Microstructure and electrochemical properties of Ti-containing AB₂ type hydrogen storage electrode alloy

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Abstract

The microstructure and electrochemical properties variation of alloy Zr(MnVNi)₂ after Ti substitution for Zr was investigated. The microstructures of Zr₁₋ₓTiₓ(MnVNi)₂ (x = 0, 0.5) alloys were determined with X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution electron microscopy (HREM) and energy dispersive spectrum (EDS) analysis. The systematic structural analysis shows that there are two phases in the Ti-substituted alloy Zr₀.₅Ti₀.₅(MnVNi)₂, the C₁₄ Laves and the Ti containing “premartensite” R phase, Ti₀.₈Zr₀.₂Ni. The variation in electrochemical properties of the alloy Zr(MnVNi)₂ after partial Ti substitution can be attributed to the Ti substitution for some Zr sites in C₁₄ Laves phase, the formation of Ti₀.₈Zr₀.₂Ni R-phase and the disappearance of Zr–Ni binaries. © 2000 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical properties; Laves phase; Premartensite R phase; Zr–Ni binaries

1. Introduction

The AB₂ (A = Zr, Ti; B = V, Cr, Mn) hydrogen storage intermetallic compounds have been investigated extensively because of their potential application in high capacity negative electrodes for nickel-metal hydride batteries [1,2]. The common interests are concentrated on the compositional substitution of metallic elements in ZrMn₂, ZrCr₂ and ZrV₂ Laves phases, to improve the hydrogen absorbing/desorbing kinetics and to increase the electrochemical capacity [1–4]. It has been shown that substitution of Zr by Ti in Laves phase results in not only the decrease of the lattice parameter of Laves phase [4], but also the formation of Ti₀.₈Zr₀.₂Ni R-phase [1]. However, so far the mechanism for the change of the electrode properties due to Ti substitution has not been made clear.

In the present work, we report on the effect of Ti partial substitution on the electrochemical properties and microstructure for Zr–Mn–V–Ni system alloys. Particular attention has been paid to the influence of substructures of the Laves phase and the non-Laves phase on the electrode performance of reversible hydrogen capacity and the absorption/desorption activation.
2. Experimental procedures

The alloys were synthesized by arc melting pure metals (Zr 99%, Ti 99.5%, Ni 99.9%, Mn 99.75%, V 99.5%) on a water cooled copper crucible under argon atmosphere. Alloys were remelted four times to ensure compositional homogeneity. Working electrodes were prepared by cold pressing the mixtures of the alloy and Cu powders of 360 mesh with a weight ratio of 2:1 to pellets under 15 MPa. The electrochemical behavior of each sample was tested in a three-chamber glass vessel filled with 6 M KOH electrolyte solution. A NiOOH/Ni(OH)2 counter electrode of large excess capacity and a Hg/HgO reference electrode were employed.

X-ray diffraction was carried out by using a Rigako/max-B type diffractometer. The Rietveld refinement method was used for the quantitative analysis of phase abundance and the determination of lattice parameters.

Thin foil specimens for TEM and HREM observation were prepared by mechanical tinning and ion milling. TEM observations and EDS analysis were carried out on a Philips CM12 electron microscope operated at 120 kV with a point resolution of 3.4 Å. The HREM experiment was carried out by using a JEOL 2010 microscope with a point resolution of 0.197 nm.

3. Experimental results

3.1. Electrochemical properties of Zr_{1-x}Ti_x(MnVNi)_2 (x = 0, 0.5) alloys

Fig. 1 shows the electrochemical capacity variation and activation process of Zr_{1-x}Ti_x(MnVNi)_2 (x = 0, 0.5) alloys.
0.5) alloys at the room temperature. At the discharge current of 60 mA/g, the discharge capacity of Zr(MnVNi)\(_2\) reaches only 280 mAh/g after 30 activation cycles. After Ti substitution for 50% Zr, the discharge capacity of Zr\(_{0.5}\)Ti\(_{0.5}\)(MnVNi)\(_2\) reaches 375 mAh/g after 10 cycles and decreases to 350 mAh/g after 30 cycles. It is apparent that the alloy Zr\(_{0.5}\)Ti\(_{0.5}\)(MnVNi)\(_2\) has both higher capacity and better activation property than alloy Zr(MnVNi)\(_2\).

