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# Hydrogenation characteristics of $Ti_2Ni$ and $Ti_4Ni_2X$ (X=O, N, C)

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## Abstract

Ternary $Ti_4Ni_2X$ (X=O, N, C) compounds and a binary $Ti_2Ni$ compound were compared based on their hydrogen pressure–composition–temperature (PCT) relations. It was demonstrated that the ternary compounds desorbed most of the absorbed hydrogen under moderate conditions such as room temperature and atmospheric pressure. The hydrogen desorption pressures of the $Ti_4Ni_2X$ compounds were more than two orders of magnitude higher than the desorption pressure of the binary compound. In spite of the significant increase in the hydrogen desorption pressure, the slope of the PCT curve of each ternary compound was not large compared with that of the $Ti_2Ni$ one. These four $Ti_2Ni$-based compounds and their corresponding hydrogen occlusion ones were discussed in terms of their relative thermal stability. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogen storage materials; Intermetallics; Electrochemical reactions; Thermodynamic properties

## 1. Introduction

$Ti_2Ni$ can absorb a large amount of hydrogen by gas–solid reaction [1] and electrochemical reaction [2], and its hydrogenation properties have been investigated by many researchers [3–5]. The hydrogen desorption of $Ti_2Ni$ has been observed at high temperatures such as 423 K [1], which means that its hydride is too stable for the application to hydrogen storage tanks. Mintz et al. have shown that the addition of oxygen up to the nominal composition of $Ti_4Ni_2O_{0.66}$ to the $Ti_2Ni$ compound is effective for the decrease in the stability of its hydrogen occlusion phase [6]. The oxometallic (oxygen-stabilized) compound with the stoichiometric composition of $Ti_4Ni_2O$ has a $Ti_2Ni$-type $Fd\bar{3}m$ structure (more strictly η-carbide one) [7]. In a previous paper, we have shown that the addition of not only oxygen but also nitrogen and carbon to $Ti_2Ni$ leads to a significant increase in the hydrogen desorption pressure of their corresponding ternary alloys and that $Ti_2Ni$-based ternary phases expressed as $Ti_4Ni_2X$ (X=O, N, C), where also the $Ti_4Ni_2N$ and $Ti_4Ni_2C$ have a $Ti_2Ni$-type $Fd\bar{3}m$ structure, are responsible for the reversible hydrogen absorption and desorption of the alloys under moderate conditions such as room temperature and atmospheric pressure [8].

One of the aims of the investigation about the $Ti_2Ni$-based compounds containing the non-metal elements was to determine the systematic change in their hydrogenation properties with the types of additive non-metal light elements. In a previous paper, however, the comparison among the four $Ti_2Ni$-based compounds ($Ti_4Ni_2O$, $Ti_4Ni_2N$, $Ti_4Ni_2C$ and $Ti_2Ni$) based on their hydrogenation properties has not been systematically performed because of (i) difficulty in measuring the hydrogen desorption pressure of the binary compound at the same temperatures as the ternary samples, and (ii) the existence of minor phases such as TiNi in the ternary alloy samples [8].

The objective of the present study is to provide more extensive data about the difference in stability of the hydrogenated $Ti_4Ni_2X$ and $Ti_2Ni$ compounds. For this purpose, an electrochemical measurement technique was applied to the measurement of the pressure–composition–temperature (PCT) relation of the $Ti_2Ni$ compound at room temperature and the correction of the PCT relations was conducted to obtain the hydrogenation properties of the pure $Ti_4Ni_2X$ compounds.

## 2. Experimental details

The details of sample preparation are described in a previous paper [8]. The constituent phases of the samples were confirmed to be $Ti_4Ni_2X$, TiNi and TiX (X=O, N,

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C) by X-ray diffraction analysis using Cu-K$\alpha$ radiation and with a scanning electron microscope equipped with an energy dispersive X-ray spectroscope (SEM-EDS). The PCT relations were obtained with a conventional Sieverts'-type apparatus and by an electrochemical method.

