



Hydrogenation characteristics of ternary alloys containing Ti_4Ni_2X ($X=O, N, C$)

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Abstract

Ti_2Ni -based alloys containing oxygen, nitrogen and carbon were investigated regarding their metallographic structures and hydrogenation characteristics. The alloy samples containing these non-metal elements had multi-phase structures composed of Ti_4Ni_2X , $TiNi$ and TiX ($X=O, N, C$) phases. The ternary alloy samples reversibly absorbed and desorbed hydrogen under moderate conditions such as room temperature and atmospheric pressure. The hydrogenation properties of the alloy samples containing the non-metal elements were compared with those of the binary Ti_2Ni compound. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ti_2Ni is one of the promising materials for application to hydrogen storage tanks and Ni-MH batteries because it possesses various merits such as a good hydrogen storage capacity [1], relatively low cost and an ability for electrochemical hydrogen storage [2]. However, the hydride of the Ti_2Ni compound is too stable to desorb hydrogen absorbed at ambient temperature under atmospheric pressure [3]. Ti_2Ni can absorb oxygen up to 14 atomic percent (at%) [4] without changing its cubic $E9_3(Fd\bar{3}m)$ -type crystal structure [5]. According to Mintz and his co-workers, oxygen addition to the binary Ti_2Ni compound leads to an increase in the hydrogen desorption pressure of the alloy [6]. However, the effects of adding non-metal light elements on the hydrogenation properties of the Ti_2Ni compound have not been systematically investigated. In the case of nitrogen and carbon, no information is available even for their solubility in Ti_2Ni .

The objective of the present study is to provide exten-

sive data on the hydrogenation properties of the Ti_2Ni -based alloys containing several non-metal elements such as oxygen, nitrogen and carbon.

2. Experimental details

2.1. Samples containing oxygen, nitrogen and carbon

The starting materials were Ti (99.9%), Ni (99.9%), TiO_2 (99%), TiN (99%) and TiC (99%) powders. The powders were weighed and mixed so that the alloy samples with the overall compositions of $Ti_{57.1}Ni_{28.6}X_{14.3}$ ($X=O, N, C$) were obtained. The mixtures were cold-pressed into tablets under vacuum using a rotary pump. The tablets were set on a water-cooled copper hearth and alloyed by arc melting in an argon atmosphere. The Ar gas was purified in advance by melting a titanium getter. The alloy samples were turned over and remelted three times. In order to improve the homogeneity of the samples, heat treatments were conducted as follows: (1) An alloy ingot was annealed for 336 h at a temperature of 900°C in a high vacuum furnace equipped with a diffusion pump; (2) the annealed ingot was mechanically crushed into a powder with a grain size smaller than 75 μm ; (3) the powder was well mixed and cold-pressed into tablets under vacuum;

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(4) the tablets were annealed for 72 h at 900°C in a high-vacuum furnace; (5) the heat treatment was conducted by again following the procedure from (2) to (4). After the treatment, the obtained alloy samples were mechanically pulverized for the analyses. The grain sizes of the pulverized samples were less than 75 μm for the X-ray diffraction (XRD) analysis and about 1 mm for the pressure–composition–temperature (PCT) relation measurements.

The crystal and metallographic structures of the samples were examined by XRD analysis using Cu-K α radiation and with a scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (SEM-EDS), respectively. The composition of each constituent phase in the samples was determined by averaging nine measurement values obtained by Phi-Rho-Z correction in the SEM-EDS analysis.

The measurements of the PCT relations were conducted with a conventional Sieverts'-type apparatus equipped with a turbomolecular vacuum pump and two hydrogen pressure sensors with 4 and 0.1 MPa maximum measurement pressures. The initial hydrogenations of the samples were easily accomplished by holding them at a temperature of 100°C in a pure hydrogen atmosphere at a hydrogen pressure of 4 MPa. Some of the samples were initially hydrogenated even at room temperature and 4 MPa. The sample was degassed at 300°C and 1×10^{-2} Pa for 3 h before each measurement. The measurements of the PCT relations at temperatures ranging from 0 to 80°C were performed over the hydrogen pressure range from 0.003 to 2 MPa. The hydrogen pressure normally became stable within 5 min after the sample started to react with the hydrogen gas. Each equilibrium hydrogen pressure was determined after at least 15 min had passed since the pressure became stable.