3.2. Lattice parameters and crystalline characteristics of each phase

3.2.1. X-ray Rietveld analysis results

The lattice parameters of Laves phase components and the abundance of non-Laves phase components of the two alloys determined by X-ray Rietveld analysis are listed in Table 1.

3.2.2. Substructure of Laves phase and EDS analysis results of each phase in alloy Zr(MnVNi)\(_2\)

As indicated in Table 1, C14 and C15 Laves phase are coexisting in Zr(MnVNi)\(_2\), for which high density of stacking faults were observed in the C15 Laves phase, as shown in Fig. 2. According to TEM observation, the stacking faults in the C15 phase were regarded as the main defect that would affect the hydrogen absorbing/desorbing behavior of the electrode alloys during electrochemical process. EDS results show that no diffraction peaks of Mn and V appear in the CDS of Zr-Ni binaries as shown in Fig. 3(a).

3.2.3. Composition and crystalline characteristics of each phase in Zr\(_{0.5}\)Ti\(_{0.5}\)(MnVNi)\(_2\) alloy

There are only two phases in the Zr\(_{0.5}\)Ti\(_{0.5}\)(MnVNi)\(_2\) alloy. One is the Laves phase and the other is the bcc phase. EDS results show that some Ti exists in C14 Laves phase as shown in Fig. 3(b). The bcc phase, which determined to be Ti\(_{0.8}\)Zr\(_{0.2}\)Ni according to quantitative EDS analysis, contains only Ti, Zr and Ni elements and no Mn and V as shown in Fig. 3(c). EDS results of Fig. 3 for the investigated alloys also reveal that Mn and V exist only in Laves phase. Thus, the B side atom construction of Laves phase with AB\(_2\) structure in Zr(MnVNi)\(_2\) alloy is consistent after Ti substitution for Zr. As it is known that the lattice parameters of laves phase are related to the radii of atoms located in A and B sites [2,4], when the substitution atom radius for A or B side is smaller than the original one, the lattice will be contracted. The lattice

![Fig. 2. Morphology and substructure of C14 and C15 Laves phase in Zr(MnVNi)\(_2\) alloy: (A) stacking faults of C15 Laves phase; (B) C14 Laves phase.](image-url)
parameters of C14 Laves phase in alloy Zr_{0.5}Ti_{0.5}(MnVNi)$_2$ are apparently decreased in comparison with those in alloy Zr(MnVNi)$_2$ as shown in Table 1. From both the structural model and the experimental measurement of the lattice parameters of alloys with different chemical compositions, we believe that Ti atoms ($r_{Ti}=0.147$ nm) can only substitute the Zr atoms ($r_{Zr}=0.161$ nm [5]) in the A side of AB$_2$ Laves phase in alloy Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_2$. The results also reveal that the alloying elements in multicomponent alloys are re-distributing among the coexisting Laves phase and non-Laves phase. In addition, the experimental result reveals that the compositions of either C14 Laves phase or the bcc phase are different from the nominal alloy composition.

Furthermore, after Ti substitution, the substructure of C14 Laves phase in alloy Zr(MnVNi)$_2$ is also changed. High density dislocations in C14 Laves phase can be observed in Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_2$ alloy as shown in Fig. 4. The island-like Ti$_{0.8}$Zr$_{0.2}$Ni phase homogeneously distributed in the C14 laves phase matrix. The tweed-like contrast of the Ti$_{0.8}$Zr$_{0.2}$Ni phase was

Fig. 3. EDS results of different phases: (a) Zr-Ni phases in the alloy Zr(MnVNi)$_2$; (b) C14 Laves phase in the alloy Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_2$; (c) Ti containing bcc phase in the alloy Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_2$. 
Fig. 4. Dislocations of C14 laves phase and morphology of Ti–Zr–Ni phase in the alloy Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_2$: (A) C14 Laves phase matrix; (B) Ti–Zr–Ni phase.