For the measurements using the Sieverts'-type apparatus, the initial hydrogenation of the samples was easily accomplished by holding them at a temperature of 373 K under a hydrogen atmosphere of 4 MPa and they were activated enough to obtain reproducible data by only one hydrogenation–dehydrogenation cycle. The degassing conditions were 573 K for temperature, 0.01 Pa for pressure and 3 h for holding time. The measurements of the PCT relations were performed at temperatures ranging from 273 to 353 K over the hydrogen pressure range from 0.003 to 2 MPa.

In order to experimentally compare the hydrogenated $Ti_4Ni_2X$ obtained by gas–solid reaction with the hydrogenated $Ti_2Ni$ for their stabilities at room temperature, the electrochamical measurements were performed for the binary $Ti_2Ni$ and oxygen-containing samples, where the latter sample was measured to confirm the validity of the experimental conditions. For the electrochemical measurements, the alloy sample was pulverized into powder with a particle size less than 150 μm in diameter. One g of alloy powder was adequately mixed with 3 g of the Cu one, then 1 g of the mixture was cold-pressed into a pellet with a 13 mm diameter. The pellet was sandwiched between nickel mesh and spot-welded with a nickel wire. Thus the negative electrode containing 0.25 g of the alloy was prepared. NiOOH–$Ni(OH)_2$ and Hg–HgO were used as the counter and reference electrodes, respectively. The negative electrode was placed in the central compartment of a Pyrex cell with three compartments and the two counter electrodes were placed into the adjacent compartments which were separated from the central compartment by porous glass filters. A 6 M KOH solution was used as the electrolyte. The potential of the negative electrode was given with respect to the reference in the 6 M KOH solution. The charges and discharges were limited by the negative electrode.

The conditions of the electrochemical measurements for the PCT relations are listed in Table 1. It may be worth to note that the oxygen-containing sample was easily activated by only one cycle of activation treatment. For the measurements, the equilibrium potentials were obtained by repeating a pulse charge and a discharge rest until the potential reached a cut-off voltage, after full charging. The electrochemical PCT relations were obtained by converting the equilibrium potentials to hydrogen pressures using a Nernst equation and discharge capacities to hydrogen contents using the Faraday equation.

Table 1
Experimental conditions of electrochemical PCT measurements at 293 K (20°C)

(a) Experimental conditions for electrochemical activation of alloy electrode

| Charge[a] | | | Discharge | | Cycles |
|---|---|---|---|---|---|
| Current | Time | Rest[b] | Current | Cut-off | |
| 25 mA | 4 h | 0.5 h | 25 mA | −0.65 V[c] | 1 |

(b) Experimental conditions for measurement of PCT relation

| Charge[a] | | | Discharge | | | |
|---|---|---|---|---|---|---|
| Current | Time | Rest[b] | Current | Time | Rest[d] | Cut-off |
| 5 mA | 20 h | 0.5 h | 2 mA | 1 h | 0.5 h | −0.60 V[c] |

[a] Nominal electric charge capacity of 400 mA·h per 1 g of alloy.

[b] Interval time from end of electric charge to beginning of electric discharge.

[c] With respect to the Hg–HgO reference electrode in 6 M KOH solution.

[d] Interval time from end of electric discharge to measurement of equilibrium potential.

Assuming that the hydrogen contents of the alloy samples are the weighed average of those of the constituent $Ti_4Ni_2X$, TiNi and TiX phases, we can obtain the PCT relations of the $Ti_4Ni_2X$ compounds using the following equations:

$$c_{\mathrm{H}}^{\mathrm{Ti_4Ni_2X}}(P_{\mathrm{H_2}},T) = \frac{1}{x_{\mathrm{Ti_4Ni_2X}}}\{c_{\mathrm{H}}^{\mathrm{alloy}}(P_{\mathrm{H_2}},T) - x_{\mathrm{TiNi}} \cdot c_{\mathrm{H}}^{\mathrm{TiNi}}(P_{\mathrm{H_2}},T) - x_{\mathrm{TiX}} \cdot c_{\mathrm{H}}^{\mathrm{TiX}}(P_{\mathrm{H_2}},T)\}, \quad (1)$$