2.2. Binary Ti–Ni samples

Two binary Ti–Ni alloy samples with the compositions of TiNi and Ti₂Ni were prepared in order to compare the hydrogenation properties with those of the samples containing the non-metal elements. The Ti (99.9%) and Ni (99.9%) granules were weighed so as to obtain samples with the target compositions. These granules were alloyed by arc melting in an argon atmosphere purified in advance by melting a titanium getter and then annealing for 72 h at 900°C in the vacuum furnace described in Section 2.1. After the heat treatment, the obtained ingots were crushed into a powder with the same grain size as described Section 2.1. It was confirmed by XRD and SEM-EDS analyses that these two samples possessed single-phase structures composed of TiNi and Ti₂Ni phases, respectively. The crystal structure of the TiNi compound was monoclinic.

The initial hydrogenation of these samples was performed at a temperature of 130°C under a hydrogen

pressure of 4 MPa. Before starting the measurements of the PCT relations, the samples were degassed at 400°C and 1×10^{-2} Pa for 3 h. For the PCT relations, the samples were measured under the same conditions as described for the ternary alloys, except using a temperature of 180°C for the Ti₂Ni sample.

3. Results and discussion

3.1. Constituent phases

Figs. 1 and 2 show the XRD profiles and metallographic structures of the alloy samples with the nominal compositions of Ti_{57.1}Ni_{28.6}X_{14.3} (X=O, N, C), respectively. It was found from these analyses that all the ternary samples possessed multi-phase structures. For each XRD profile shown in Fig. 1, most of the diffraction peaks were indexed as a cubic structure of the $E9_3(Fd\bar{3}m)$ type, i.e., the Ti₂Ni type. The lattice constant and standard deviation, which were obtained by averaging the values calculated for the three measurements were 11.33 ± 0.01 Å for the

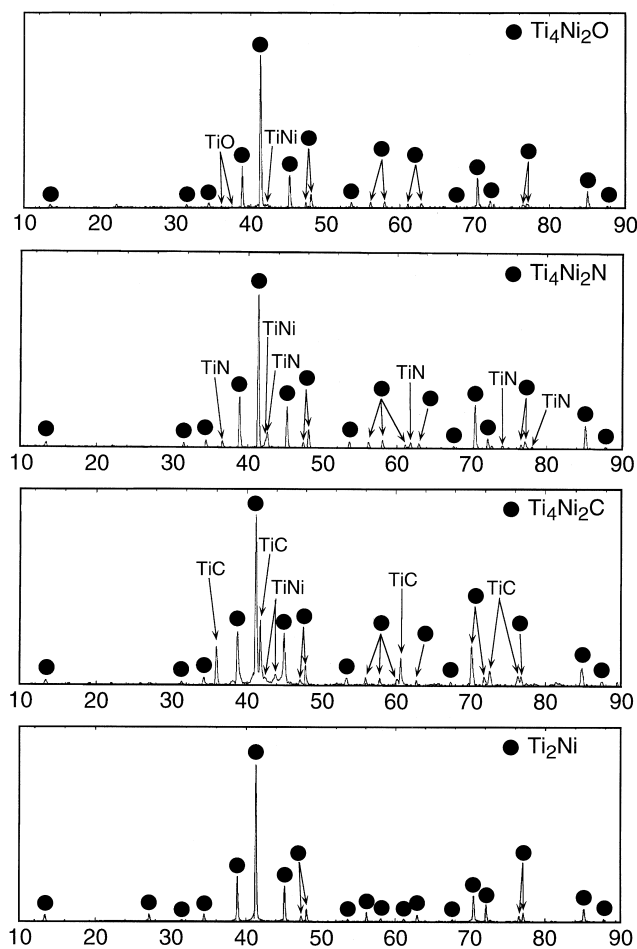


Fig. 1. X-ray diffraction profiles of the alloy samples with nominal compositions of Ti_{57.1}Ni_{28.6}X_{14.3} (X=O, N, C) and the Ti₂Ni compound prepared for comparison.

