

Influence of heat treatment on electrochemical properties of $Ti_{1.4}V_{0.6}Ni$ alloy electrode containing icosahedral quasicrystalline phase

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Abstract: The structures and electrochemical properties of the $Ti_{1.4}V_{0.6}Ni$ ribbon before and after heat treatment are investigated systematically. The structure of the sample is characterized by X-ray powder diffraction analysis. Electrochemical properties including the discharge capacity, the cyclic stability and the high-rate discharge ability are tested. X-ray powder diffraction analysis shows that after heat treatment at 590 °C for 30 min, all samples mainly consist of the icosahedral quasicrystal phase (I-phase), Ti_2Ni phase (FCC), V-based solid solution phase (BCC) and C14 Laves phase (hexagonal). Electrochemical measurements show that the maximum discharge capacity of the alloy electrode after heat treatment is 330.9 mA·h/g under the conditions that the discharge current density is 30 mA/g and the temperature is 30 °C. The result indicates that the cyclic stability and the high-rate discharge ability are all improved. In addition, the electrochemical kinetics of the alloy electrode is also studied by electrochemical impedance spectroscopy (EIS) and hydrogen diffusion coefficient (D).

Key words: quasicrystal; $Ti_{1.4}V_{0.6}Ni$ alloy; electrochemical properties; cyclic stability; high-rate discharge; discharge capacity

1 Introduction

The quasicrystalline phase formation is observed in 1984 by SHECHTMAN et al. Many kinds of quasicrystalline materials have been discovered and investigated extensively during the past three decades. I-phase may have better physical properties for hydrogen-storage applications since some of its atoms have an adequate affinity for hydrogen. The hydrogen desorption performance of $Ti_{45}Zr_{38}Ni_{17}$ I-phase is investigated by using high temperature XRD. The result validates the potential utility of Ti-based I-phase alloy [1]. The $Ti_{45}Zr_{38}Ni_{17}$ I-phase can absorb a large amount of hydrogen, up to about two hydrogen atoms per metal atom, while the $Ti_{41.5}Zr_{41.5}Ni_{17}$ I-phase alloy can reach up to three hydrogen atoms per metal atom [2,3]. The electrochemical maximum hydrogen storage capacity of

$Ti_{45}Zr_{35}Ni_{17}Cu_3$ I-phase alloy of 240 mAh/g was reported at the discharge current density of 30 mA/g [4–6]. HU et al [7] systematically investigated the electrochemical hydrogen storage properties of Ti–V–Ni–Co I-phase alloys [7]. Our previous works reported that the electrochemical performance of $Ti_{1.4}V_{0.6}Ni$ I-phase alloy is improved when AB_3 -type hydrogen storage alloy is added to $Ti_{1.4}V_{0.6}Ni$ I-phase alloy [8]. Up to the present, few investigations of hydrogen storage properties have been focused on the other Ti-based I-phase alloys.

At present, the Ti-based Laves phase alloys [9,10] and the V-based solid solution alloys [11,12] are regarded as promising materials for electrodes of the Ni–MH rechargeable batteries due to their higher discharge capacity. The V-based solid solution with BCC structure could absorb and desorb a large amount of hydrogen in the alkaline electrolyte. For example, the

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C14 Laves phase or the TiNi phase exhibits high electrocatalytic activity [13,14]. AKIBA and IBA [15] found the Laves phase alloys with a large amount of hydrogen capacity (above 2% in mass fraction) and fast hydrogen absorption and desorption kinetics at appropriate condition [15]. Some studies have discovered that a well-designed multiphase hydrogen storage alloys might greatly improve their electrochemical properties [13–16]. OVSHINSKY and FETCENRO [16] pointed out that some multielement, multiphase disordered hydrogen storage alloys provided the electrode surface with exceptionally good electrochemical catalytic activity.

In this work, multiphase Ti–V–Ni hydrogen storage alloy containing I-phase is formulated, and the structures and electrochemical properties of the alloy is investigated.