where $c_{\mathrm{H}}^{\mathrm{Ti_4Ni_2X}}(P_{\mathrm{H_2}},T)$, $c_{\mathrm{H}}^{\mathrm{alloy}}(P_{\mathrm{H_2}},T)$, $c_{\mathrm{H}}^{\mathrm{TiNi}}(P_{\mathrm{H_2}},T)$ and $c_{\mathrm{H}}^{\mathrm{TiX}}(P_{\mathrm{H_2}},T)$ are the hydrogen contents under an equilibrium hydrogen pressure $P_{\mathrm{H_2}}$ at a temperature $T$ for the $Ti_4Ni_2X$, the alloy sample, the TiNi and the TiX, respectively, and $x_{\mathrm{Ti_4Ni_2X}}$, $x_{\mathrm{TiNi}}$ and $x_{\mathrm{TiX}}$ are the molar ratios of the $Ti_4Ni_2X$, TiNi and TiX phases in the sample, respectively. For the molar ratios, the following relation is established:

$$x_{\mathrm{Ti_4Ni_2X}} + x_{\mathrm{TiNi}} + x_{\mathrm{TiX}} = 1. \quad (2)$$

The molar ratios of the constituent phases were calculated using Avogadro's number, the number of atoms per unit cell, the lattice volumes and the calculated volume ratios from the metallographic structures obtained by SEM-EDS analysis. Since the TiX compounds did not react with hydrogen under the present conditions [8], we regarded the value of $c_{\mathrm{H}}^{\mathrm{TiX}}(P_{\mathrm{H_2}},T)$ as zero. The $c_{\mathrm{H}}^{\mathrm{alloy}}(P_{\mathrm{H_2}},T)$ and $c_{\mathrm{H}}^{\mathrm{TiNi}}(P_{\mathrm{H_2}},T)$ values were taken from the PCT relations of the ternary alloy samples and those of the TiNi ones [8], respectively.

We examined the enthalpy change ($\Delta H_{\mathrm{H_2}}$) and entropy change ($\Delta S_{\mathrm{H_2}}$) of hydriding using van't Hoff's equation, $\ln P_{\mathrm{H_2}} = \Delta H_{\mathrm{H_2}}/R \cdot T^{-1} - \Delta S_{\mathrm{H_2}}/R$, where $R$ is the gas constant. The hydrogen pressure at the hydrogen content of 0.30 H/M (H/M; the atomic ratio of hydrogen to metal) was used to calculate the thermodynamic values for each hydrogenated $Ti_4Ni_2X$ compound.

## 3. Results and discussion

The results obtained for the alloy samples containing $Ti_4Ni_2X$ (X=O, N, C) phases are summarized in Table 2 [8]. The corrected PCT relations for the $Ti_4Ni_2X$ compounds, which were calculated using Eq. (1), are shown in Fig. 1. The reversible hydrogenation and dehydrogenation accompanied by the sloping hydrogen pressure plateaus were observed for these three compounds. The lower limits of the plateau regions were judged to be in the range from 0.05 H/M to 0.1 H/M, independent of the contained non-metal elements. On the other hand, it was found difficult to determine the upper limits because the slope of each PCT curve was not very large at any hydrogen content over 0.1 H/M. The maximum hydrogen content at a pressure of 2 MPa was 0.43 H/M at 0°C for the $Ti_4Ni_2O$, 0.67 H/M at 0°C for the $Ti_4Ni_2N$ and 0.69 H/M at 40°C for the $Ti_4Ni_2C$; however, the small slope of each PCT curve at 2 MPa indicated that these compounds did not absorb hydrogen up to their true maximum hydrogen content under the present conditions. An insignificant hysteresis was observed in these PCT relations.

Fig. 2 shows the PCT relations obtained by the electrochemical method for the $Ti_2Ni$ and $Ti_4Ni_2O$ compounds with the relation measured by Sieverts' method for the $Ti_4Ni_2O$ compound. For the $Ti_4Ni_2O$ compound, the electrochemical PCT relation was in good agreement with the PCT relation obtained using Sieverts'-type apparatus, which indicated that the PCT relations electrochemically obtained were available to comparison for the hydrogen desorption pressure. The equilibrium hydrogen pressure at 0.3 H/M for the $Ti_4Ni_2O$ compound is more than two orders of magnitude higher than that for the $Ti_2Ni$ one. Moreover, the slope of the plateau for the $Ti_4Ni_2O$ compound is smaller than that for the $Ti_2Ni$ one, although $Ti_4Ni_2O$ exhibited the largest slope of the three ternary compounds.

