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Phase composition and electrochemical performances of the $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloys with $0.1 \leq x \leq 0.3$

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Abstract

The effects of substituted Zr by Ti on phase composition, microstructure and electrochemical performances of the $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy have been investigated. The XRD results show that the main phase of the $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy consists of C15 Laves phase, coexisting with a little C14 Laves phase and second phase Zr_7Ni_{10}. With increasing Ti content, abundance of C15 Laves phase and second phase Zr_7Ni_{10} decreases and that of C14 Laves phase increases, and the cell volume of both C15 and C14 Laves phase decreases gradually. From SEM results, the microstructures of the $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ ($x = 0.1$–0.2) alloys are found to be dendrite. When $x = 0.3$, the dendrite of the alloy disappears. The $Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy exhibits maximum discharge capacity 354 mAh/g and high rate discharge ability. However, it is also found that the Ti substitution for Zr decreases activation properties of the alloys. It is believed that the increase in capacity and high rate discharge capability ascribes to the increase of the amount of C14 Laves phase and the decrease of hydride formation heat.

Keywords: Zr-based alloy; Phase structure; Dendrite; Alloying; Electrochemical performance

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1. Introduction

Zr-based AB_2 Laves phase alloy can be used as the active material for the negative electrode in the Ni/MH secondary battery due to its higher theoretical charging–discharging capacity and good cycling durability. However, there are some problems still remained, e.g. poor activate process and high rate dischargeability (HRD), which need to be improved for electric vehicle commercial application. It is well known that multi-component substitution in alloys is an effective method to improve the electrochemical properties of hydrogen storage alloys [1–3]. For the Zr-based AB_2 alloys, some effects of the substitution of Ti for Zr on electrochemical performances are still controversial for the different systems. Su et al. [4] reported that the Ti substitution for $Zr(NiVMnCr)_2$ has no effect on the microstructure and the activation process, but can improve their discharge capacity and cycle life. Jisang et al. [5] found that the discharge capacity of $Zr_{1-x}Ti_x(NiVMnCo)_2$ alloys has the maximum value with increasing Ti content. In the Ti additive alloys the HRD had been improved and the cycle life was deteriorated with Ti content. With Zr substituted by Ti in Zr-based AB_2 alloys, the discharge capacity of alloys can be improved because the atomic weight of Ti is less than that of Zr. Meanwhile, decreasing the stability of alloy hydride with substitution of Zr by Ti also results in the increase of the dynamic of hydrogen desorption. Both factors are positive effect on the discharge capacity of the alloys. On the other hand, the volume of hydrogen storage interstitial site can be contracted because the radius of Ti atom is smaller than that of Zr atom; the absorption/desorption plateau can be consequently raised and the capacity may be decreased. The electrochemical performances of the alloys may be closely related to the above factors. So it is important to determine the substituted amounts of Zr element with Ti element in a specific alloy system and to clarify the effect of substitution Ti for Zr on the surface properties of the alloys.

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In our previous work, the $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy from Zr–Cr–Ni system [6] had been developed, which exhibited good cycle stability and better discharge capacity [7]. But its HRD was still very poor. In the present study, we attempt the substitution of Zr with Ti to reduce the hydride stability and increase the C14 Laves phase content, which may improve the HRD of the alloy, and to investigate the effects of substituted amounts of Ti for Zr on the phase composition, microstructure and electrochemical performances.

2. Experimental details

The alloys were synthesized from pure element 99.9% (except Mn 99.7%) by arc melting in an argon atmosphere. To ensure homogeneity, these alloys were remelted four times and mechanically pulverized in air to 275 mesh. Phase identifications were performed using a D/max-3A diffractometer with Co Kα radiation. a piece of ingot was polished, and then etched with a solution of 80 ml $CH_3CH_2OH + 10$ ml $HCl + 10$ ml HF. The morphology was observed by Philips XL-30 scanning electron microscopy (SEM).