Fig. 5. Tweed-like morphology of R phase.
clearly seen in the dark field images as shown in Fig. 5. According to X-ray Rietveld analysis, the lattice parameter of the Ti$_{0.8}$Zr$_{0.2}$Ni bcc phase, which coexists with the C14 phase in the Zr$_{0.5}$Ti$_{0.5}$(MnVNi)$_{2}$, is 3.01 Å. This result is well in agreement with those from other research groups [6,7]. However, the composition of the present bcc phase is significantly different from those reported in the literature. From the model for X-ray Rietveld analysis of the series alloys Zr$_{1-x}$Ti$_x$Ni$_{1.3}$Mn$_{0.7-y}$V$_y$ ($x = 0, 0.1, 0.2, 0.5; y = 0, 0.1, 0.2, 0.4, 0.7$), the bcc phase was assumed as a solid solution of all the alloying elements Zr, Mn, V, Ni and Ti with a structure of Im3 m space groups by Yoshida and Akiba [4].

In order to determine the crystalline characteristics of the present bcc phase, SAED patterns were obtained from the same region of the sample as illustrated in Fig. 6. There are seven patterns along the zone axis within the [001]–[011]–[111] stereographic projection triangles for the bcc phase. Similar to the diffraction spots in normal ordered phases, the spots with the strongest intensity are contributed from the basic structure, while those with weaker intensities are results from the superstructure by atomic ordering. According to the diffraction spots with the strongest intensity, the basic structure of the bcc phase can be determined to have a lattice parameter of $a = 0.3$ nm. Furthermore, super lattice diffraction spots located in 1/3, 2/3 positions between the neighboring fundamental diffraction spots from the basic structure are also observed. These “1/3 reflections” are the characteristic diffraction of the “premartensite” R phase for Ti–Ni shape memory alloy [8–10]. It has been notified previously that there are four distinct R-phase variants re-
lated to each other by twin relationship. The coexisting variants are often superimposed. For \([111]_{B2}\) SAED pattern, namely 1/3 reflections from a single variant of R-phase can appear on just one \([011]_{B2}\) directions or they can appear along all three \([011]_{B2}\) directions. The observation of 1/3 reflections on two \([011]_{B2}\) directions is considered as a superimposed pattern from two variants [10]. In order to distinguish the superimposing variants, the microstructure of the R phase in the atom scale was observed by HREM as shown in Fig. 7. A conventional Fourier transformation was performed from different area in the HREM image of \([111]\) direction (as shown in Fig. 6(e)) of the R phase, and the Fourier space (SAED pattern) corresponding to the area was obtained. Two variants of the R phase with 1/3 reflections in different directions were obtained as shown in Fig. 7(a, b). It was shown in fig. 6(e) that 1/3 reflections appear along all three \([011]_{B2}\) directions. Thus, there are at least three R phase variants coexisting in the observed Ti0.8Zr0.2Ni. In addition, diffraction patterns of the R phase in Fig. 6 are accompanied by strong localized diffused scattering, which was caused by the large-amplitude, short-wavelength atomic displacements [12]. The localized diffuse scattering reflects the incipient mechanical instability in the parent cubic lattice during the R phase transformation [11,12].

4. Discussion

As we have indicated in Section 3.1 that the alloy Zr0.5Ti0.5(MnVNi)2 has a higher electrochemical capacity and a better activation property than Zr(MnVNi)2, we are attempting to analyze the mechanism for the electrochemical property variation in the following passages.