For application of hydrogen storage alloys to hydrogen storage tanks, it is indispensable that they possess flatter plateaus. The addition of metal elements to the hydrogen storage alloys for the control of the hydrogen desorption pressure often leads to a more sloping hydrogen pressure plateau. It can be expected from the present results that the addition of non-metal light elements is more effective for the hydrogen desorption pressure control of the hydrogen storage alloys for hydrogen storage tanks than the addition of metal elements.

The enthalpy and entropy changes of hydriding at 0.3 H/M for each ternary compound were calculated in order to compare the relative stability of their corresponding hydrogen occlusion phases. The calculated values are listed in Table 3. The enthalpy change decreased in the order of $Ti_4Ni_2O$, $Ti_4Ni_2N$ and $Ti_4Ni_2C$. Since the hydrogenated $Ti_2Ni$ is much more stable than the hydrogenated $Ti_4Ni_2C$, the stability of the hydrogen occlusion compound decreases in the order of $Ti_2Ni$, $Ti_4Ni_2C$, $Ti_4Ni_2N$ and $Ti_4Ni_2O$.

We estimated the relative stability of the $Ti_2Ni$-based compounds using the following two procedures. In the first method, the formation enthalpy of the compound was obtained by the calculation based on Miedema's semi-empirical model [9–11]. The calculated enthalpy was $-40.2\ \mathrm{kJ \cdot (mol\ atoms)^{-1}}$ for $Ti_2Ni$, $-71.3\ \mathrm{kJ \cdot (mol\ atoms)^{-1}}$ for $Ti_4Ni_2C$ and $-108.0\ \mathrm{kJ \cdot (mol\ atoms)^{-1}}$ for $Ti_4Ni_2N$. However, no value was obtained for $Ti_4Ni_2O$ because there was no available oxygen data in Ref. [9].

Nitrogen and carbon atoms occupy the interstitial sites which are the center of the irregular octahedron composed of six titanium atoms in the $Ti_2Ni$ lattice [8], as well as oxygen [7]. Since nickel atoms are too distant (3.364 Å

Table 2
Summary of experimental results for alloy samples containing $Ti_4Ni_2X$ (X=O, N, C) phases

| | Constituent phase | Alloy sample | | | |
|---|---|---|---|---|---|
| | | $Ti_{57}Ni_{29}O_{14}$ | $Ti_{57}Ni_{29}N_{14}$ | $Ti_{57}Ni_{29}C_{14}$ | $Ti_2Ni$ |
| Crystal structure | $Ti_4Ni_2X$<br>or $Ti_2Ni$ | Cubic*<br>$Ti_2Ni$-type* | Cubic*<br>$Ti_2Ni$-type* | Cubic*<br>$Ti_2Ni$-type* | Cubic*<br>$Ti_2Ni$-type* |
| Content of X | $Ti_4Ni_2X$ | 14%* | 14%* | 14%* | |
| Lattice constant | $Ti_4Ni_2X$ | 11.33(1) Å* | 11.32(1) Å* | 11.36(1) Å* | 11.33(1) Å* |
| H capacity at 2 MPa | | 0.45 H/M<br>(0°C) | 0.67 H/M<br>(0°C) | 0.59 H/M<br>(40°C) | 0.88 H/M*<br>(180°C) |
| Molar ratio | $Ti_4Ni_2X$ | 98% | 90% | 50% | 100% |
| | TiNi | 2% | 5% | 35% | 0% |
| | TiX | <1% | 5% | 15% | 0% |

