Short Communication

Effect of adding chromium to Ti–Zr–Ni–V–Mn alloy on its cycle life as an Ni/metal-hydride battery material

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Abstract

Chromium is added to Ti–Zr–Ni–V-based AB_2-type alloys to investigate its effect on the cycle-life performance of Ni/metal-hydride batteries made from these alloys. It is found that the addition of chromium significantly reduces the discharge capacity although it has only a limited effect on the hydrogen absorption/desorption performance. Presumably, chromium has a negative effect on the discharge kinetics. In addition, chromium controls the dissolution of V and Zr and hence, extends cycle life. An optimal material, $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Mn_{0.2}Cr_{0.2}$ is identified and prepared. This possesses acceptable performance with respect to both discharge capacity and cycle life.

Keywords: Hydrogen absorption; Metal-hydride alloys; Hydrogen desorption

1. Introduction

Numerous metals, alloys or intermetallic compounds have been studied extensively as hydrogen-storage materials, among which Ti-based AB_2-type alloys with Laves' structure are considered to be highly promising [1,2].

These AB_2 Laves' phase alloys have an atom radii ratio (d_A/d_B) around 1.2 [3]. According to Girgis [4] and Bernauer et al. [5], the structure is also affected by the average number of outer electrons (ANOE). A Ti-based AB_2 alloy can form a C14 Laves' structure if the ANOE is between 5.4 and 7. If the ANOE exceeds 7, it becomes a C15 Laves' structure.

In the authors' laboratory, an alloy has been found, namely, $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Mn_{0.2}$, that shows good hydrogen-absorption/desorption behaviour and fairly good discharge performance. Unfortunately, however, it has a poor cycle life [6]. Since several previous papers [7,8] indicate that the addition of Cr can inhibit the dissolution of V in the Ti–Zr–Ni–V-type alloy, an attempt has been made to modify the alloy by replacing part of the V or Mn by Cr, and to study its effect on discharge performance.

2. Experimental

Hydrogen-absorbing alloys were prepared in an arc-melting furnace under an argon atmosphere. The ingots were then pulverized by hydriding/dehydriding and, finally, by ball milling. Detailed procedures of the preparation and P–C–T measurements have been described previously [6].

Different compositions of the alloy powder were mixed with nickel powder and polytetrafluoroethylene (PTFE) dispersion and pressed on to a nickel mesh. The apparent surface area of the electrode was 2.5 cm × 2.5 cm and the thickness of the electrode was about 1.6 mm.

The test cell consisted of a working electrode (metal-hydride alloy powder electrode), a counter nickel electrode, and a reference electrode (Hg/HgO electrode). The negative working electrode was enclosed in a non-woven Nylon separator and then inserted between two positive electrodes. The electrolyte was 31 wt.% KOH solution and the temperature was maintained at 30 °C. The discharging and charging were controlled at a constant current of 25 mA g^{-1}. The cut-off voltage for discharging was set at −0.7 V with respect to the Hg/HgO electrode.

3. Results and discussion

3.1. Study of $Ti_{0.35}Zr_{0.65}Ni_xV_{2-x-y}Cr_y$

Four kinds of alloy with varying Cr contents were prepared and tested. According to Bernauer et al. [5], the electronic concentration greatly affects the structure of AB_2 Laves' phase alloys. Table 1 shows the values of ANOE of these

Table 1

ANOE and structure of $Ti_{0.35}Zr_{0.65}Ni_xV_{2-x-y}Cr_y$ ($x = 1, 1.2; y = 0.2, 0.4$)

Alloy	Composition	ANOE	Structure identified by XRD
A	$Ti_{0.35}Zr_{0.65}Ni_{1.0}V_{0.8}Cr_{0.2}$	6.4	C14
B	$Ti_{0.35}Zr_{0.65}Ni_{1.0}V_{0.6}Cr_{0.4}$	6.47	C14
C	$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Cr_{0.2}$	6.73	C14
D	$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.4}Cr_{0.4}$	6.8	C14

Fig. 1. SEM of $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.4}Cr_{0.4}$.

four samples. Obviously, they all fall within the range between 5.4 and 7 and should form a C14 structure [9]. This was confirmed by X-ray diffraction (XRD) analysis.