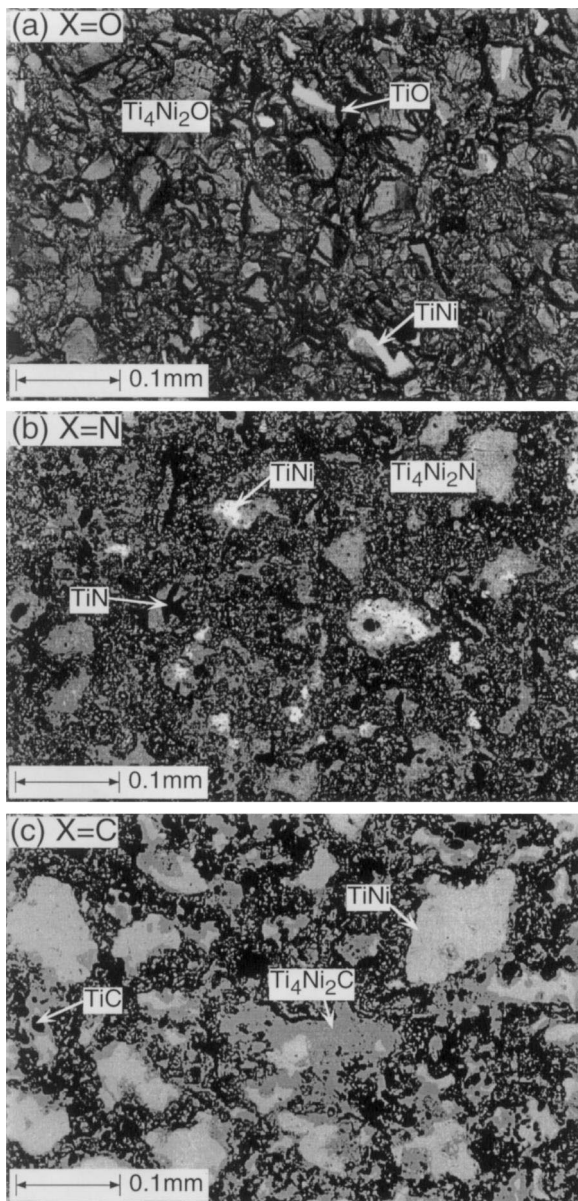


Fig. 2. Metallographic structures of alloy samples with nominal compositions of $\text{Ti}_{57.1}\text{Ni}_{28.6}\text{X}_{14.3}$ ($\text{X}=\text{O}, \text{N}, \text{C}$).

oxygen-containing sample, $11.32 \pm 0.01 \text{ \AA}$ for the nitrogen-containing one, $11.36 \pm 0.01 \text{ \AA}$ for the carbon-containing one and $11.33 \pm 0.01 \text{ \AA}$ for the binary Ti_2Ni compound prepared for comparison. The averages and the three X standard deviations for the oxygen, nitrogen and carbon contents in the Ti_2Ni -type phases, which were obtained by the quantitative SEM-EDS analysis, were 14 ± 3 , 14 ± 2 and 14 ± 3 atomic percent, respectively. It was found from this quantitative analysis that the compositions of the Ti_2Ni -type phases could be expressed as $\text{Ti}_4\text{Ni}_2\text{X}$ ($\text{X}=\text{O}, \text{N}, \text{C}$).

The minor phases in the ternary samples were found to be TiNi and TiX ($\text{X}=\text{O}, \text{N}, \text{C}$) based on the XRD and quantitative SEM-EDS analyses. The crystal structure of the TiNi phase was cubic ($B2$ -type) for the oxygen- and

nitrogen-containing samples, whereas it was monoclinic for the carbon-containing sample. The amount of these minor phases in the ternary sample tended to increase from the oxygen-containing sample to the carbon-containing one.

