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A study of the development of a high capacity and high performance Zr–Ti–Mn–V–Ni hydrogen storage alloy for Ni–MH rechargeable batteries

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Abstract

Extensive investigations have been carried out for developing a Zr-based Laves phase alloy with high capacity and high rate-capability for electrochemical application. In order to increase the discharge capacity of the $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ alloy, which is optimized in our previous work [11], Ti was partially substituted for Zr and the stoichiometry was also changed. This change also increases the rate-capability. After such careful alloy design reached by substitution and changing stoichiometry, $Zr_{0.9}Ti_{0.1}(Mn_{0.7}V_{0.5}Ni_{1.4})_{0.92}$ alloys with high capacity and high rate-capability have been developed. This alloy has a discharge capacity of 392 mA h g^{-1} at 0.25 C discharge rate and shows high rate-capability equalling that of commercialized AB_5 type alloys.

Keywords: High capacity; High performance; Hyper-stoichiometry; Zr-based Laves phase; Ni–MH battery

1. Introduction

Recently, nickel–metal hydride (Ni–MH) batteries are rapidly replacing nickel–cadmium (Ni–Cd) batteries because of their advantages of high energy density, high rate-capability, long cycle life and better environmental compatibility. Many kinds of hydrogen storage alloys have been examined as potential electrodes for Ni–MH batteries [1–4]. Among them, Zr-based Laves phase metal hydrides have been attracting much attention because their hydrogen storage capacity is larger than that of commercialized AB_5 type alloys and because of their relatively long electrochemical charge–discharge cycle life [5,6]. In general, however, most of Zr-based Laves phase alloys are disappointing as to the rate-capability compared with the conventional AB_5 type alloys. Therefore, many researches have been focused on the development of Zr-based alloy with high capacity and especially with high rate-capability for electrochemical application. It has been reported that the rate-capability is mainly controlled by surface reaction kinetics and this surface reaction kinetics depends on the metallic Ni or some Ni-rich phase on the alloy surface [7,8]. On the other hand, it was reported recently that some hyper-stoichiometric Zr-based Laves phase alloys showed excellent hydriding and electrochemical characteristics compared with that of the stoichiometric alloys [9,10].

In our previous work [11], the hydrogen storage performance and discharge characteristics of the hyper-stoichiometric $ZrMn_{0.5}V_{0.5}Ni_{1.4+y}$ ($y=0.0$, 0.2, 0.4 and 0.6) alloys with variable Ni content were determined. The Ni content is believed to be of influence on the catalytic activity. From the study of SEM, BET and measurement of the exchange current density, it was found that the major factor affecting the rate-capability of this alloy system was the total reaction surface area of the alloy, not the specific surface catalytic activity of the alloy surface. Based on the above results, the alloy composition was optimized to $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ which had a capacity of about 330 mA h g^{-1} and a rate-capability of about 82% at 1 C rate. However, the above properties of the $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ alloy should be further improved in view of the discharge capacity and rate-capability for electrochemical application.

In this work, extensive studies have been carried out continuously on developing the Zr-based Laves phase alloy with high capacity and high rate-capability for electro-

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chemical application. The relationship between the discharge performance and the alloy characteristics is also discussed.

2. Experimental details

The alloys were prepared by arc-melting of the components with a purity of more than 99.5% under argon atmosphere and remelted several times to obtain a homogeneous phase. Then the alloys were mechanically crushed into a powder of less than 37μm. The crystal structures of the alloys were confirmed by X-ray powder diffraction analysis. In order to investigate the hydrogen storage performance of the alloys, the pressure–composition–temperature (PCT) curves were measured using an automatic Sieverts-type apparatus made by ourselves. About 1 g sample powder with the size of less than 80 mesh was taken for each test run. For activation, the alloy powder was first brought into a vacuum and then exposed to a hydrogen atmosphere at a pressure of about 40 $\mathrm{kg\,cm^{-2}}$ and heated at about 400°C for several minutes at the same time. The following dehydriding was performed by evacuation and by heating the hydrided powder up to about 400°C for several minutes. After three cycles of activation process, the P–C–T data were recorded.

The metal hydride electrode was fabricated by mixing alloy powder with Cu powder (about 1 μm) at a weight ratio of 1:0.25. The mixture was cold pressed to a pellet with a diameter of 10 mm and a thickness of about 1 mm at a compacting pressure of 10 $\mathrm{ton\,cm^{-2}}$.