2 Experimental

Blend of Ti, V and Ni (99.9% purity) corresponding to the nominal composition of $Ti_{1.4}V_{0.6}Ni$ was prepared by arc-melting under argon atmosphere on a water cooled copper hearth. The ingots were turned over and remelted three times to ensure the homogeneity. Then they were melt-spun onto a copper wheel rotating at 34 m/s to produce ribbon. The phase transformation temperature of the ribbon was investigated in an alumina pan under a purified argon atmosphere with a heating rate of 0.17 K/s by a differential scanning calorimeter (DSC). Alloy ribbons were mechanically crushed into fine powders of 0.038–0.075 μm for testing. The powders were treated at 590 $^{\circ}C$ for 30 min under vacuum. Structure of each heat treated sample was examined by XRD analysis with Cu K_{α} radiation on D/Max-rB X-ray diffractometer using JAD5 software.

The metal hydride electrode as the working electrode was prepared by mixing 0.15 g alloy powder and 0.75 g carbonyl nickel powder, then cold-pressing the mixture to form pellets under a pressure of 15 MPa with 10 mm in diameter and about 1.5 mm in thickness. For electrochemical measurements, the charge-discharge test was conducted in a half-cell consisting of a metal-hydride electrode, a $Ni(OH)_2/NiOOH$ counter electrode, and a Hg/HgO reference electrode in a 6 mol/L KOH solution electrolyte, with DC-5 battery testing instrument under computer control. During the charge/discharge test, the electrodes were fully charged (the over-charged ratio approximately 30%) at a current density of 60 mA/g for 6 h, and then discharged to -0.6 V vs Hg/HgO at 30 mA/g and 303 K. After every charge/discharge, the rest time was 5 min. For evaluating the high-rate dischargeability, discharge capacities of the

alloy electrode at different discharge current densities were measured. The electrochemical impedance spectroscopy (EIS) analysis was taken at the 50% depth of discharge (DOD) using a Solartron 1287 Potentiostat/Galvanostat and a Solartron 1255B frequency response analyzer with Z-PLOT software for WINDOWS. In this work, potentiostatic discharge technique was selected to estimate the hydrogen diffusion coefficient through a given electrode. After being fully charged and followed by 30 min open-circuit lay-aside, the tested electrodes were discharged with 500 mV potential-step for 3600 s on the EG & G PARC Model 273 Potentiostatic/Galvanostat, using the M352 corrosion software.

3 Results and discussion

3.1 Alloy structures

Figure 1 shows the DSC curve of the melt-spun $Ti_{1.4}V_{0.6}Ni$ alloy ribbon. The DSC trace is obtained at a heating rate of 0.17 K/s from 400 to 800 $^{\circ}C$. The crystallization takes place through a small sharp exothermic peak reaction for this alloy ribbon, and the main DSC exothermic peak shows a straight base line. The tardy peak of the exothermic reaction is due to the transformation from the I-phase to the C14 Laves phase, and the transfer peak temperature ranges from 564 $^{\circ}C$ to 613 $^{\circ}C$.

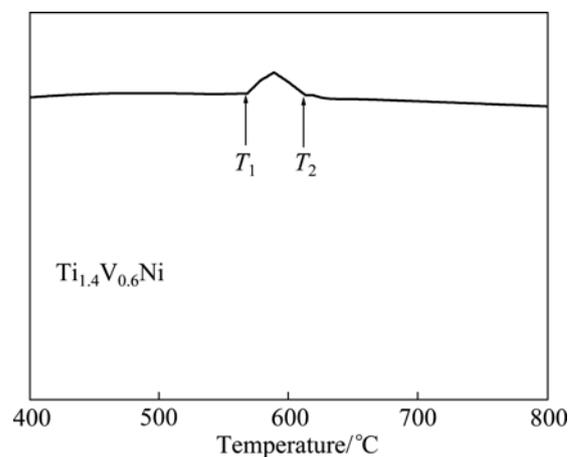


Fig. 1 DSC curve of original melt-spun $Ti_{1.4}V_{0.6}Ni$ alloy ribbon

Figure 2 shows the XRD patterns of the $Ti_{1.4}V_{0.6}Ni$ alloy. It is found that the $Ti_{1.4}V_{0.6}Ni$ alloy consists of I-phase, face centered cubic (FCC) phase with Ti_2Ni -type structure in space group $R-3m$ and V-based solid solution phase with body centered cubic (BCC) structure in space group $Im3m$. After heat treatment, the alloy also contains the C14 Laves phase with $MgZn_2$ type hexagonal structure in space group $P63/mmc$ except for I-phase and V-based solid solution phase. It can be found

that the peak intensity of I-phase becomes weak, which means that the transformation from the I-phase to the C14 Laves phase occurs.