Fig. 3 shows a schematic diagram for the crystal structure of the Ti_2Ni -based compound, where the $8a$ position is taken as the present origin for the crystal structure of the $E9_3$ type [5]. For the $\text{Ti}_4\text{Ni}_2\text{O}$ compound, oxygen atoms occupy the $16c$ positions which are the center of the irregular octahedrons composed of six titanium atoms [5]; however, no information is available for the positions of the nitrogen and carbon atoms in the $\text{Ti}_4\text{Ni}_2\text{N}$ and $\text{Ti}_4\text{Ni}_2\text{C}$ compounds, respectively. The calculated diffraction peak patterns of the $\text{Ti}_4\text{Ni}_2\text{X}$ ($\text{X}=\text{O}, \text{N}, \text{C}$) compounds in which the non-metal atoms occupy the $16c$ positions are shown with the calculated pattern of the Ti_2Ni compound without any atom at the $16c$ position in Fig. 4. The effect of these light elements on the diffraction patterns is mainly observed at low diffraction angles. Compared with the binary compound, the intensity of the (111) , (222) and (331) peaks decreases, whereas the (311) peak appears and the intensity of the (400) peak increases. The XRD profiles measured for the four samples are redrawn in the 2θ range between 10 and 35° in Fig. 5. The tendency observed in the measured profiles is in a good agreement with that observed in Fig. 4. It is considered that not only oxygen but also nitrogen and carbon atoms occupy the $16c$ positions in the Ti_2Ni -based compounds.

3.2. Pressure–composition isotherms of alloy samples

Fig. 6 shows the PCT relations of the oxygen-, nitrogen- and carbon-containing samples. The three samples reversibly absorbed and desorbed hydrogen at temperatures ranging from 0 to 80°C for the change in hydrogen pressure ranging between 0.003 and 2 MPa . The maximum hydrogen content at the hydrogen pressure of 2 MPa was 0.45 H/M at 0°C for the oxygen-containing sample, 0.67 H/M at 0°C for the nitrogen-containing one and 0.59 H/M at 40°C for the carbon-containing one. These samples exhibited hydrogen pressure plateau-like regions in which the slopes of the curves were smaller than those in other hydrogen-content ranges. The plateau-like regions were observed in the range of hydrogen content from 0.1 in the atomic ratio of hydrogen to metal (H/M) to 0.4 H/M for the oxygen-containing sample, from 0.15 H/M to 0.5 H/M for the nitrogen-containing sample and from 0.3 H/M to 0.5 H/M for the carbon-containing sample. The ‘hysteresis’ effect, which was observed as the difference between hydrogen absorption and desorption pressures, was only slightly observed in the PCT relations.

Fig. 7 shows the PCT relations of the TiNi and Ti_2Ni compounds prepared for comparison. These compounds did not show any hydrogen pressure plateau under the present conditions. The TiNi compound with the mono-