4.1. Effect of Ti substitution on Laves phase in Zr(MnVNi)2 alloy

The X-ray Rietveld results show that the abundance of laves phase (C14: 55 wt% plus C15: 30 wt%) was 85% for Zr(MnVNi)2 alloy. But for the bcc phase containing alloy Zr0.5Ti0.5(MnVNi)2, the only one type of laves phase is the C14 Laves phase and the abundance of C14 laves phase reaches 86 wt%. Although the C14 and C15 Laves phase are coexisting in the Zr(MnVNi)2 alloy, the abundance of entire Laves phase keeps almost unchanged before and after the Ti substitution. It has been proven that there is no significant difference in the hydrogen capacity and electrocatalytic property between C14 and C15 Laves phase in multicomponent Zr-based alloys [2,4]. So, the electrochemical properties variation of Zr(MnVNi)2 alloy after Ti substitution was not caused by the change of abundance of Laves phase.

The substructure of laves phase should also be taken into account because the activation and discharge capacity of an electrode alloy all depend on the rate of diffusion of hydrogen, and the rate of nucleation and growth of hydride in alloy matrix as well as alloy in the hydride matrix [13,14]. Our study indicates that there are lots of stacking faults in C15 Laves phase and grain boundaries between
the C14 and C15 Laves phase in the Zr(MnVNi)2 alloy. And for Zr0.5Ti0.5(MnVNi)2 alloy, there are some dislocations existing in the C14 Laves phase. Through TEM observations we regard that the density of defects in Zr(MnVNi)2 alloy was slightly higher than that in Zr0.5Ti0.5(MnVNi)2 alloy. Accordingly, the higher capacity and easier activation tendency of Zr0.5Ti0.5(MnVNi)2 alloy compared with Zr(MnVNi)2 alloy cannot be attributed to the difference in phase abundance and defect density of the Laves phase.

As we mentioned in Section 3.2, the Ti atoms introduced in Zr0.5Ti0.5(MnVNi)2 are believed to substitute the Zr atoms in the A side of Laves phase. The reason for the improvement in hydrogen absorbing capacity and absorbing/desorbing kinetics after Ti substitution for Zr in multicomponent alloys, can be partially attributed to the Ti substitution effect in C14 Laves phase for Zr0.5Ti0.5(MnVNi)2 alloy [3,6,7].

4.2. The non-Laves phase effect on the electrochemical properties of multicomponent alloys

The reversible capacities for Zr–Ni binaries are lower than 100 mAh/g [2]. In the capacity and durability study of Ti–Ni hydride electrodes, the Zr-substituted Ti1-xZrxNi alloys show sufficiently large charging capacity and good durability [15]. The reversible discharge capacity of Ti0.8Zr0.2Ni phase is 240 mAh/g [15] and much better than that of Zr–Ni binaries. For multiphase alloy, the hydrogenation property of alloy is the combination of these properties of all constitutional phases [2]. The hydrogen desorbing capacity should be reasonably enhanced due to the presence of the bcc phase precipitates in the Zr0.5Ti0.5(MnVNi)2 alloy. Furthermore, the premartensite R phase could play a favorable role on the hydriding kinetics [16]. The premartensite R phase are believed to act as nucleation centers for the hydride formation [16]. Therefore, the existence of premartensite R phase will accelerate the Zr0.5Ti0.5(MnVNi)2 alloy activation process.

5. Conclusion

1. For the Ti substitution for 50% Zr in Zr(MnVNi)2, the lattice parameters, substructure of Laves phase as well as non-Laves phase components are all found varied. In Zr0.5Ti0.5(MnVNi)2 alloy the non-Laves phases Ti0.8Zr0.2Ni contains no Mn and V and is of bcc structure. The TEM and HREM analysis results reveal that the bcc phase is a typical premartensite R-phase of Ti–Ni intermetallic compound and contains at least 3 R phase variants.

2. After Ti substitution for 50% Zr, the hydrogen absorbing capacity and electrochemical activation of the alloy Zr(MnVNi)2 are both improved. The electrochemical property improvements can be attributed to the formation of Ti0.8Zr0.2Ni phase, disappearance of Zr–Ni binaries as well as the substitution of Ti for Zr on Zr sites in C14 Laves phase.

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