***** Reported in previous paper [8]

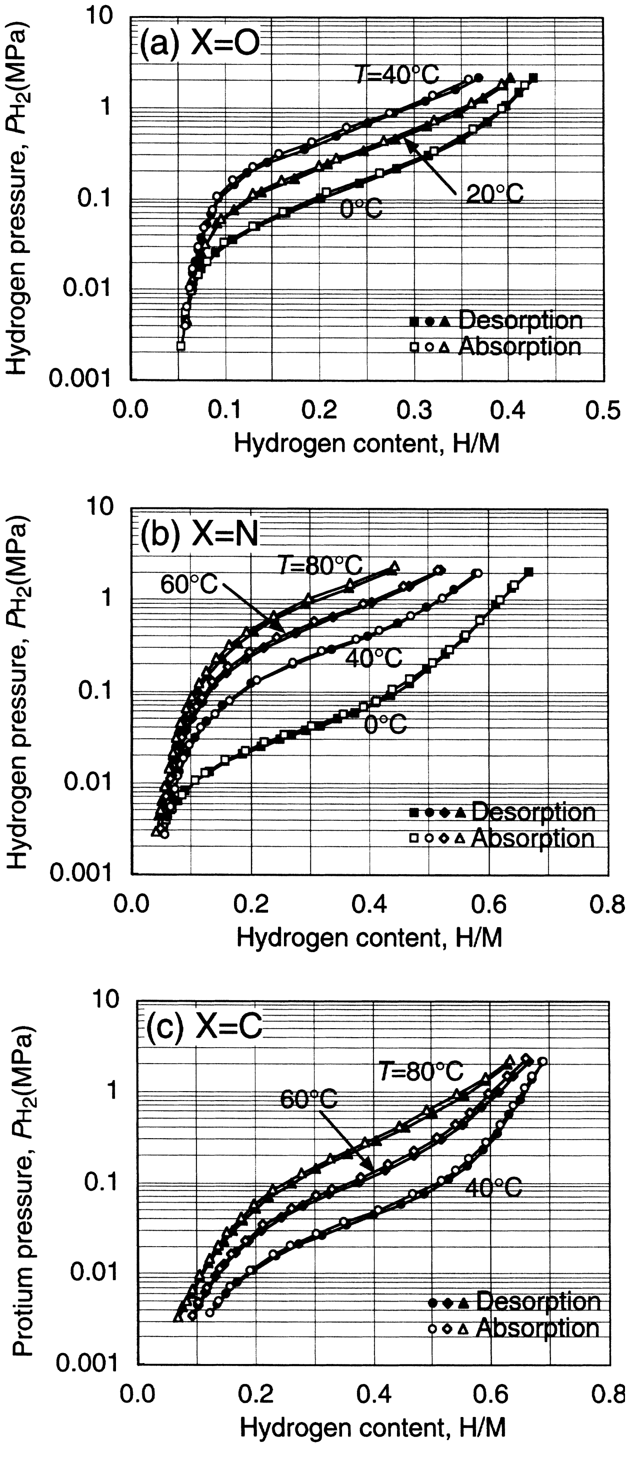

Fig. 1. Pressure–composition–temperature (PCT) relations of $Ti_4Ni_2O$ (a), $Ti_4Ni_2N$ (b) and $Ti_4Ni_2C$ (c) compounds, which are measured by Sieverts' method and corrected using Eq. (1).

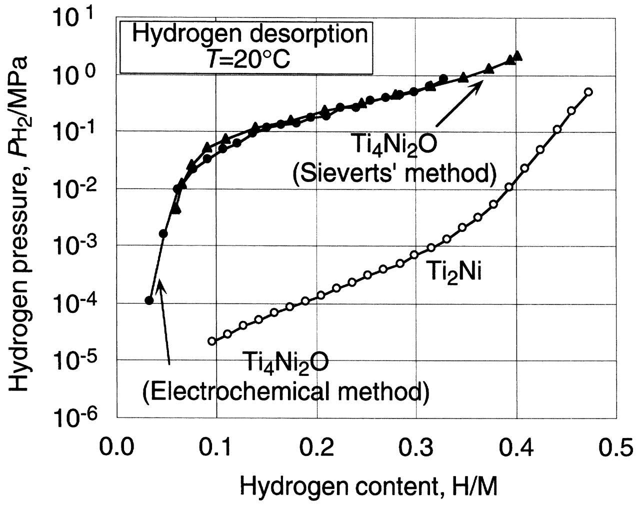

Fig. 2. PCT relations of $Ti_2Ni$ and $Ti_4Ni_2O$ compounds, which are obtained by the electrochemical method, and the PCT relation of $Ti_4Ni_2O$ for comparison, which is obtained by Sieverts' method and shown in Fig. 1.

