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# Improved electrochemical hydrogen storage capacity of $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal by addition of $ZrH_2$

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ABSTRACT

$Ti_{45}Zr_{38}Ni_{17} + xZrH_2$ ($x$ = 5, 10, 15 and 20 wt%) composite materials are produced by ball milling for 20 min. The results of XRD measurement show that the composite materials contain icosahedral quasicrystal phase (I-phase), FCC phase with a $Ti_2Ni$ type crystal and C14 Laves phase. After adding $ZrH_2$, the composite materials include not only the individual phases mentioned above, but also the ZrH phase. These composite materials are used as the negative electrode material of the nickel-metal hydride batteries. The electrochemical hydrogen storage characteristics of the material after adding ZrH is investigated. The $Ti_{45}Zr_{38}Ni_{17} + xZrH_2$ ($x$ = 5, 10, 15 and 20 wt%) composite material has reached the maximum discharge capacity (83.2 mA h/g) when $x$ equals 10. This maximum discharge capacity is much higher than that of $Ti_{45}Zr_{38}Ni_{17}$ alloy without ZrH. After adding $ZrH_2$, the high-rate discharge ability and the cycling stability are enhanced simultaneously. The improvement of the electrochemical properties can be attributed to the synergistic effects of $ZrH_2$, and the synergistic effects in the composite electrodes are probably attributed to the entry of most of hydrogen atoms from weakly bond strength of the Zr-H to the I-phase structure in electrochemical reaction.



## 1. Introduction

Absolutely, hydrogen storage is clearly one of the key challenges for developing hydrogen economy. Ti-Zr-Ni icosahedral (I) quasicrystal alloys with a new type of translational long-range order are promising negative electrode material for Ni/MH batteries and display non-crystallographic rotational symmetry [1]. Stroud et al. [2] firstly reported that the hydrogen desorption from $Ti_{45}Zr_{38}Ni_{17}$-H was observed by using high-temperature XRD, demonstrating the potential utility of Ti-based I-phase alloy. Kelton et al. [3–5] investigated the properties of $Ti_{45}Zr_{38}Ni_{17}$ I-phase alloy which serves as hydrogen storage material. However, high hydrogen desorption temperature and unfavorable cycling stability inhibit its application.

Takasaki et al. [6] has reported the electrochemical hydrogenation/dehydrogenation properties of $Ti_{45}Zr_{38}Ni_{17}$ I-phase electrode, and the maximum discharge capacity of the I-phase electrode at a current density of 15 mA/g is 23.9 mA h/g under room temperature. Compared with the theoretical charge capacity of the $Ti_{45}Zr_{38}Ni_{17}$ I-phase electrode which is estimated to reach 795 mA h/g [6,7], the true discharge capacity is relatively low. The Ni in the $Ti_{45}Zr_{38}Ni_{17}$ can be substituted by adding other 3d transition metals [8] such as Fe [9] and Co [10]. Although the structural properties do not change in a significant way as a result of such substitution, the hydrogen storage properties can be altered apparently, particularly the variations of the maximum concentration and the desorption temperature. The effect of mechanical milling on the discharge performance of electrodes, which consist of $Ti_{45}Zr_{38-x}Ni_{17+x}$ ($x$ = 0, 8) quasicrystals, is investigated at room temperature. Discharge performance of $Ti_{45}Zr_{30}Ni_{25}$ I-phase-based electrode is better than $Ti_{45}Zr_{38}Ni_{17}$ electrode manifestly [11].

To further enhance discharge capacity, we have studied electrochemical hydrogen properties of Ti-V-Ni quasicrystal and metal hydride composite materials [12]. In this paper, electrochemical hydrogen properties of $Ti_{45}Zr_{38}Ni_{17}$ icosahedral quasicrystals, negative electrode materials for Ni/MH batteries, are given, following

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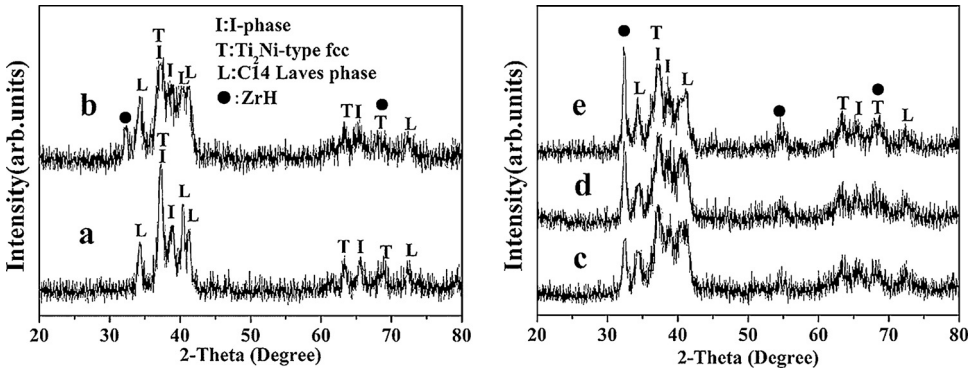


**Fig. 1.** XRD patterns of $Ti_{45}Zr_{38}Ni_{17}$ alloy (a) and composite materials corresponding to $x$ = 5 wt% (b), $x$ = 10 wt% (c), $x$ = 15 wt% (d) and $x$ = 20 wt% (e).

with a discussion about the effect of $ZrH_2$ on the discharge performance of I-phase-based electrodes.