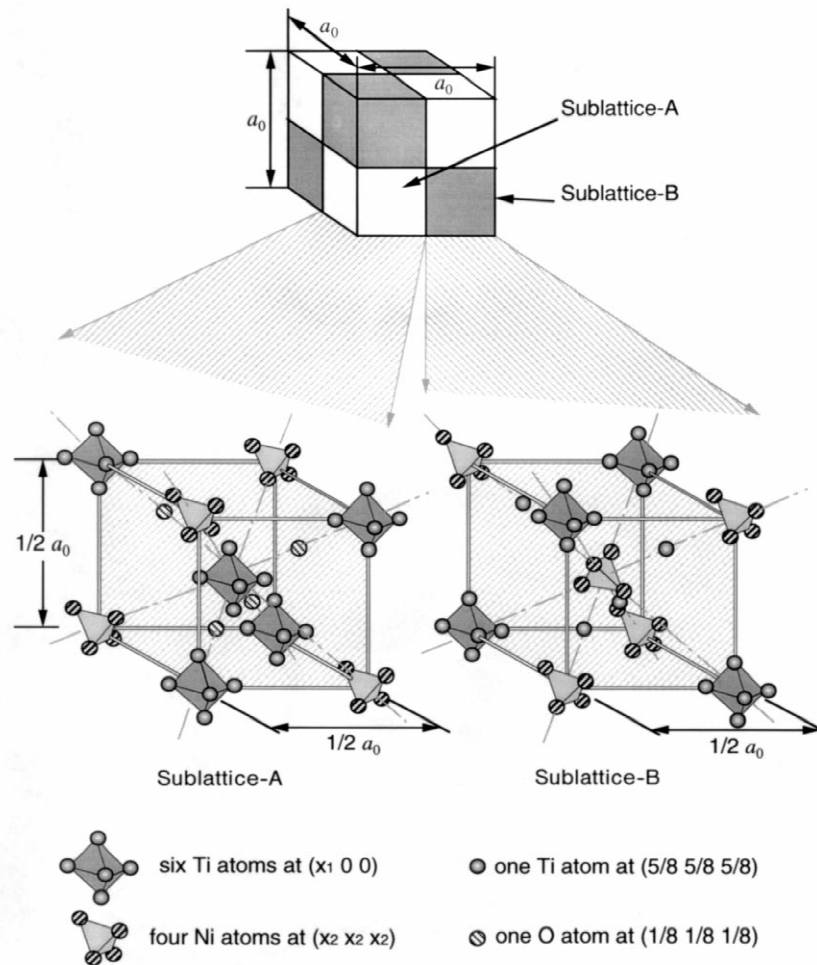


Fig. 3. Schematic diagram for the crystal structure of the Ti_2Ni -based compound [5].

clinic structure only slightly desorbed hydrogen absorbed under the same experimental conditions as did the ternary alloy samples. From the comparison of the PCT relations of this monoclinic compound with those of the $B2$ -type compound, which were reported by Burch and Mason [7], it was considered that the PCT relations of the $TiNi$ compound were not dependent on its crystal structure at the temperatures below $80^\circ C$. The Ti_2Ni compound desorbed only 30% of the hydrogen absorbed even at temperatures as high as $180^\circ C$ when the hydrogen pressure decreased from 3 to 0.007 MPa, although it showed a large hydrogen storage capacity of 0.9 H/M.

The hydrogenation of TiO , TiN and TiC was conducted at temperatures ranging from 0 to $80^\circ C$ at hydrogen pressures ranging from 0.003 to 2 MPa; however, no evidence for their reaction with hydrogen gas was observed.

The results mentioned above indicate that the Ti_4Ni_2X ($X=O, N, C$) phases are responsible for the hydrogen pressure plateau-like regions observed in the PCT relations of the ternary alloy samples. This means that the hydrogen occlusion phases of the ternary Ti_4Ni_2X compounds are

very unstable compared with those of the binary Ti_2Ni one. As well as oxygen [6], nitrogen and carbon contribute to decreasing the stability of the hydrogen occlusion phases of the Ti_2Ni -based compounds.

4. Conclusion

Oxygen-, nitrogen- and carbon-containing Ti_2Ni alloys have been investigated with respect to their constituent phases and hydrogenation characteristics. The results obtained are summarized as follows:

1. Ti_2Ni alloys can absorb 14 atomic percent of nitrogen and carbon to form Ti_4Ni_2N and Ti_4Ni_2C , respectively. The nitrogen and carbon atoms occupy the $16c$ positions of the $E9_3$ -type (Ti_2Ni -type) structure as well as the oxygen atoms.
2. Ti_2Ni alloys containing non-metal elements possess multi-phase structures composed of Ti_4Ni_2X , $TiNi$ and TiX ($X=O, N, C$) even after two heat treatments.
3. The alloy samples containing the Ti_4Ni_2X ($X=O, N,$

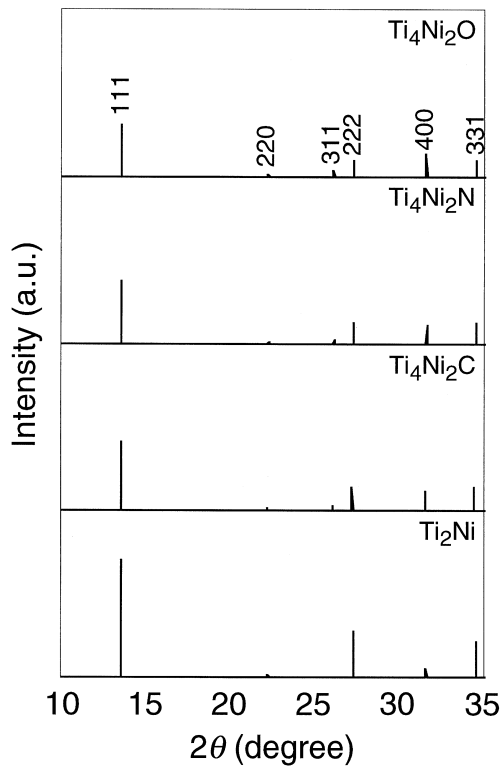


Fig. 4. Comparison of calculated X-ray diffraction peak patterns for Ti_4Ni_2X ($X=O, N, C$) compounds in which non-metal X atoms occupy 16c positions with calculated diffraction peak pattern of binary Ti_2Ni compound without any atom at the 16c position.