A half-cell was constructed using a metal hydride alloy powder electrode as a working electrode, a platinum wire as a counter electrode and a mercury/mercury oxide (Hg/HgO) electrode as a reference electrode in 30 wt % KOH electrolyte. The charge–discharge was controlled by the potential of the working electrode with respect to the reference electrode with an automatic galvanostatic charge–discharge apparatus. The electrode was charged with a current density of 100 $\mathrm{mA\,g^{-1}}$ for 6 h and discharged with the same current density to −0.75 V vs. Hg/HgO. The discharge capacity was expressed in milliampere hours (mA h) per gram of alloy. The rate-capability of each alloy was obtained by measuring the discharge capacity at various discharge current densities such as 25 $\mathrm{mA\,g^{-1}}$, 50 $\mathrm{mA\,g^{-1}}$, 100 $\mathrm{mA\,g^{-1}}$, 200 $\mathrm{mA\,g^{-1}}$ and 400 $\mathrm{mA\,g^{-1}}$.

3. Results and discussion

3.1. Compositional optimization of Zr–Ti–Mn–V–Ni alloys

The $\mathrm{ZrMn_{0.7}V_{0.5}Ni_{1.2}}$ alloy of which the composition was optimized in our previous work [11] shows a discharge capacity of about 330 $\mathrm{mA\,h\,g^{-1}}$ and a rate-capability of about 82% at 1 C discharge rate. In the above alloy system, it is found that the major factor affecting the rate-capability is the total reaction surface area of the alloy, not the specific surface catalytic activity of the alloy surface. We also found that Mn has the role of enlarging the reaction surface of the alloy associated with its increased brittleness [11]. However, the discharge capacity and the rate-capability of the $\mathrm{ZrMn_{0.7}V_{0.5}Ni_{1.2}}$ alloy should be improved in view of those of similar alloy systems.

In order to improve the discharge capacity of the $\mathrm{ZrMn_{0.7}V_{0.5}Ni_{1.2}}$ alloy, Zr was partially replaced by Ti. Zr in the $\mathrm{ZrMn_{0.7}V_{0.5}Ni_{1.2}}$ alloy has higher hydrogen affinity and larger atomic weight than Ti. Therefore, if Zr is replaced by Ti of which atomic weight is only the half of that of Zr, it may be possible to increase the discharge capacity per unit weight. Fig. 1 shows the electrochemical discharge curves of $\mathrm{Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}}$ (x=0.0, 0.1, 0.15 and 0.2) alloys with respect to the Ti content at 30°C. It is seen in this figure that the electrochemical discharge capacity passes through a maximum with Ti content in the alloy. To analyze the above phenomena, the PCT curves were measured for the $\mathrm{Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}}$ (x=0.0, 0.1, 0.15 and 0.2) alloys. Fig. 2. shows the PCT curves of $\mathrm{Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}}$ (x=0.0, 0.1, 0.15 and 0.2) alloys at 30°C. It is observed in this figure that the hydrogen storage capacity decreases and hydrogen equilibrium pressure increases with increasing Ti content in the alloys. In

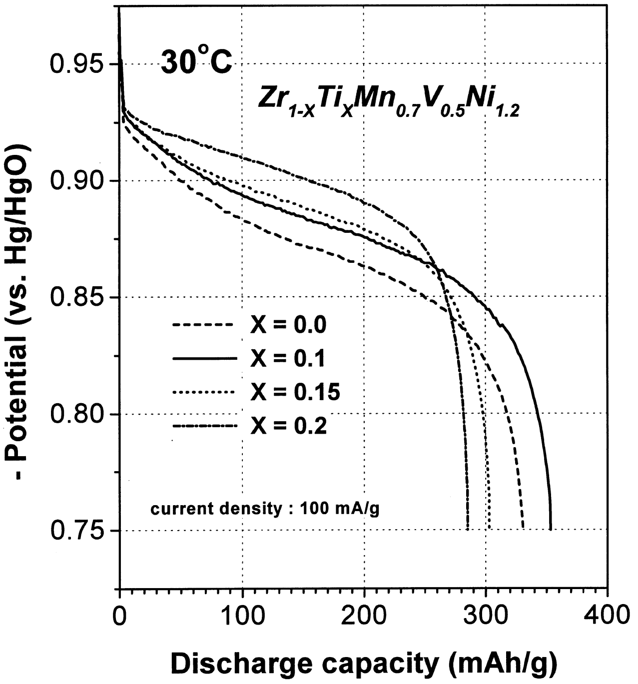

Fig. 1. Discharge curves of $\mathrm{Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}}$ (x=0.0, 0.1, 0.15 and 0.2) alloys with respect to substituted Ti content in the alloy at the current density of 100 $\mathrm{mA\,g^{-1}}$.

