[Article ID] 1003- 6326(2002)05- 0826- 03

Properties of Zr-Ti-V-Mn-Ni hydride alloy①

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[Abstract] Six kinds of Zr-based hydride alloy were designed. XRD analyses show that the main phase of $Zr_{1-x}Ti_x(NiCoMnV)_{2.1}$ alloy is Laves C15 when x is between 0 and 0.5, but the more the content of Ti, the more the Laves C14 phases. The amount of Laves C14 can be up to the amount of Laves C15 after substituted V and Fe by V-Fe alloy in $Zr_{0.6}Ti_{0.4}(NiCoMnVFeCr)_{1.7}$ alloy. The electrochemical measurements show that the discharge capacity of $Zr_{0.9}Ti_{0.1}(NiCoMnV)_{2.1}$ electrode is about 340 mA·h/g at 60 mA/g, but with increasing the amount of Ti, the discharge capacity of alloy electrode abruptly decreases; at 300 mA/g current density, its K_r can be up to 91%. The discharge capacity of $Zr_{0.6}Ti_{0.4}(NiCoMn(V-Fe)Cr)_{1.62}$ alloy electrode is about 200 mA·h/g at first cycle, the maximum capacity is more than that of the electrode with pure V, and about 315 mA·h/g.

[Key words] Zr-based hydride alloy; XRD; Laves phase; discharge capacity
[CLC number] TQ 343 [Document code] A

1 INTRODUCTION

With the development of economics and city traffics, more and more oil-powered vehicles appear, resulting more serious pollution to the city environment. Developing electric vehicles has become an important theme in the world. Rechargeable battery with high energy density is the key to the advanced electric vehicle.

It is obvious that high-capacity hydrogen storage alloys are essential to the NiMH batteries with high energy density. Since the commercialized AB_5 alloys are limited by their relatively low hydrogen storage capacity and low cycle life and others[1~3], Zr-based AB_2 Laves phase alloys as a new generation of NiMH electrode materials, are attracting more and more interests for their high capacity and long cycle life[4~6], but their low initial discharge capacity and high cost obstacle their developing. The object of this paper is to prime alloy composing, decrease cost, and substitute Ti for a part of Zr, and (V-Fe) alloy for pure V.

2 EXPERIMENTAL

The hydrogen storage elements can be classified as follows[7]:

1) increasing hydrogen storage, such as Mg, Ti, V, Zr, Nb, La;

2) raising kinetics, for example V, Mn, Zr(adjusting metal-hydride bond intensity);

3) improving surface properties, hole rate and specific conductance, for instance, Cr, Mo and W. According to above principle, six AB_2 type hydrogen storage alloys were designed.

Alloy samples of $Zr_{1-x}Ti_x(Ni, Co, Mn, V)_{2+\alpha}$ $\{x = 0, 0.1, 0.3, 0.5, -0.1 < \alpha < 0.2\}$, $(Zr_{0.6}Ti_{0.4})(Ni, Mn, Co, V, Fe, Cr)_{1.7}$ and $(Zr_{0.6}Ti_{0.4})(Ni, Mn, Co, (V-Fe), Cr)_{1.7}$ (V, Fe substituted by V-Fe alloy) were prepared by vacuum induction furnace in the protective argon. In air, the as-cast alloy pieces were mechanically ground to powder of 74 μm. In order to discuss easily, the samples were named: $T_0(x = 0)$, $T_1(x = 0.1)$, $T_2(x = 0.3)$, $T_3(x = 0.5)$, $T_4((Zr_{0.6}Ti_{0.4})(Ni, Mn, Co, V, Fe, Cr)_{1.7})$, $T_5((Zr_{0.6}Ti_{0.4})(Ni, Mn, Co, (V-Fe), Cr)_{1.7})$.

The electrochemical properties were determined at BT-2043 battery testing system made by Arbin Company, USA. Preparing total mass of 3.000 g powders of hydrogen storage alloy and nickel with the ratio of 1:3, the powders were cold-pressed into an electrode pellet of 25 mm in diameter. The pellet was sandwiched between two $NiOOH/Ni(OH)_2$ electrodes with excessive capacity, and then put into a beaker with 6 mol/L KOH containing 0.02 mol/L LiOH solution at (298 ± 1) K, the sample was charged at current density of 60 mA/g for 8 h, and then discharged at the same current density to a cut-off voltage of 1 V.

After all electrodes were activated completely, the charge-discharge cycle life was measured at 300 mA/g current density. The cut-off voltage was 1 V.

XRD was carried out on the Rigaku D/max-γ_A diffractometer. CuK_α radiation and optical filtering

① [Foundation item] Project(715- 004- 0233) supported by the National Advanced Materials Committee of China
[Received date] 2001- 10- 18; [Accepted date] 2002- 01- 28;

with the graphite monochrometer. SEM was finished on the S-360 type scanning electron microscope made intheCambridgeInstrumentLtd, andEDXcarriedoutatthe same time.

