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Metal hydride electrodes using titanium–iron-based alloys

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Abstract

The characteristics of metal hydride electrodes using partially substituted TiFe alloys were studied. By substituting the alloy with nickel, the alloy became electrochemically rechargeable. The rechargeable capacity strongly depended on the discharge current density. Measuring at a constant discharge current density, the capacity increased with increasing concentration of nickel in the alloy. The strong dependence of the rechargeable capacity on the current density was attributed to the poor discharge kinetics. The higher capacities of nickel-rich alloy electrodes can be attributed to the hydrogen dissociation kinetics on alloy electrodes.

Keywords: Metal hydride electrodes; Titanium–iron-based alloys

1. Introduction

TiFe-based alloys are promising materials for hydrogen storage, because of their high hydrogen storage capacities and low cost [1–4]. However, their activation (initial hydrogenation) is difficult compared with other hydrogen storage alloys such as rare-earth nickel-based alloys. Temperatures higher than 700 K and hydrogen pressures higher than 1 MPa are required for their activation. The addition or partial substitution of other elements has been found to be effective in improving the poor activation characteristics. Not only metallic elements, but also the addition of small amounts of oxygen has been found to be effective for improving the activation characteristics [4].

Because of the difficulty of activation, the alloys are rarely used as materials for metal-hydride electrodes (MH electrodes). Recently, Yamashita et al. [5] reported that partial substitution of iron by platinum greatly improved the activation characteristics and the alloy became electrochemically rechargeable. This suggests that the difficulty in the electrochemical activation of TiFe-based alloys can be attributed to the poor catalytic effect of the electrode surface on hydrogen dissociation. On the other hand, Jurczky et al. reported a different method. They reported that ball milling was effective for improving the initial hydrogen absorption rate [6], and makes the alloy electrochemically active. The reason for this is thought to be a reduction in particle size and the creation of fresh surface due to ball milling.

These results suggest that once the TiFe electrode can be activated, it can be used as an electrode material like other metal hydride materials. Therefore, in order to use TiFe-based alloys for MH electrodes, the dissociation of hydrogen on the electrode surface should be improved.

When considering the use of metal hydrides as electrode materials, the catalytic effect for hydrogen dissociation on the alloy surface is important. The addition or partial substitution of the alloy by nickel would be effective, because nickel promotes the recombination reaction on the alloy surface. In the present work, the electrode characteristics of some nickel-substituted TiFe alloys were studied. The microstructures and the hydrogenation behavior in the gas–solid reaction were also investigated.

2. Experimental

2.1. Alloy preparation

The alloys were prepared by the arc melting of high-purity metal elements into ingots under an argon atmosphere. The alloy ingots were pulverized into powder with a particle size of about 60 μm diameter. Microstructures were investigated using X-ray diffractometry (Philips

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"X'Pert" system) with Cu Kα radiation with a carbon monochromator.

2.2. P–C isotherms

The pressure–composition isotherms (*P–C* isotherms) for the hydrogenation of the alloys were determined at 333 K using a Sieverts'-type apparatus. About 0.5 g of each alloy powder was placed in a small container, and the sample was evacuated down to 1.0×10^{-3} Torr for 30 min by a rotary pump. The initial hydrogenation (activation) was carried out by maintaining the sample at 523 K under 3.5 MPa hydrogen gas. After activation, each sample was degassed at 523 K for 2 h, followed by cooling to the measuring temperature (333 K) and *P–C* isotherm measurement.

2.3. Electrochemical measurement

Each alloy powder was made into an electrode. First, the alloy powders were sieved to an average particle size of about 60 μm diameter. The alloy powders were then mixed with copper powder (Fukuda Metal Foil & Powder MFG Co.; 'FCC-1100MH') which functioned as both a binder and a current collector. The mixing ratio of copper to alloy powder was 3:1. Each mixed powder was then pressed into a pellet of 13 mm diameter, which contained about 0.2 g alloy powder. The copper-bound pellet was then enveloped by a small piece of nickel net which was connected to a nickel wire, thus forming a working electrode.

The alloy electrodes were tested in an open cell, using 6 M KOH as electrolyte, a $Ni(OH)_2$/NiOOH counter electrode, and a Hg/HgO reference electrode. The electrode characteristics were measured by monitoring the electrode potentials during charge/discharge cycles. Rechargeable capacities were evaluated by discharging the electrode from the fully charged state to the cut-off potential of −0.65 V vs. Hg/HgO. The charge/discharge currents were controlled by a conventional galvanostat (Hokuto-denkoh HA-151) with a small computer system. All electrochemical measurements were carried out at 298 K.

3. Results and discussion

3.1. Microstructures

Figs. 1 and 2 show the XRD profiles of $TiFe_{1-x}Ni_x$ and $Ti_{1-x}FeNi_x$ alloys, respectively. The $TiFe_{1-x}Ni_x$ alloys (iron-site substituted alloys) have a CsCl-type structure, which is the same structure as that of the starting material, TiFe. On the other hand, the $Ti_{1-x}FeNi_x$ alloys (titanium-site substituted alloys) are a mixture of CsCl-type and a C14 Laves phase compound.