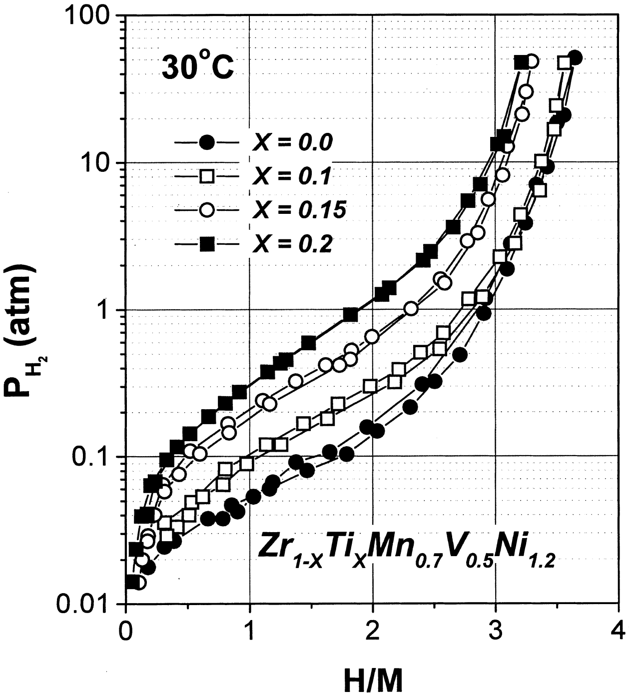

Fig. 2. PCT curves of $Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}$ (x=0.0, 0.1, 0.15 and 0.2) alloys for variable Ti content at 30°C.

general, the hydrogen storage capacity and the hydrogen equilibrium pressure of the alloy are closely related to the size of hydrogen sites (i.e. tetrahedral interstices) and the change of the chemical affinity of alloy for hydrogen. The crystal structure and the size of hydrogen sites(i.e. tetrahedral interstices)of $Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}$ (x=0.0, 0.1, 0.15 and 0.2) alloys were investigated by XRD analysis. From the XRD results shown in Fig. 3(a), all of these alloys are identified to be almost single phase with the C14-type hexagonal structure. On the other hand it is also observed in Fig. 3(b) that the lattice parameters decreases with the increasing amount of substituted Ti. This means that both the lattice volume and the size of hydrogen sites (i.e. tetrahedral interstices) decrease. Therefore it seems that the increase of the hydrogen equilibrium pressure and the decrease of the hydrogen storage amount is attributed to the lattice shrinkage and the change in chemical affinity for hydrogen of the metals.

Nevertheless, the hydrogen storage capacity decreased with respect to the amount of substituted Ti and the electrochemical discharge capacity passes through a maximum. Therefore it is thought that there exists another factor affecting the electrochemical discharge capacity. And this factor is supposed to be the discharge kinetics, i.e. the rate-capability. Fig. 4 shows the rate-capabilities of $Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}$ (x=0.0, 0.1, 0.15 and 0.2) alloys for various Ti contents at 30°C. As expected, the rate-capability increases as the amount of substituted Ti increases. Therefore the maxima phenomenon of the electrochemical discharge capacity of the alloy is attributed to a competition between decreasing hydrogen storage capacity and increasing of rate-capability with increasing Ti content. On the other hand, the increase of the rate-capability of this alloy system with respect to increasing Ti content may be due to the formation of a Ti-oxide film on the MH surface, which is believed to be more porous than the Zr-oxide film and to let the hydrogen penetrate easily through its porous surface [13].