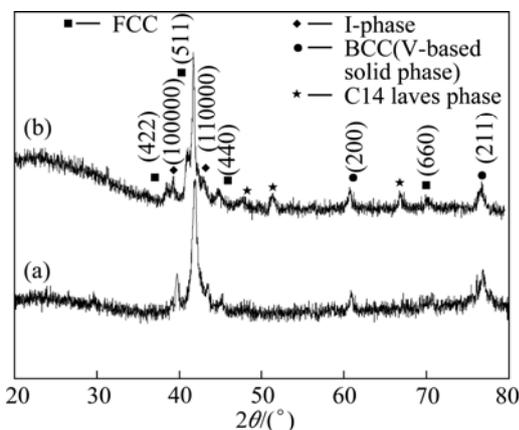


Fig. 2 XRD patterns of original (a) and treated $Ti_{1.4}V_{0.6}Ni$ (b) alloys

3.2 Discharge capacity

Figure 3 shows the discharge capacity as a function of the cycle number at a current density of 30 mA/g and 30 °C for the original and the heat treated alloy electrodes. The maximum electrochemical capacities of the above alloys are summarized in Table 1. The original $Ti_{1.4}V_{0.6}Ni$ alloy and the heat treated alloy give a discharge capacity of 276.3 and 330.9 mA·h/g, respectively. This can be explained by that the heat treated alloy contains the C14 Laves phase with $MgZn_2$ type, which acts as a catalyst and a micro-current collector, Ti_2Ni phase (FCC), V-based solid solution phase (BCC) and I-phase which is activated to reversibly absorb and desorb a considerable amount of hydrogen in KOH electrolyte. The discharge capacity of the treated alloy is higher than that of the untreated one, and the cyclic stability of the alloy electrode is little improved.

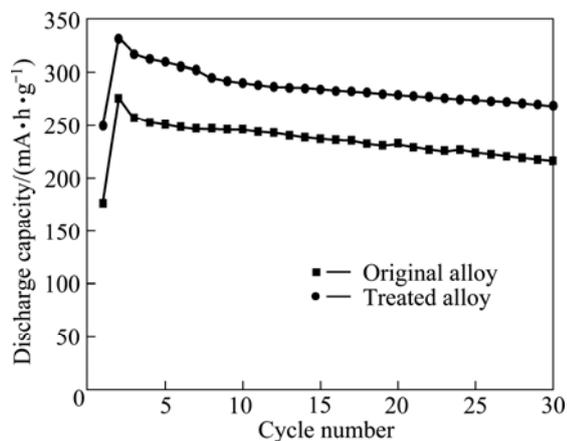


Fig. 3 Discharge capacity as function of cycle number for original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes

Table 1 High-rate discharge abilities of original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes

Alloy	Current density/($mA \cdot g^{-1}$)						HRD (C_{240}/C_{30})/ %
	30 mA/G	60 mA/G	90 mA/G	120 mA/G	180 mA/G	240 mA/G	
Original alloy	276.3	248.3	245.9	244.6	230.9	205.1	74.2
Treated alloy	330.9	310.5	300.2	295.6	280.1	261.4	79

3.3 High-rate discharge ability and electrochemical kinetics

Figure 4 shows the high-rate discharge ability (HRD), which denotes the discharge properties of the fully activated alloys at large discharge current densities. The HRD is an important kinetic property for the metal hydride electrode. To evaluate the HRD, the charging current density is kept constant of 60 mA/g, the discharge capacities are noted as C_i at different discharge current densities. The HRD is defined as the ratio of the C_i to the maximum discharge capacity C_{30} when the discharge current density is 30 mA/g. It can be observed that the HRD of the treated alloy is superior to that of the original alloy under the same discharge condition, as summarized in Table 1. For example, the HRD increases from 74.2% to 79 % after heat treatment at the discharge current density of 240 mA/g. The significant improvement of the HRD of the heat treated alloy is probably attributed to the C14 Laves phase which acts as a catalyst.