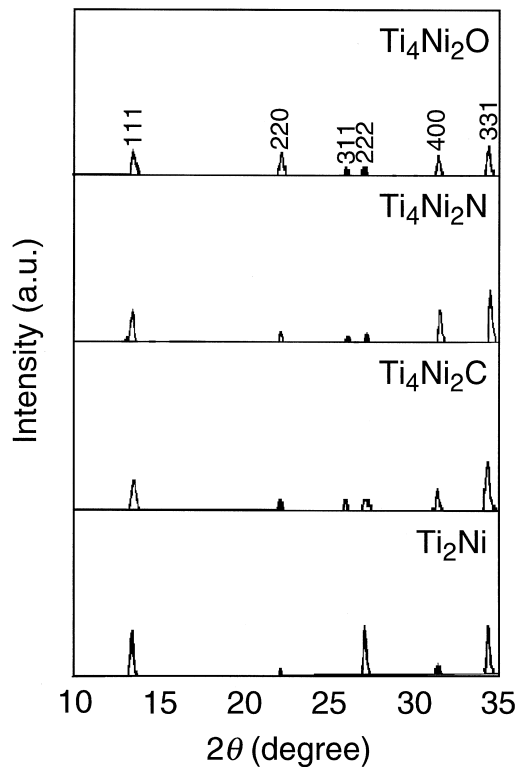


Fig. 5. X-ray diffraction profiles in 2θ range between 10 and 35° for alloy samples with nominal compositions of $Ti_{57.1}Ni_{28.6}X_{14.3}$ ($X=O, N, C$) and Ti_2Ni compound prepared for comparison.