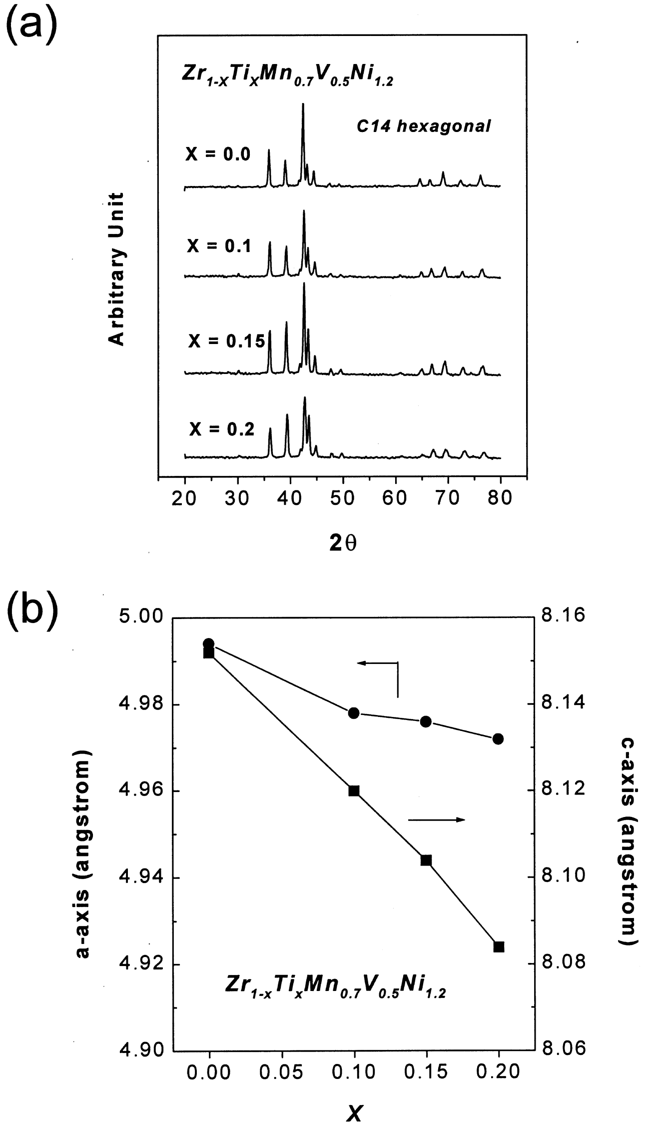

Fig. 3. (a) XRD patterns; and (b) lattice parameters of $Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}$ (x=0.0, 0.1, 0.15 and 0.2) alloys for variable Ti content.

When investigating Ti substitution, it is found that the Zr–Ti–Mn–V–Ni alloy system reveals the best electrochemical properties at the composition of $Zr_{0.9}Ti_{0.1}Mn_{0.7}V_{0.5}Ni_{1.2}$ which has a discharge capacity of about 360 mA h g^{-1} at a current density of 100 mA h g^{-1}.

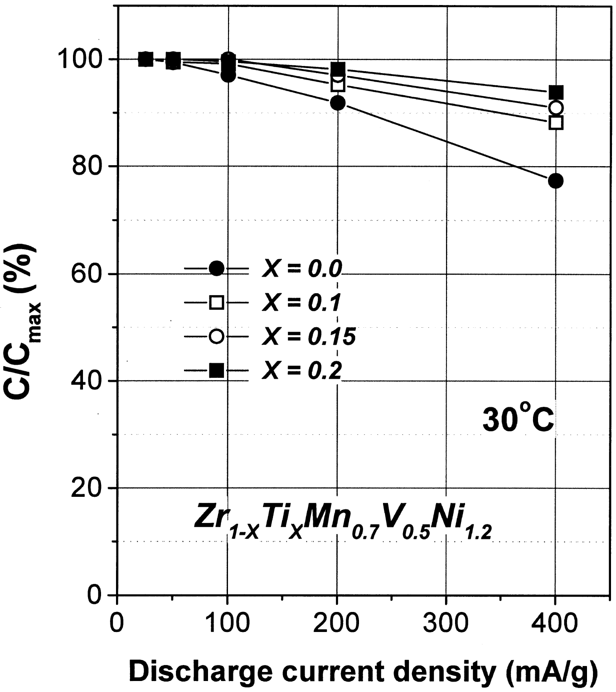

Fig. 4. Rate-capabilities of $Zr_{1-x}Ti_xMn_{0.7}V_{0.5}Ni_{1.2}$ (x=0.0, 0.1, 0.15 and 0.2) alloys for variable Ti content at 30°C.