A scanning electron micrograph (SEM) of $Ti_{0.35}Zr_{0.65}$-$Ni_{1.2}V_{0.4}Cr_{0.4}$ is given in Fig. 1. In addition to the main C14 structure, there is another phase in the form of dispersed dark dots. An electron-probe microanalysis (EPMA) technique was used to analyse the composition of the second phase, found to be rich in V and Cr. This is because Cr and V tend to form a body-centred cubic solid solution [10]. Hence, Cr is very low in C14 structure, i.e., about less than 2 at.%. Miyamura et al. [11] studied $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Cr_{0.2}$ and obtained similar results.

Table 2 shows the P–C–T results of the four alloys. Comparison of alloy A with alloy B, or alloy C with alloy D, shows clearly that the replacement of V by Cr tends to reduce hydrogen absorption. A comparison between alloy A and alloy C, or between alloy B and alloy C, also leads to the deduction that replacement of V by Ni decreases hydrogen absorption. Hence, V is very effective for hydrogen storage. Bernauer and Halene [12] studied the hydrogen absorption of Ti–Cr–Mn, Ti–Ze and Ti–V–Mn alloys and found that the amount of hydrogen absorbed is a function of the valence electrons, especially the electron concentration (DEC). As DEC increases, the amount of hydrogen absorbed decreases. Based on the data in Table 2, the system examined here also displays the same behaviour.

When the four alloys are used as electrode materials, the discharge capacities did not exactly match the absorption/desorption behaviour. All the alloys required at least 40 cycles before the peak capacity was reached. This means that the alloys are rather difficult to activate. Among the four alloys,

Table 2

P–C–T data of alloys and their DEC values

Alloy	Composition	Absorption, 10 atm, H_2 (wt.%)	Desorption, 10–0.05 atm (wt.%)	DEC
A	$Ti_{0.35}Zr_{0.65}Ni_{1.0}V_{0.8}Cr_{0.2}$	1.59	0.3	4.467
B	$Ti_{0.35}Zr_{0.65}Ni_{1.0}V_{0.6}Cr_{0.4}$	1.46	0.4	4.6
C	$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Cr_{0.2}$	1.42	0.47	4.8
D	$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.4}Cr_{0.4}$	1.28	0.46	4.93

only alloy C can have a peak capacity at 276 mAh g^{-1} alloy which is close to the existing material in industrial applications. The other three alloys have lower peak capacities as follows, namely, 148, 158 and 180 mAh g^{-1} for alloys A, B and D, respectively.

The alloys all exhibit good cycle life and no significant capacity deterioration was observed for well over 100 cycles. A comparison between alloy A and alloy C indicates that the substitution of Ni for V leads to an increase in discharge capacity, although there is actually a decrease in hydrogen absorption. This means that the amount of hydrogen absorbed is only one of the controlling factors of discharge performance. It provides a thermodynamic upper limit. Kinetically, however, Ni has high catalytic activity and provides good surface conductivity [1], which strongly enhances the dischargeability.

3.2. Study of $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Mn_{0.2}Cr_{0.2}$

Based on the above results, it seems that alloy C ($Ti_{0.35}$ $Zr_{0.65}Ni_{1.2}V_{0.6}Cr_{0.2}$) has fairly good cycle life and discharge performances. A major shortcoming is its long activation period. Since Mn has been found to be rather effective in activation [6], Mn was added to alloy C to give a six-component alloy, viz., $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Mn_{0.2}Cr_{0.2}$. The new alloy, designated as alloy E has an $AB_{2.2}$ composition rather than the conventional AB_2 type. SEM of alloy E is shown in Fig. 2. It shows that the alloy has two phases. Yang et al. [6] reported that for $Ti_{0.35}Zr_{0.65}Ni_xV_{2-x-y}Mn_y$ alloy, the addition of Mn favours the formation of a simple phase. In the present system, however, the Cr added tends to form a body-centred