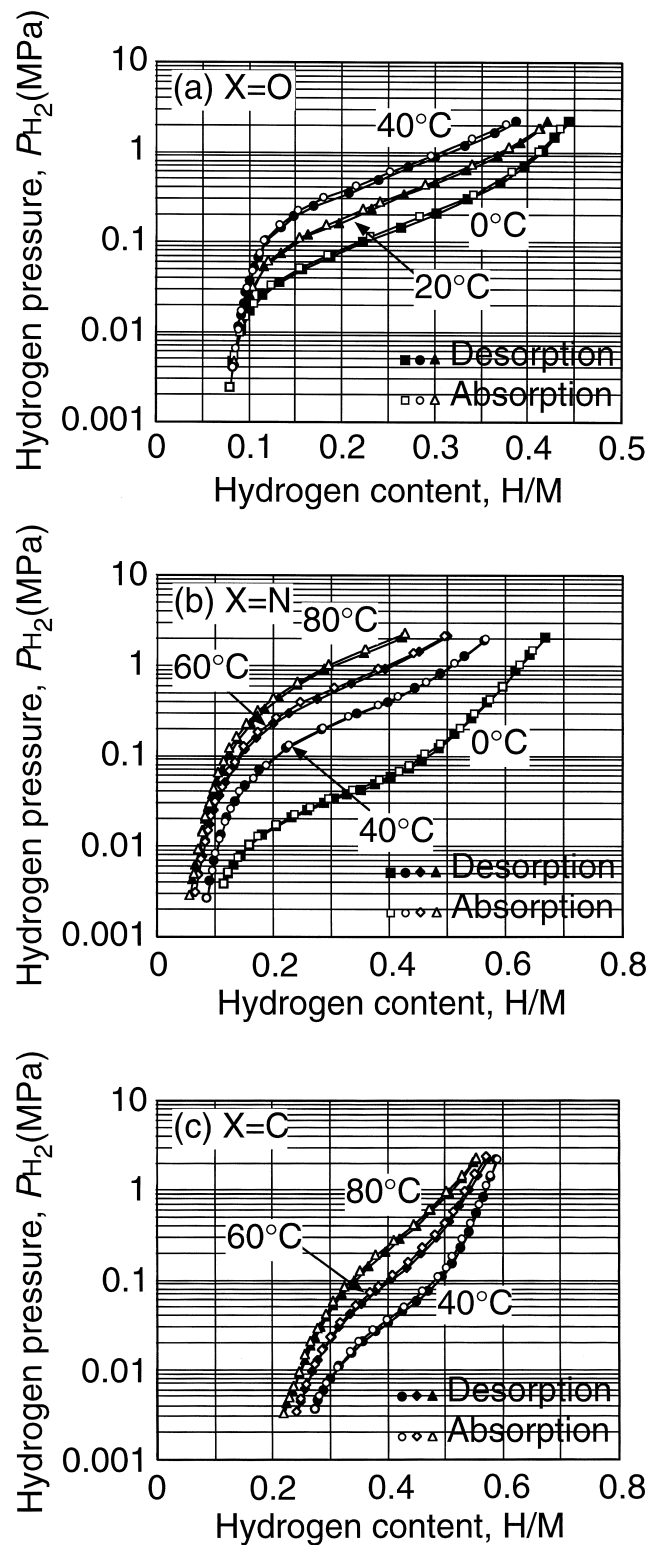


Fig. 6. Hydrogen pressure–composition–temperature relations of alloy samples with nominal compositions of $Ti_{57.1}Ni_{28.6}X_{14.3}$ ($X=O, N, C$).

C) phases desorb much of the hydrogen absorbed at ambient temperature at hydrogen pressures in the range between 0.003 and 2 MPa. The ternary Ti_4Ni_2X ($X=O,$

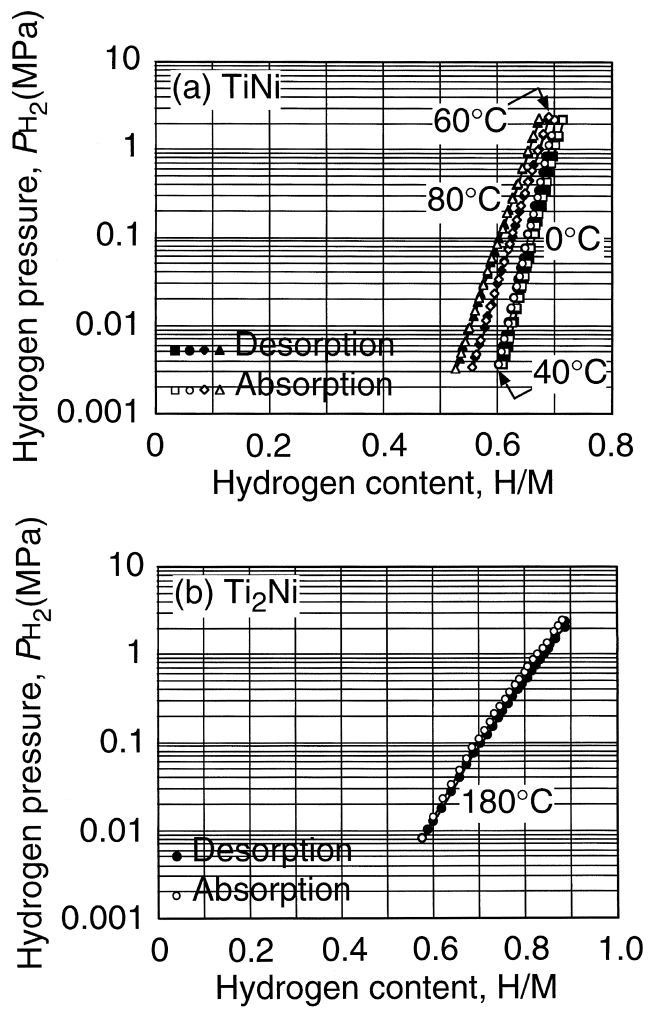


Fig. 7. Hydrogen pressure–composition–temperature relations of TiNi and Ti_2Ni compounds prepared for comparison.

N, C) phases are responsible for the hydrogen desorption of these samples.

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