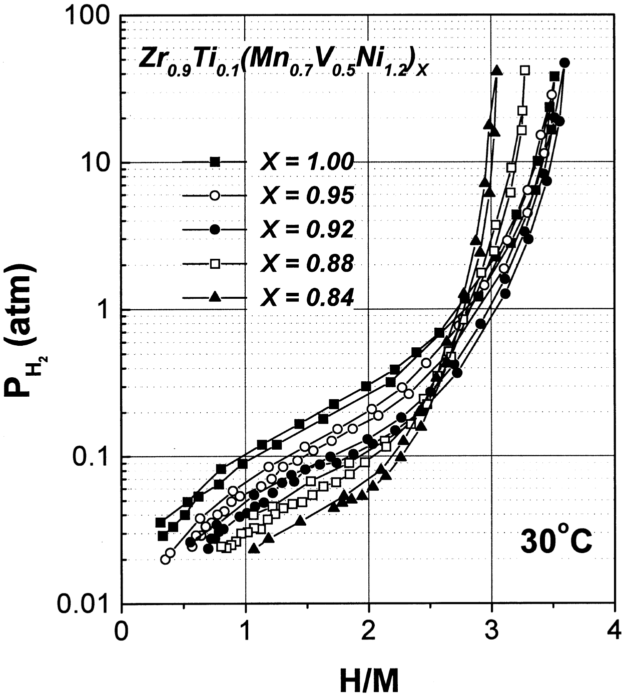

Fig. 5. PCT curves of $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ (x=1.0, 0.95, 0.92, 0.88 and 0.84) alloys for variable stoichiometric ratio at 30°C.

3.2. The optimization of the stoichiometry of (Zr–Ti)(Mn–V–Ni)$_x$ alloys

In this work, the discharge efficiency of a hydrogen storage alloy is defined as the ratio of discharge capacity at a current density of 25 mA g^{-1}(i.e. at the low discharge current density) to the theoretical capacity calculated from PCT curves. The discharge efficiency of the $Zr_{0.9}Ti_{0.1}Mn_{0.7}V_{0.5}Ni_{1.2}$ alloy is as high as about 92% because the discharge capacity at a current density of 25 mA g^{-1} is 361 mA h g^{-1} and the theoretical capacity calculated from the PCT curve is 393 mA h g^{-1}. Considering the high discharge efficiency of the $Zr_{0.9}Ti_{0.1}$-$Mn_{0.7}V_{0.5}Ni_{1.2}$ alloy, for increasing the discharge capacity, it is necessary to increase the theoretical capacity rather than to increase the discharge efficiency. On the other hand, it is well known that the amount of hydrogen stored reversibly in the alloy between the equilibrium pressure range of about 0.01 and 5 atm attributes to the theoretical capacity to be discharged electrochemically in KOH solution [14]. In general, the hydrogen equilibrium pressure can be easily changed by substitution of some elements because of their different chemical affinity for hydrogen, or by varying the stoichiometric ratio of the hydride forming element part ‘A’(i.e. Zr, Ti) to the transition element part ‘B’ (i.e. Mn, V, Ni). Because the alloy has been optimized until now by substitution, it is necessary to vary the hydrogen equilibrium pressure by changing this stoichiometric ratio. In order to adjust the hydrogen equilibrium pressure of the $Zr_{0.9}Ti_{0.1}Mn_{0.7}V_{0.5}$-$Ni_{1.2}$ alloy in above mentioned pressure range, the PCT curves were measured for the $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ alloys with the various stoichiometric ratios, i.e. x=1.0, 0.95, 0.92, 0.88 and 0.84. Fig. 5 shows the PCT curves of these alloys. As expected, the hydrogen equilibrium pressure also decreases with increasing x, i.e. with decreasing amount of $(Mn_{0.7}V_{0.5}Ni_{1.2})$. However, the theoretical capacity shows a maximum with respect to x (Table 1). On the other hand, as shown in Fig. 6, the rate-capability is hardly changed with x. Accordingly, it is shown in Fig. 7 that the discharge capacity passes through a maximum with respect to x and that the highest discharge capacity is obtained at the stoichiometric ratio $Zr_{0.9}Ti_{0.1}(Mn_{0.7}V_{0.5}Ni_{1.2})_{0.92}$.