3 RESULTS AND DISCUSSION

3.1 XRD analyses

Fig. 1 is the XRD patterns of T_4 and T_5. From the plot, it is clear that T_4 and T_5 alloys consist of large amount of Laves C14, which is almost equal to Laves C15 and the content of Laves C15 in T_5 is more than that of T_4.

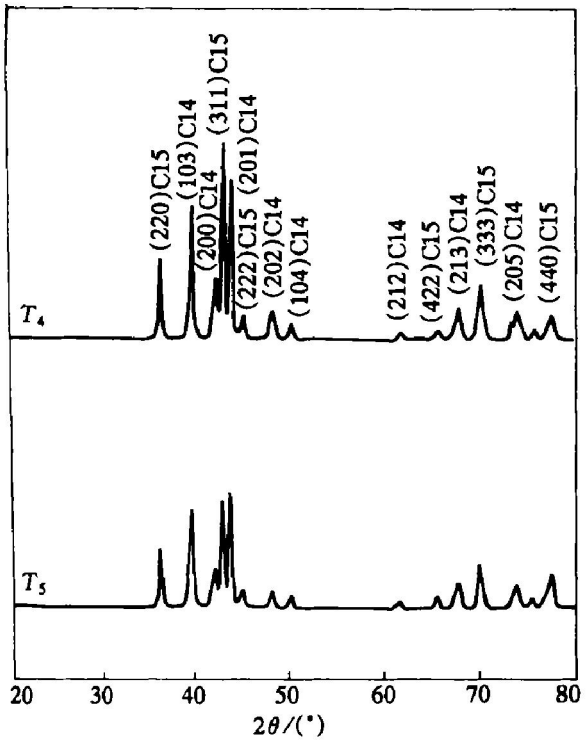

Fig. 1 XRD patterns of Zr-based hydride alloy with different contents of V
T_4 —$Zr_{0.6}Ti_{0.4}(NiCoMnFeVCr)_{1.7}$;
T_5 —$Zr_{0.6}Ti_{0.4}(NiCoMn(Fe-V)Cr)_{1.62}$

Fig. 2 shows that all alloys consist of a great deal of cubic C15 Laves phase. In T_0 alloy, the non-Laves phase is Zr_9Ni_{11}, while in T_1 alloy, it is Zr_7Ni_{10}; except T_1 alloy, with increasing the content of T_i, the intensity of (311) peak is decreasing, however, the intensity of hexagonal C14 Laves phase rises.

3.2 Laves phase formation

The ratio of atom radius is the main factor, which has effect on the formation of Laves phase. The theoretic radius ratio (R_A/R_B) is 1.225, in fact , Laves C15 and Laves C14 are mixed in most situation. When the ratio R_A/R_B is more than 1.24, the alloy structure tends to Laves C15 type, while lower than 1.24, the crystal structure inclines to Laves C14[8].

On the other hand, the crystal structure type is related to the alloy average outer-electrons number n[9]. In Zr-based and Ti-based alloys, when $n<4.67$, no Laves phase formed; when $4.67<n<5.4$, the C15 Laves phase formed in Zr-based alloys, when n is between 5.4~ 7.0, Laves C14 phase formed, while n is more than 7.0, Laves C15 phase formed in Zr-based and Ti-based alloy.

The crystal structure type is also related to the alloy average outer elements concentration (e/a)[10]. When e/a is more than 2.3, Laves C15 phase type is formed easily.

Table 1 is Laves phase formation conditions of six alloys. It shows that T_0 and T_1 alloys belong to Laves C15 type on the above principles, while the radius ratio of T_2 and T_3 are less than 1.24, which shows T_2 and T_3 alloy type are mixture of Laves C14 and C15, the result is the same as Fig. 2. It is clear that in T_4 and T_5 alloy, the crystal structures tend to Laves C14 phase, which is identical with Fig. 1.