These figures show that, in the TiFe compound, iron is more readily substituted by nickel than by titanium, because the atomic radius of nickel is closer to that of iron than to that of titanium. No structure other than the CsCl or C14 Laves phase was observed.

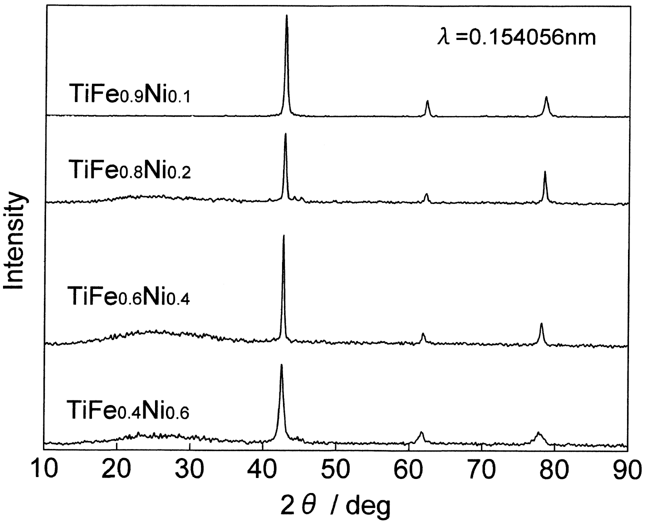

Fig. 1. XRD profiles of $TiFe_{1-x}Ni_x$ alloys.

3.2. P–C isotherms

Fig. 3 shows the pressure–composition isotherms of $TiFe_{1-x}Ni_x$ alloys (iron-site substituted alloys) measured at 333 K. The plateau pressure decreased and the absorption capacity at the same dissociation pressure higher than 0.1 MPa increased with increasing nickel content.

Fig. 4 shows the pressure–composition isotherms of $Ti_{1-x}FeNi_x$ alloys. Contrary to the iron-site substituted alloys, the absorption capacity decreased with increasing nickel content. Moreover, the $Ti_{0.6}FeNi_{0.4}$ alloy was not activated.

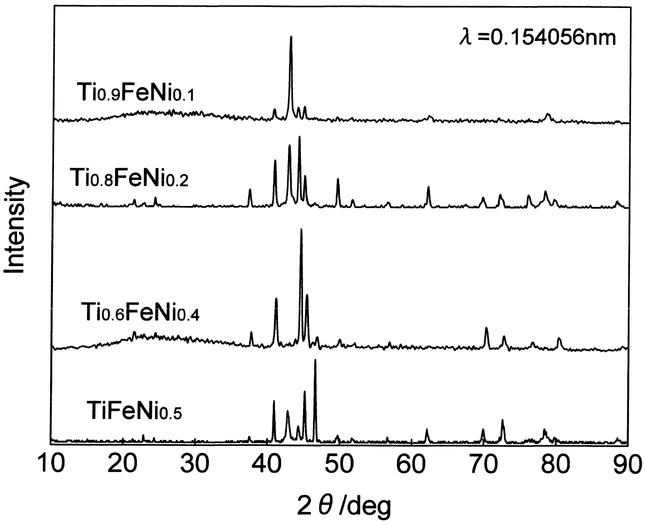

Fig. 2. XRD profiles of $TiFeNi_{0.5}$ and $Ti_{1-x}FeNi_x$ alloys.

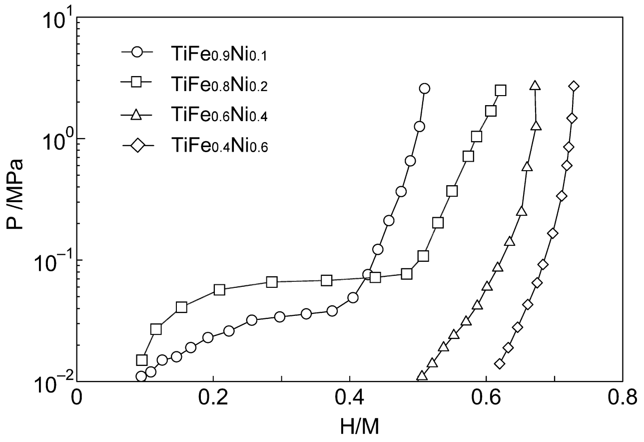

Fig. 3. *P*–*C* isotherms of $TiFe_{1-x}Ni_x$ alloys (333 K).