In this work, as shown in Fig. 8, we developed the $Zr_{0.9}Ti_{0.1}(Mn_{0.7}V_{0.5}Ni_{1.2})_{0.92}$ alloy. It has a discharge capacity of 392 mA h g^{-1} at a discharge current density of

Table 1
Theoretical capacities and discharge efficiencies of $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ (x=1.0, 0.95, 0.92, 0.88 and 0.84) alloys for the variable stoichiometric ratio

x	1.0	0.95	0.92	0.88	0.84
[a]Theoretical capacity (mA h g^{-1})	393	414	433	409	399

[a] Calculated from the amount of hydrogen stored reversibly in the pressure range between 0.01 and 5 atm in PCT curves at 30°C; theoretical capacity=$(\Delta(H/M)/M_w)\times 96500/3.6$; $\Delta(H/M)$: the amount of hydrogen stored reversibly in the pressure range between 0.01 and 5 atm in PCT curves; M_w: molecular weight.

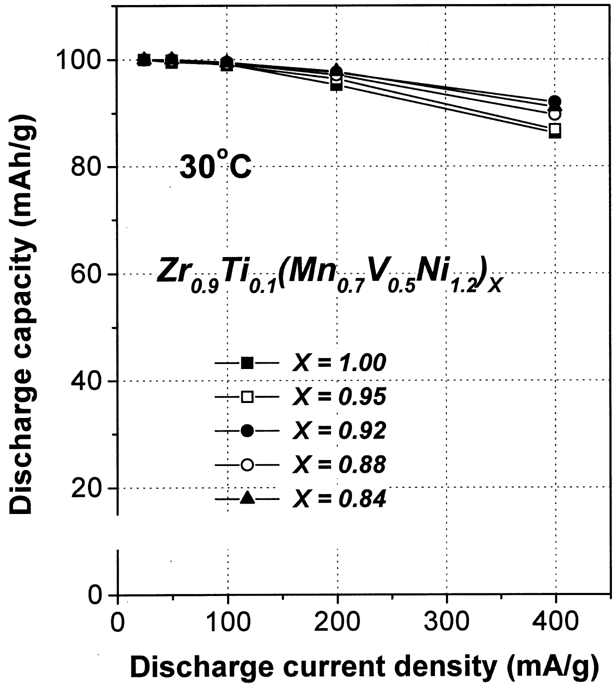

Fig. 6. Rate-capabilities of $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ (x=1.0, 0.95, 0.92, 0.88 and 0.84) alloys with respect to stoichiometric ratio.

0.25 C, i.e. its capacity is higher by about 35% than that of the commercialized AB_5 type alloy, and it shows a high rate-capability equalling that of the commercialized AB_5 type alloy.

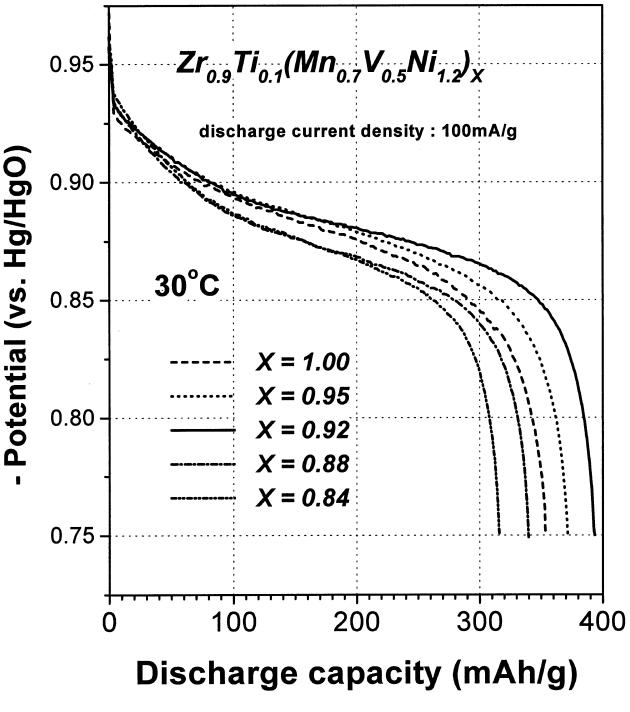

Fig. 7. Discharge curves of $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ (x=1.0, 0.95, 0.92, 0.88 and 0.84) alloys with respect to stoichiometric ratio.