Fig. 2. SEM of $Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.6}Mn_{0.2}Cr_{0.2}$.
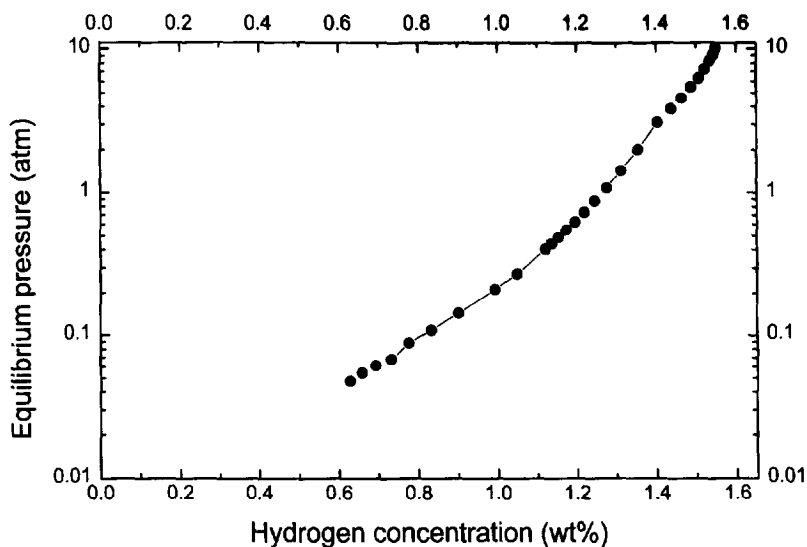
Fig. 3. Equilibrium hydrogen pressure vs. hydrogen concentration (wt.%) at 30 °C for alloy E.
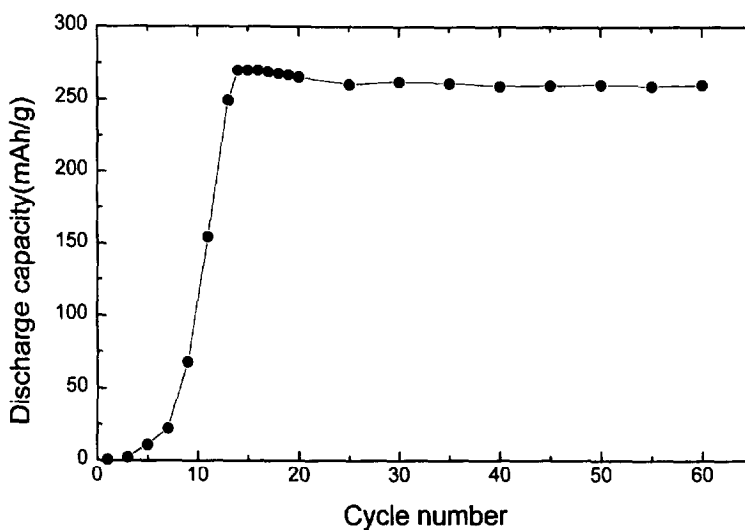

Fig. 4. Discharge capacity vs. life cycles of electrode made from alloy E.

solid solution as previously described [11], hence a second phase appears. The P–C–T curve for alloy E at 30 °C is presented in Fig. 3. Apparently, the alloy has fairly good hydrogen absorption (10 atm, 1.54 wt.%) and desorption (10 to 0.05 atm, 0.9 wt.%) ability. This improvement is due to the addition of Mn, as reported by Yang et al. [6].

The cycling performance of an electrode made from alloy E is given in Fig. 4. It is obvious the addition of Mn reduces significantly the number of cycles required for activation. The electrode reaches its peak capacity after only 14 cycles. For alloys A to D, i.e., alloys without Mn, over 40 cycles are required for activation. In addition, the electrode maintains fairly stable cycle life due to the inclusion of Cr. Hence, an appropriate balance of Mn and Cr can help prepare a Ti–Zr–Ni–V-based alloy with both quick activation and long cycle life.

Kim et al. [13] found in the case of Zr–Cr–Ni–La-based alloy that Cr can form a dense oxide film that prevents hydro-

gen penetration, and, hence, results in a longer activation period. For Ti–Zr–Ni–V-based alloy, Fetcenko et al. [14] also found that cycling can cause a dissolution of Zr and V, which results in microporosity in the oxide layer and, consequently, an increase in discharge activity. Excessive dissolution of Zr and V could, however, lead to decay of capacity and shortened cycle life. Table 3 shows the effect of Cr on controlling the dissolution of Zr and V. Hence, the results reported here confirm Fetcenko's finding that Cr can lengthen the cycle life but introduces a longer activation period.

Table 3
Content of Zr and V dissolved in KOH electrolyte after cycling

	Zr (ppm)	V (ppm)
$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.4}Mn_{0.4}$	35.2	181.3
$Ti_{0.35}Zr_{0.65}Ni_{1.2}V_{0.4}Mn_{0.2}Cr_{0.2}$	7.7	30.7

4. Conclusions

For a Ti–Zr–Ni–V-based AB$_2$-type alloy, the addition of Mn could reduce the activation period and improve the discharge activity. On the other hand, an appropriate amount of Cr tends to reduce the dissolution of Zr and V, which results in longer cycle life without sacrifice of the activation period.

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