The hydride electrodes were prepared by cold pressing the mixtures of alloy powders with powdered electrolytic copper (200 mesh) in the weight ratio of 1:2 to form porous 10 mm diameter pellets. Electrochemical charge–discharge tests were carried out in a standard open tri-electrode cell, in which the counter electrode was Nickel hydroxide, the reference electrode was Hg/HgO/6 M KOH, and the electrolyte was 6 M KOH solution. A detail description of electrochemical measurements was given in Ref.[6]. The rate dischargeability was defined as $HRD_n = (C_n/C_{50}) \times 100\%$, where C_n is the discharge capacity under current densities (n mA/g) and C_{50} is the discharge capacity at current 50 mA/g.

3. Results and discussion

3.1. Phase composition and microstructure

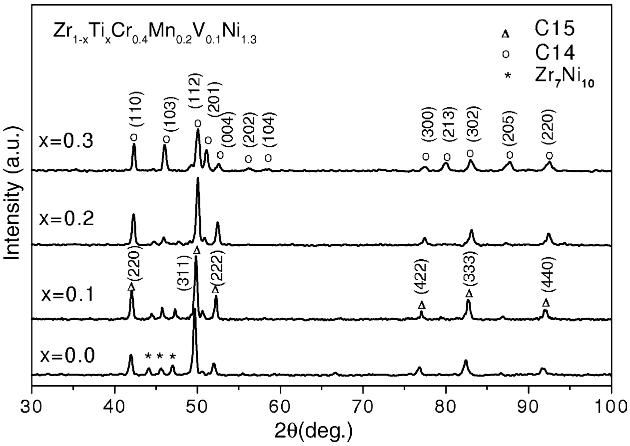

Fig. 1. X-ray diffraction patterns of alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$.

Fig. 1 shows the X-ray diffraction patterns of the $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ ($x = 0.0$–0.3) alloys. It can be seen that the main phase of the alloy $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ consists of C15 Laves phase, coexisting with a little C14 Laves phase and second phase Zr_7Ni_{10}. With increasing Ti content, abundance of the (2 2 2) and (3 3 3) peaks of the C15 Laves phase decreases, that of (1 0 3) and (2 0 1) peaks of the C14 Laves phase increases gradually, and that of the Zr_7Ni_{10}decreases and disappears at $x = 0.3$. The results show that high Ti content avails to the stability of C14 Laves phase and restrain the second phase Zr_7Ni_{10}.

Table 1 lists the lattice parameters and cell volume of the $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloys. With increasing Ti content, the lattice parameters and cell volume of both C15 and C14 Laves phase of the alloys reduce with $x < 0.3$. This is attributed to the smaller atomic radius of Ti than that of Zr. It is worthy noting that there is a critical substitution ($x = 0.3$), the cell volume of C15 Laves phase of the alloy does not contract, but that of C14 Laves phase of the alloy only contracts. It indicates that Ti atom mainly enter C14 Laves phase with high Ti content alloy at $x = 0.3$.

Fig. 2 shows the microstructures of the alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ ($x = 0.0$–0.3). It can be seen that the microstructures of the $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy are dendrites and there are some microcracks in the alloy surface. With increasing Ti content ($x = 0.1, 0.2$), there is little effect on the dendrite, but the microcracks decrease gradually. When $x = 0.3$, the surface ($x = 0, 0$) of the alloy turns to be porous. It may indicate that the active property of surface of alloys decreases with increasing Ti content.

3.2. Electrochemical performance

The discharge capacity and activation process of alloys are shown in Fig. 3. Among the alloys, the $Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$alloy has the maximum

Table 1
Lattice parameters and cell volume of the $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloys

Sample	C15		C14		
	a (nm)	V (nm^3)	a (nm)	c (nm)	V (nm^3)
$ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$	0.7053	0.3509	0.5002	0.8186	0.1774
$Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$	0.7034	0.3480	0.4997	0.8152	0.1763
$Zr_{0.8}Ti_{0.2}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$	0.7008	0.3442	0.4978	0.8108	0.1740
$Zr_{0.7}Ti_{0.3}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$	0.7009	0.3443	0.4955	0.8118	0.1726