## 2. Experimental

Under an argon atmosphere, $Ti_{45}Zr_{38}Ni_{17}$ alloy ingots were prepared by arc-melting the mixture of spongy bulk Ti, Zr, and Ni on a Cu hearth with circulating water cooling system. In order to minimize the oxygen contamination, the sample chamber was evacuated to the level of $10^{-5}$ Pa and filled with a high-purity argon gas sequentially for three times. The ingots were melted and then turned over at least three times for homogenizing the chemical compositions. From the mother alloy ingot, ribbons were prepared by the single roller melt-spinning technique at the wheel speed of 25 m/s under argon atmosphere. The obtained ribbons with 30–40 μm thickness, 6–10 cm length, and 2 mm width around are crushed mechanically to make alloy powders with a size range of 200–400 mesh. As one of the starting materials, $ZrH_2$ (98% purity) was purchased from Aldrich, and the $Ti_{45}Zr_{38}Ni_{17} + xZrH_2$ ($x$ = 5, 10, 15 and 20 wt%) were prepared by ball-milling in the stainless steel vial with an argon atmosphere for 20 min. From 20° to 80° ($2\theta$) with the step size of 0.04°, XRD measurements were conducted by using an ARL X-ray diffractometer with Cu$K\alpha$ radiation at 40 kV and 40 mA. Furthermore, the surface morphology of samples was characterized by the JSM-5610LV scanning electron microscope (SEM).

Working electrodes, a half-cell consists of a $Ni(OH)_2$/NiOOH counter electrode and a Hg/HgO reference electrode under a 6 M KOH aqueous solution, were prepared by pressing 0.15 g active powders and 0.75 g Ni powders into a pellet with 10 mm in diameter and 1.0 mm in thickness under a pressure of 15 MPa. The electrochemical tests were performed on an automatic galvanostatic charge-discharge apparatus (DC-5) at 303 K. The electrode was charged at 60 mA/g for 6 h, allowed to rest for 5 min sequentially, and then discharged at 30 mA/g and cut-off voltage of −0.6 V (*vs.* Hg/HgO). High-rate discharge ability (HRD) was measured after the cycles of charging and discharging at various specific current densities. HRD (%) is evaluated from the following equation: HRD (%) = $C_n \times 100/C_{30}$, where in $C_n$ ($n$ = 60, 90, 120, 180 and 240).

## 3. Results and discussion

### 3.1. Phase structure

Fig. 1 shows X-ray diffraction (XRD) patterns of the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal and $Ti_{45}Zr_{38}Ni_{17} + xZrH_2$ ($x$ = 5, 10, 15 and 20 wt%) composite materials. According to Fig. 1(a), it can be seen that the $Ti_{45}Zr_{38}Ni_{17}$ alloy contains the I-phase, the C14 Laves phase, and the face centered cubic (FCC) phase with the $Ti_2Ni$-type structure. The XRD peaks corresponding to the I-phase are indexed by using a six-index scheme proposed by Bancel et al. [13]. The composite material appears ZrH phase except for the I-phase, C14 Laves phase, and face centered cubic (FCC) phase with $Ti_2Ni$-type structure in space group R-3m, and the intensity of the peaks corresponding to ZrH phase increase with the increasing of the value of $x$. Fig. 1(b)–(e) which are corresponding to $x$ = 5, 10, 15 and 20 wt% respectively. Meanwhile, we find that all diffraction peaks prone to broader slightly after adding $ZrH_2$, which suggests that there is a decomposition reaction of $ZrH_2$ and some of hydrogen atoms, enter the interspaces of quasicrystal, are released during the process of the ball milling, resulting in the expansion of lattice.

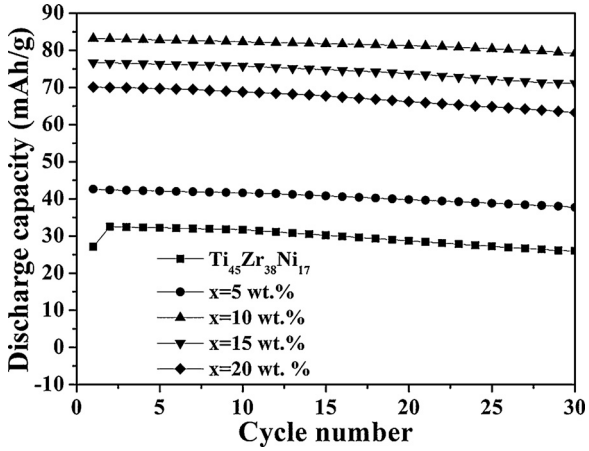


**Fig. 2.** Discharge capacities of $Ti_{45}Zr_{38}Ni_{17}$ alloy and composite material electrodes as a function of cycle number.

### 3.2. Electrochemical hydrogen storage characteristics

As a function of cycle number at room temperature, discharge capacities of the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal and composite materials electrodes are shown in Fig. 2. The charge process is performed for 6 h. The $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal electrode have a stable discharge capacity of 32.5 mA h/g around after secondary charge and discharge cycles at discharge current density of 30 mA/h and 303 K for activation. These achieved maximum discharge capacities are approximately stable until the 10th cycle, and they slightly increase after 10th cycle. It is suggested that the Laves phase, facilitates the charge-transfer reaction and the hydrogen storage capacity, can work as the electro-catalyst and the hydrogen storage phase in the Ti-based alloy electrode. These maximum discharge capacities after adding different amount of $ZrH_2$ are given in Table 1. The maximum discharge capacity increases initially and then decreases as the content of $ZrH_2$ in the composite material electrodes increases. The achieved maximum discharge capac-

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