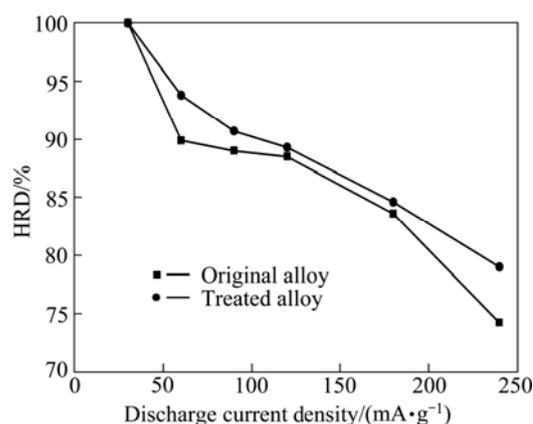


Fig. 4 High-rate dischargeability of original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes

Figure 5 shows the EIS curves of the original and the treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes at 50% depth of discharge (DOD) and the equivalent circuit. It can be seen clearly that all the EIS curves consist of two semicircles and a straight line. The semicircle in the high frequency region relates to the contact resistance between the current collector and the alloy pellet, and in the low frequency region corresponds to the charge

reaction resistance [17]. On the basis of the circuit and fitting program Z-VIEW [18], R_{ct} is obtained. The charge-transfer resistance R_{ct} is shown in Table 2. It can be seen that the R_{ct} decreases from 0.218 Ω to 0.175 Ω by heat treatment, which results in a great improvement of the reactive activity, thus, the discharge capacity increases dramatically.

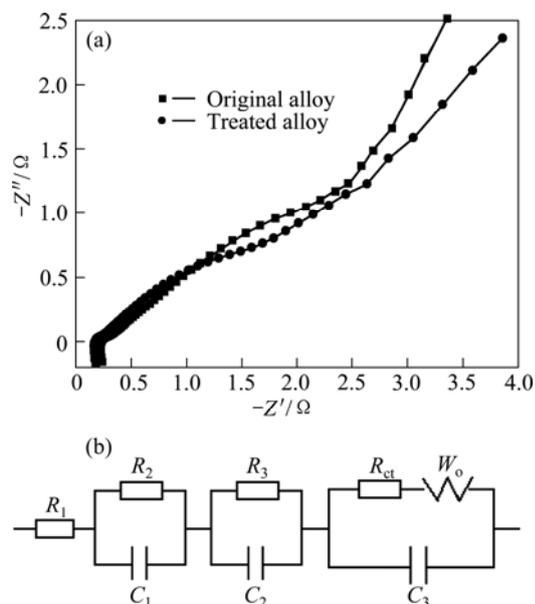


Fig. 5 EIS curves of original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes (a) and equivalent circuit (b)

Figure 6 shows the semi-logarithmic curves of anodic current vs time response for the original and the treated $Ti_{1.4}V_{0.6}Ni$ alloys. According to the model of ZHENG et al [19], the diffusion coefficient of the hydrogen atoms in the bulk alloy can be estimated through the slope of the linear region of the corresponding plots by the following formula:

$$\lg i = \lg \left(\frac{6FD(C_0 - C_s)}{da^2} \right) - \frac{\pi^2 Dt}{2.303a^2} \quad (1)$$

where D is the hydrogen diffusion coefficient; a is the radius of the spherical particle; i is the diffusion current density; C_0 is the initial hydrogen concentration in the bulk electrode; C_s is the hydrogen concentration on the surface of alloy particles; d is the density of the hydrogen storage materials; t is the discharge time. With the average particle radius of 15 μm , the hydrogen diffusion coefficients D in the bulk alloy electrodes are calculated by Eq. (1) and listed in Table 2, respectively.