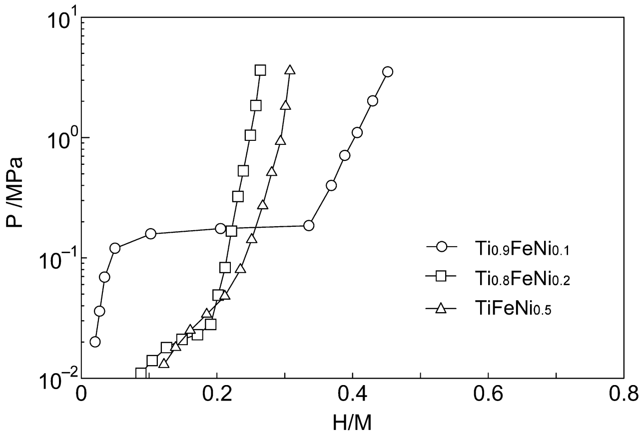

Fig. 4. *P*–*C* isotherms of $TiFeNi_{0.5}$ and $Ti_{1-x}FeNi_x$ alloys (333 K).

3.3. Electrochemical hydrogenation

Fig. 5 shows the rechargeable capacities of the alloy electrodes plotted against the number of charge/discharge cycles. All of the alloys could be activated by electrochemical charging within the initial 10 cycles. For both the iron-site and titanium-site substituted alloys, the rechargeable capacities increased with increasing nickel content. The capacities increased with increasing nickel concentration in the alloy.

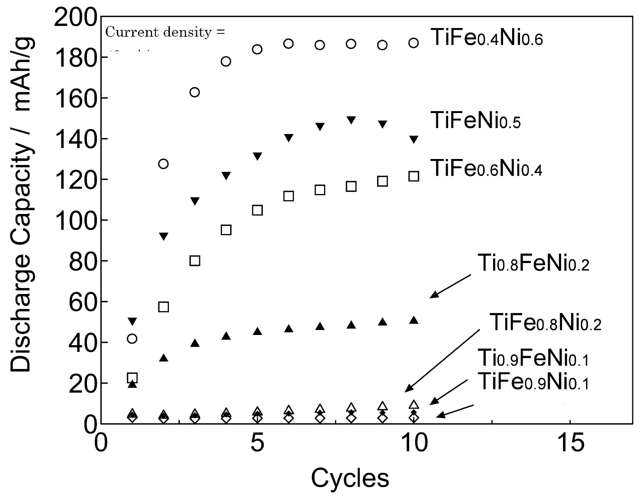

Fig. 5. Capacity–cycle plot of the alloy electrodes (298 K).

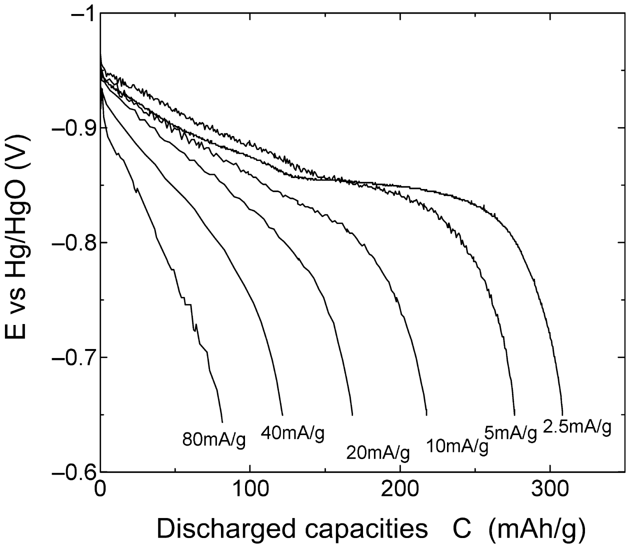

Fig. 6. Discharge capacity of $TiFe_{0.6}Ni_{0.4}$ alloys at various current densities (298 K).

Fig. 6 shows the rechargeable capacities of $TiFe_{0.6}Ni_{0.4}$ alloy electrodes discharged by a variety of discharge current densities. The rechargeable capacity increased with decreasing discharge current density and approached about 300 mAh/g, which is close to the capacity calculated using the *H*/*M* obtained by Sieverts' apparatus. Each alloy electrode became dischargeable at higher current densities with increasing amount of nickel substitution. When the discharge current densities were reduced down to <5 mA/g, the discharge capacities of iron-site substituted alloy electrodes reached about 300 mAh/g, regardless of nickel content. This means that the apparent rechargeable capacities were controlled by the discharge kinetics and the kinetics depend on the amount of nickel substitution, suggesting that nickel substitution improved the hydrogen dissociation kinetics on the electrode surface.

4. Conclusion

The microstructures and hydrogenation behaviors of partially substituted TiFe alloys were studied. Almost half of the iron atoms in CsCl-type TiFe could be substituted by nickel atoms without changing its CsCl-type structure. The plateau pressure decreased and *H*/*M* increased with increasing substitution. On the other hand, substitution of titanium by nickel changed the crystal structure to a C14 Laves phase structure. With increasing nickel substitution, the plateau pressure became lower and the absorption capacities strongly decreased.

The CsCl-type TiFe alloys became electrochemically rechargeable by nickel substitution. On discharging at high current densities, the rechargeable capacities increased with increasing nickel substitution. By decreasing the discharge current densities, the rechargeable capacities increased and approached the theoretically expected values calculated from H/M obtained by a Sieverts'-type apparatus. This means that nickel substitution improves the hydrogen dissociation kinetics on the electrode surface.

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