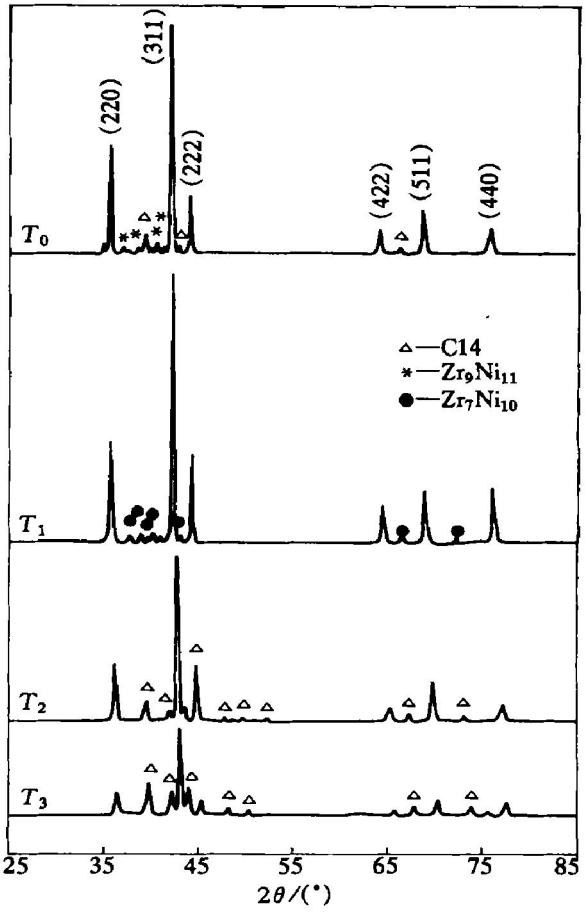

Fig. 2 XRD patterns of $Zr_{1-x}Ti_x(NiCoMnV)_{2.1}$ hydride alloys with different contents of Ti

Table 1 Conditions of Laves phase formation

alloy	R_A/R_B	e/a	n
A	1.251	2.957	7.12
B	1.240	2.957	7.09
C	1.218	2.957	7.09
D	1.196	2.957	7.09
E	1.072	2.789	6.14
F	0.929	2.621	6.57

3.3 Electrode active behavior and discharge capacity

Fig. 3 shows the variation in discharge capacity with cycle number for different electrodes. It is clearly seen that the discharge capacities of T_0 and T_1 are obviously higher than others, in which T_1 is little higher than T_0, up to 340 mA·h/g. But the maximum capacity of T_2 is only 160 mA·h/g, T_3 only 80 mA·h/g. The main reason is the content of Zr substituted by Ti, the more the Zr atom was replaced by Ti atom, the lower the stability of metal-hydride[11], which induces that hydrogen storage alloy desorbing hydrogen easily, was. Therefore, the discharge capacity decreases.

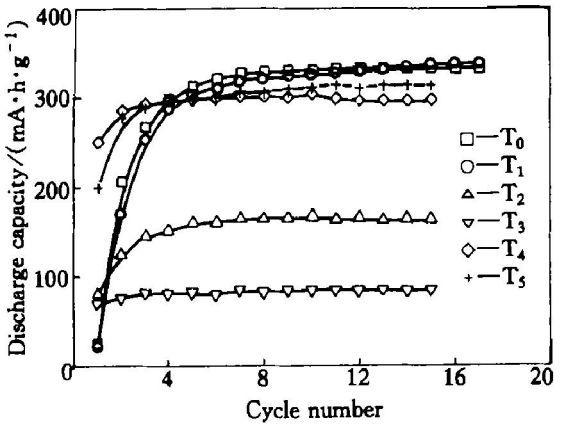

Fig. 3 Discharge capacity of hydride electrodes as function of cycle number

In Fig. 3, it can also be seen that the initial discharge capacity of T_5 electrode is up to 200 mA·h/g, while that of T_4 electrode is about 250 mA·h/g, which are higher than those of T_0, T_1, T_2 and T_3 electrodes. The more the laves C14 phase, the higher the initial discharging capacity.

3.4 Cycle life of electrodes

In Fig. 4, it can be seen that at 300 mA·h/g charge-discharge current density, the cycle stability of T_1 is the best, the capacity keeping rate (K_r) can be up to 91% after 300 cycles according to the following formula[12], while T_4 is the worst, whose K_r is only about 75%.

$$K_r = (C_{i,n}/C_{i,\max}) \times 100\%$$

where $C_{i,n}$ is the discharge capacity at 'i' current density at 'n' cycle number, and $C_{i,\max}$ is the maximum discharge capacity at 'i' current density.

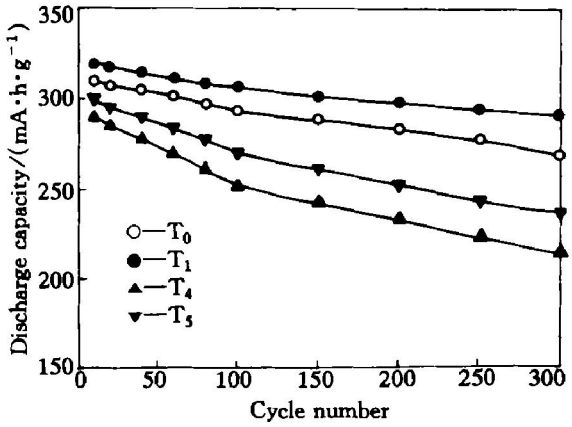

Fig. 4 Charge-discharge cyclelife of different alloy electrodes

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(Edited by HUANG Jin-song)