It can be seen that D increases from 6.47×10^{-11} to 8.23×10^{-11} cm^2/s , indicating that the hydrogen diffusion rate is enhanced by heat treatment, which is consistent with that of the high-rate of discharge ability. This suggests that the diffusion process is dominated by the electrochemical reaction. As mentioned above, the

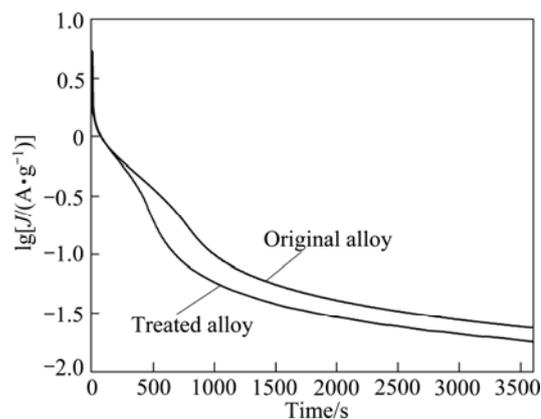


Fig. 6 Semi-logarithmic plots of anodic current vs time response of original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes

Table 2 Electrochemical behaviours of original and treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes

Electrode	Cycling stability (30)/%	Charge-transfer resistance, R_{ct}/Ω	Hydrogen diffusion coefficient/ ($10^{-11}cm^2 \cdot s^{-1}$)
Original alloy	79.4	0.218	6.47
Treated alloy	81.1	0.175	8.23

treated alloy facilitated atomic hydrogen transportation. From the above results, it is believed that the kinetics of hydriding $Ti_{1.4}V_{0.6}Ni$ alloy is greatly improved by heat treatment. Generally speaking, the kinetic properties of the hydride electrode are mainly controlled by the charge transfer resistance on the electrode surface and by the hydrogen diffusion resistance inside the electrode. In other words, the HRD is influenced by the hydrogen diffusion coefficient. In this work, D is increased markedly. The variation is virtually consistent with the HRD of the alloy electrode.

4 Conclusions

The structures and electrochemical properties of the original and the treated $Ti_{1.4}V_{0.6}Ni$ alloy electrodes were investigated systematically. The powders were treated at 590 $^{\circ}C$ for 30 min under vacuum. The result of the XRD shows that the original alloy consists of the I-phase, V-based solid solution phase with BCC structure and face centered cubic phase with Ti_2Ni -type structure; however, the treated alloy includes the above phases as well as the C14 Laves phase with a hexagonal structure. The electrochemical properties such as discharge capacity, cyclic stability and high-rate discharge ability (HRD) are improved by heat treatment. The treated alloy electrodes exhibit higher hydrogen diffusion coefficient and lower charge-transfer resistance in comparison with

the untreated one. This means that the heat treated alloy facilitates the formation of metal-hydride and hydrogen diffusion within the bulk alloy. The C14 Laves phase acts as a catalyst and a micro-current collector, and improves the electrochemical characteristics of the alloy electrode.

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热处理对包含正二十面体准晶相 $Ti_{1.4}V_{0.6}Ni$ 合金电极的电化学性能的影响

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摘要: 研究了热处理前后 $Ti_{1.4}V_{0.6}Ni$ 合金的结构和电化学性能。采用 X 射线粉末衍射(XRD)方法分析合金的结构。电化学特性包括放电容量、循环稳定性和高倍率放电性能等。XRD 衍射分析表明, 在 590 °C 热处理 30 min 的合金, 主要包含正二十面体准晶相、 Ti_2Ni (FCC)相、V 基固溶相(BCC)和 C14Laves 相(Hex)。电化学测试显示, 热处理后在 30 °C 和放电电流密度为 30 mA/g 的条件下, 合金电极的最大放电容量可达 330.9 mA·h/g, 并且循环稳定性和高倍率放电性能也得到改善。此外, 通过电化学阻抗和合金内部氢的扩散系数研究了合金电极的动力学性能。

关键词: 准晶; $Ti_{1.4}V_{0.6}Ni$ 合金; 电化学性能; 循环稳定性; 高倍率放电; 放电容量

(Edited by YANG Hua)