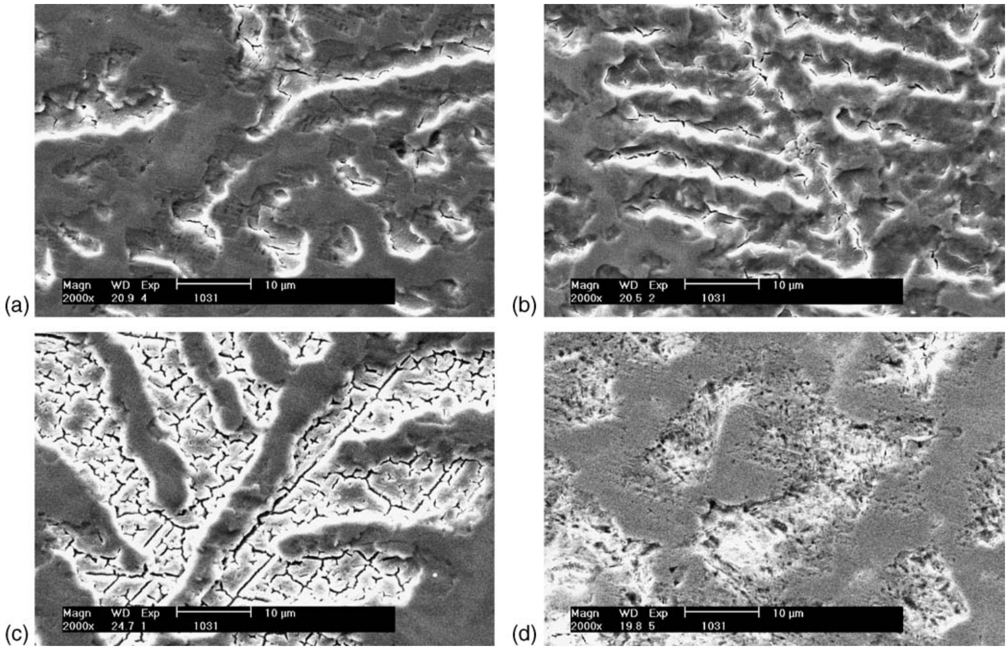

Fig. 2. SEM micrographs of the alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, and (d) $x = 0.3$.

discharge capacity 354 mAh/g, which is higher about 11% than the Ti-free alloy. However, the discharge capacities of those alloys decease sharply with the Ti content increasing further. When $x = 0.1$, the increase of the content of C14 Laves phase results in the increase of the dynamic of hydrogen desorption of alloys, so the discharge capacity of the alloy can be improved. With x increasing, the volume of the hydrogen storage interstitial site in the alloys contracts, and second phase Zr_7Ni_{10} decrease and disappears, which possesses an important catalysis on the electrochemical properties [8], so the discharge capacities of alloys decrease sharply. In addition, the activation of the alloys decreases with increasing the Ti content. From above SEM results, the microcracks on the surface of the alloys decrease with increasing Ti content. It indicates that the surface activation properties of the alloys decrease with increasing Ti content. It may be the main reason to prolong the activate process of alloys.

The HRD of $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloys are shown in Fig. 4. The discharge capacities of both of alloys decrease as the discharge current increases after totally activated. The HRD_{300} of $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ is very poor, and it only preserves about 24%.

For the $Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy, the HRD_{300} can be preserved about 42%, but HRD_{100} and HRD_{150} are kept more than 80%. It is well known that the HRD of the electrode alloy is mainly related to properties of bulk and surface of the alloy. In above XRD results, the content of

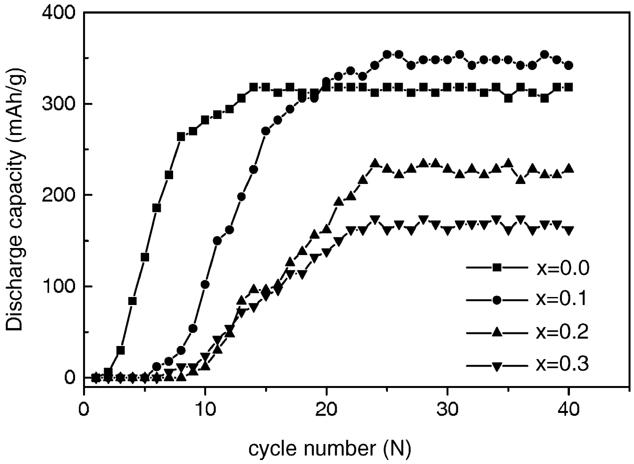

Fig. 3. Initial discharge capacity of the alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$.