[12]) from the interstitial sites to form chemical bonds with X atoms, the chemical bonding interaction between the X and Ti atoms mainly contributes to the negative enthalpy for the formation of the $Ti_4Ni_2X$ compound as a result of the reaction of the $Ti_2Ni$ with X. This means that the trends for the formation enthalpies of the $Ti_4Ni_2X$ compounds follow those for the formation enthalpies of the binary Ti–X compounds such as TiX. The formation enthalpy at 25°C is $-184.5\pm4.6$ $kJ\cdot mol^{-1}$ for TiC, $-338.1$ $kJ\cdot mol^{-1}$ for TiN and $-542.7\pm12.6$ $kJ\cdot mol^{-1}$ for TiO [13], therefore, the relative stability of the $Ti_4Ni_2X$ compound decreases in order of $Ti_4Ni_2O$, $Ti_4Ni_2N$ and $Ti_4Ni_2C$.

From the discussion described above, the stability of the $Ti_4Ni_2X$ and $Ti_2Ni$ compounds decreases in order of $Ti_4Ni_2O$, $Ti_4Ni_2N$, $Ti_4Ni_2C$ and $Ti_2Ni$. This order is a reverse of that for the stability of the hydrogenated compound, which agrees with Miedema's 'rule of reversed stability' in which the more stable original compounds form less stable hydrides [14]. The non-metal elements, O, N and C, contribute to the stabilization of the $Ti_2Ni$-based compounds and, as the result of the stabilization, lead to the formation of the relatively unstable hydrogen occlusion ones which desorb hydrogen under moderate conditions such as room temperature and atmospheric pressure.

## 4. Conclusion

The hydrogenation characteristics of oxygen-, nitrogen- and carbon-containing $Ti_2Ni$-based compounds have been

Table 3
Enthalpy and entropy changes of hydriding at 0.30 H/M for $Ti_4Ni_2X$ (X=O, N, C) compounds. These thermodynamic values are calculated using van't Hoff's equation

| | $Ti_4Ni_2O$ | $Ti_4Ni_2N$ | $Ti_4Ni_2C$ |
|---|---|---|---|
| Correlation coefficient | −0.999 | −0.999 | −0.999 |
| $\Delta H_{H_2}$($kJ\cdot mol\ H_2^{-1}$) | −25 | −32 | −38 |
| $\Delta S_{H_2}$ ($J\cdot K^{-1}\cdot mol\ H_2^{-1}$) | −101 | −110 | −106 |

compared with a binary $Ti_2Ni$ compound. These results are summarized as follows;

1. Under moderate conditions such as room temperature and atmospheric pressure, the $Ti_4Ni_2X$ ($X=O$, N, C) compounds reversibly absorb and desorb hydrogen. The hydrogen pressure–composition–temperature (PCT) relation for each compound exhibits a hydrogen pressure plateau and insignificant hysteresis.
2. The $Ti_4Ni_2X$ compounds demonstrate higher hydrogen desorption pressures by more than two orders of magnitude than the $Ti_2Ni$ does, without increasing the slopes of the PCT curves in the hydrogen pressure plateau regions.
3. The relative stability of the four $Ti_2Ni$-based compounds and their corresponding hydrogen occlusion phases decreases in order of $Ti_4Ni_2O$, $Ti_4Ni_2N$, $Ti_4Ni_2C$ and $Ti_2Ni$ and of $Ti_2Ni$, $Ti_4Ni_2C$, $Ti_4Ni_2N$ and $Ti_4Ni_2O$, respectively. The relation between the original compounds and their corresponding hydrides with respect to the order of relative stability is in agreement with 'the rule of reversed stability'.

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