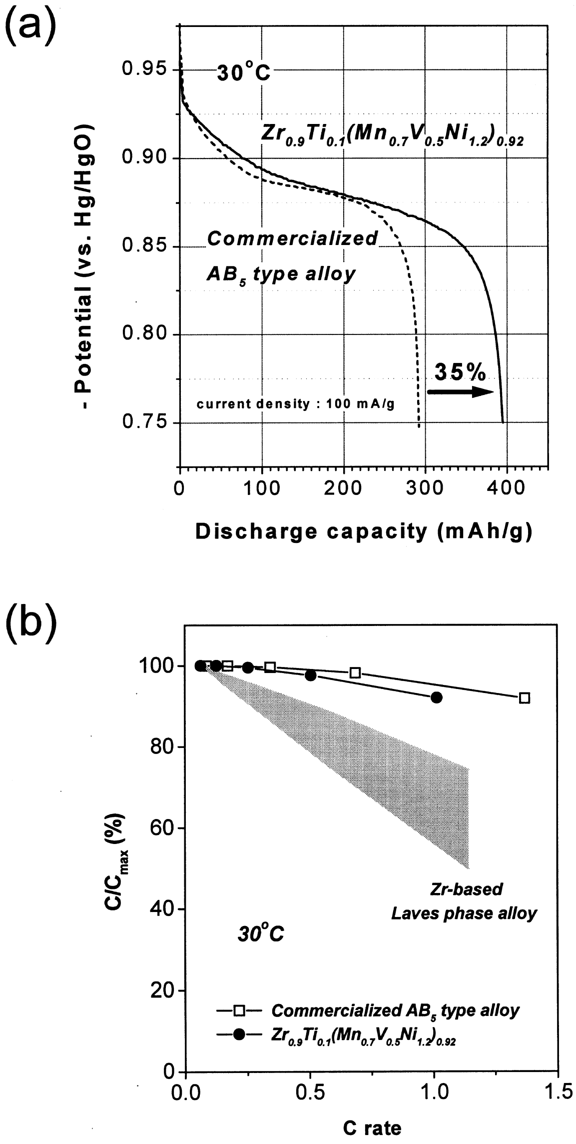

Fig. 8. (a) Discharge capacities and (b) the rate-capabilities of the commercialized AB_5 type alloy and $Zr_{0.9}Ti_{0.1}(Mn_{0.7}V_{0.5}Ni_{1.2})_{0.92}$.

4. Conclusions

In order to increase the discharge capacity and the rate-capability of the $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ alloy, of which the composition was optimized in our previous work [11], Zr has partially been replaced by Ti and its stoichiometric ratio has been changed.

The small amount of Ti substituted for Zr in the $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ alloy increased its electrochemical discharge capacity. As the amount of substituted Ti increases, the rate-capability also increases. However, the hydrogen storage capacity decreases and the hydrogen equilibrium pressure increases with increasing Ti content. Therefore the discharge capacity shows a maximum with respect to the Ti content. In the Zr–Ti–Mn–V–Ni alloy system, $Zr_{0.9}Ti_{0.1}Mn_{0.7}V_{0.5}Ni_{1.2}$ reveals the best electrochemical properties and has a discharge capacity of about 360 mA h g^{-1} at a current density of 100 mA g^{-1}.

The increase of the stoichiometric ratio of the hydride forming element part 'A' to the transition element part 'B', i.e. decreasing x value in the $(Zr_{0.9}Ti_{0.1})(Mn_{0.7}V_{0.5}Ni_{1.2})_x$ alloy, leads to a maximum in the electrochemical discharge capacity as well as in the theoretical capacity. From this result, $Zr_{0.9}Ti_{0.1}(Mn_{0.7}V_{0.5}Ni_{1.2})_{0.92}$ is chosen as the optimum alloy composition. This alloy has a discharge capacity of 392 mAh g^{-1} at 0.25 C discharge rate and shows a high rate-capability equalling that of the commercialized AB_5 type alloy [12].

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