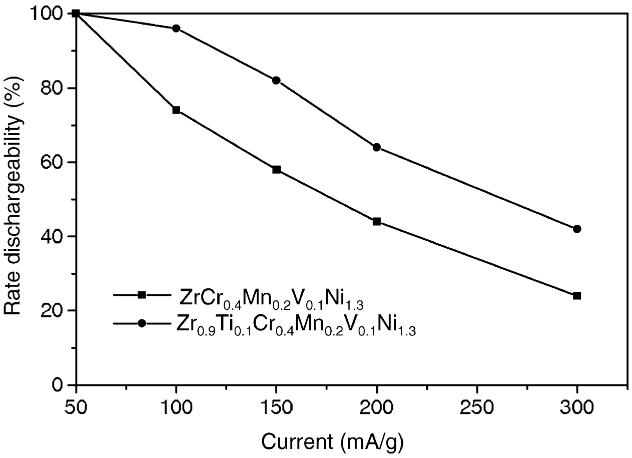

Fig. 4. The high rate dischargeability of the alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$.

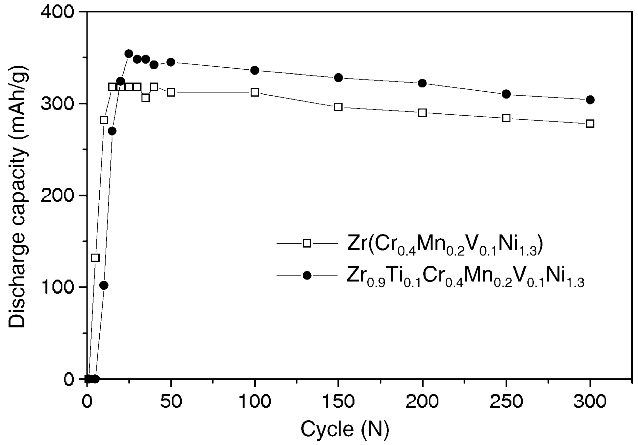

Fig. 5. The cycle life of the alloys $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$.

C14 Laves phase increases due to addition of Ti. The C14 Laves phase has better electrochemical dynamic properties, so the increase of the C14 improves the dischargeability of the alloy. However, the substitution of Ti for Zr has not a positive effect on the activation of the surface of the alloy, consequently the rate dischargeability of the alloy can only be greatly improved at low current.

The cycle durability of both $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloys change slightly, shown in Fig. 5. Both of the alloys show good cycle stability, about 13% and 14% capacity degradation after 300 cycles, respectively. It is assumed that as-cast Zr–Cr–Ni system alloys in this research was found to exhibit high capacities and good cycle life due to the Cr oxide film formation on the surface of the alloy during the charge/discharge process, which prohibit the dissolution of the other elements, such as Mn, V, Ti.

4. Conclusions

The $ZrCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ alloy consists of C15 Laves phase, coexisting with a little C14 Laves phase and second phase Zr_7Ni_{10}. With increasing Ti content, abundances of C15 Laves phase and second phase Zr_7Ni_{10} decreases and that of C14 Laves phase increases, and the cell volume of both C15 and C14 Laves phase decreases gradually. The microstructures of the alloy $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ for $x = 0.1$–0.2 are found to be dendrite. Ti substitution ($x = 0.1$) for Zr in the alloys improves the discharge capacity and rate dischargeability. When $x > 0.1$, both activation and discharge capacity of $Zr_{1-x}Ti_xCr_{0.4}Mn_{0.2}V_{0.1}Ni_{1.3}$ ($x = 0.1$–0.3) alloys decrease. All of the alloys have good cycle durability.

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