₂ B

Fig. 8 Amount of evolved hydrogen per surface area.

alloys, which exhibited high catalytic activity, were excellent materials that were prepared from aqueous solutions at low temperatures.

4. Conclusion

The compositional range of the Ni-B amorphous alloy was thermodynamically predicted from extrapolating the function of the Gibbs energy of mixing, $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$, and the activities of the Ni and B components, $a_{\text{Ni in amor.}}$, and, $a_{\text{B in amor.}}$, of the liquid phase to room temperature. The negative $\Delta_{\text{mix}}G_{\text{N-B}}^{\text{liquid}}$ was found to be from $X_{\text{Ni}} = 0.45$ to 0.92, indicating the existence of the liquid phase as metastable state, i.e. formation of amorphous alloy. $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$ showed that the strong attractive interaction acted between the Ni and B components. The Ni-B amorphous alloys were prepared from aqueous solution using reducing agent from $X_{\text{Ni}} = 0.61$ to 0.71, following the quasi equilibrium thermodynamic prediction. The Ni-B amorphous alloy showed excellent catalytic properties in the hydrogen generation reaction from ammonia borane. Moreover, the quasi equilibrium oxygen pressures, $p_{\text{O}_2}(\text{Ni in amor.})$, and, $p_{\text{O}_2}(\text{B in amor.})$, of Ni and B components in the amorphous alloys were evaluated from $a_{\text{Ni in amor.}}$ and $a_{\text{B in amor.}}$. $p_{\text{O}_2}(\text{B in amor.})$ was found to be smaller than $p_{\text{O}_2}(\text{Ni in amor.})$, revealing that B components in amorphous alloy were preferentially oxidized and inhibited Ni oxidation. Not only disordered atomic arrangement but also inhibition of oxidation of the Ni components are reasons for the excellent catalytic activity of the Ni-B amorphous alloy.

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Appendix

In our previous studies,^{30,31)} the standard electrochemical potential, E° , of molybdc acid aqueous ion ($\text{MoO}_4^{2-}(\text{aq})$) from the elements was determined from a thermodynamic cycle composed of the related substances as one of the NEA OECD nuclear waste management.³²⁾ Presently, E° of precipitation of elemental B(cr) from $\text{BH}_4^-(\text{aq})$ was

calculated. $\Delta_f G_m^\circ$ of $\text{BH}_4^-(\text{aq})$ at 298.15 K was given by eq. (A1).

$$\Delta_f G_m^\circ(\text{BH}_4^-(\text{aq})) = 114.35 [\text{kJ} (\text{mol of compd.})^{-1}]^{33)} \quad (\text{A1})$$

Hydrogen reaction is defined as

The standard Gibbs energy of reaction of precipitation of B(cr) from $\text{BH}_4^-(\text{aq})$ was defined as eq. (A3).

Namely, E° of precipitation of elemental B(cr) from $\text{BH}_4^-(\text{aq})$ was given by eq. (A4)

$$E^\circ = -\frac{\Delta_r G^\circ(\text{A3})}{-F} = -1.185 [\text{V}] \quad (\text{A4})$$

where F is Faraday constant ($9.6485 \times 10^4 [\text{C mol}^{-1}]$). C is Coulomb, that is, 1 [J] = 1 [CV].

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