Effect of microstructure on the properties of Zr–Mn–V–Ni AB₂ type hydride electrode alloys

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Abstract

The effect of the microstructure for multicomponent ZrMn₀.₉ₓVₓNi₀.₀₉ (x = 0.1–0.8) hydride electrode alloys on their hydrogen absorbing capacity, activation and high rate discharge capacity was investigated. The electrochemical properties and microstructure changed with the alloys compositions. The microstructure were determined by the combination of transmission electron microscopy (TEM) and X-ray Rietveld analysis. Hexagonal C14 type, cubic C15 type Laves phase and tetragonal body centered Zr₆Ni₁₁ coexisted in the alloys of given compositions. The metastable Zr₆Ni₁₁ phase was stabilized at room temperature as long range ordered state along (009) and (900) directions. Substructure of each phase and the orientation relations among the existing phases were investigated in detail. Stacking faults in the C15 Laves phase and precipitation of Zr–Ni binaries considerably enhanced the activation and high rate discharge capacity of Laves phase.

1. Introduction

The AB₂ (A = Zr, Ti; B = V, Cr, Mn) intermetallic compounds have been investigated extensively because of their ability to serve as high capacity negative electrodes in nickel-metal hydride batteries. Much of the work has concentrated on alloying binary Laves phase ZrMn₂, ZrCr₂ and ZrV₂ by replacing small amount of Zr, or Mn, V, and Cr in the structure to improve the hydrogen absorbed/desorbed kinetics and to increase the electrochemical capacity [1–3]. On the other hand, C14, C15 Laves phases and non-Laves phase component such as Zr–Ni binaries often coexist in the multicomponent alloys [1–5]. For example, the well-known Ovonic alloys [1] are multiphasic Zr based alloys. It was found that the electrochemical properties of multicomponent alloy are improved when the alloy is changed from single to multiphase. Similar results are also observed for multiphase Ti–Zr–Ni alloys containing different portion of Zr–Ni binary phase [5]. The hydrogen absorption/desorption behavior of Zr based multicomponent alloys varies with the element substitution in C15 and C14 Laves phase as well as the crystallography of non-Laves phase [6]. So far, no systematic studies have been reported to clarify the roles taken by C14 and C15 Laves phases and the effects of the non-Laves phase component on the electrochemical properties of Zr based multicomponent alloys. The present work deals with the effects of multiphase, substructure and interaction among the existing phases on the electrochemical behavior of Zr–Mn–V–Ni alloys. Particular attention has been paid to the hydrogen absorption/desorption capacity, electrode activation and high-rate dischargeability in alkaline electrolyte.

2. Experimental procedure

The alloys were synthesized by arc melting of the pure elements (Zr, 99.9%; Ni, 99.9%; Mn, 99.75%; V, 99.5%) in a water cooled copper crucible under argon atmosphere. Every sample was remelted four times. Each time, the ingot were inverted to ensure homogeneity. Working electrodes were prepared by cold pressing the mixtures of Cu and the alloy powders of 360 mesh with the weight

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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 with a large excess capacity and a Hg/HgO reference electrode were employed.

X-ray powder diffraction patterns were obtained using a Rigaku/Max-B type diffractometer. The Rietveld refinement method was used for the quantitative analysis of phase abundance and the determination of lattice parameters.

Specimen foils for TEM observation were cut from the cast ingots. The foils which are approximately 500 μm thick were first mechanically polished and then dimpled down to the thickness of 20 μm. Finally the samples were ion thinned 3.8 kV until perforation. TEM observations and EDS analysis were carried out on a Philips CM12 electron microscope operated at 120 kV with the point to point resolution of 3.4 Å.

3. Experimental results

3.1. Phase abundance

C14, C15 Laves phases and a small amount of the binary Zr–Ni phases were identified in the ZrMn₀·₈₉V₀·₁₁Ni₀·₀₀ alloys by X-ray diffraction analysis.

The proportions (wt%) of the Laves phases and Zr–Ni binaries as functions of content of V in the Zr–Mn–V–Ni system are shown in Fig. 1.

C14, C15 Laves phase coexist with Zr₉Ni₁₁ in the alloys ZrMn₀·₈₉V₀·₁₁Ni₀·₀₀, and the abundance (wt%) of Zr₉Ni₁₁ is about 14% in the range from x = 0.1 to x = 0.6. In Fig. 1, it is obvious that the abundance of C15 decreases, but that of C14 increases while the substitution of Mn by V increased from x = 0.1 to x = 0.6. Further substitution is accompanied by a decrease of zirconium in the Laves phases because of the formation of the ZrNi phase as x > 0.6. It is clear that the additional precipitation of ZrNi will cause changes of Laves phase abundance.

3.2. Substructure observation of Laves phase

The substructure of each Laves phase was investigated in detail by TEM. Figure 2 shows the composite electron diffraction patterns taken from the interface of C14 and C15 Laves phases in the Zr–Mn–V–Ni alloys. The orientation relationship between C14 and C15 Laves phase was deduced as (0001)₁₁₁∥[111]₁₁₁ and (1-210)₁₁₁∥(1-10)₁₁₁. For the as cast Zr–Mn–V–Ni alloys, high density of stacking faults were observed in the C15 Laves phase, as shown in Fig. 3. In contrast, few defects can be observed in the C14 Laves phase. These results reveal that in Zr–Mn–V–Ni alloys the stacking fault energies of C14 and C15 Laves phases are different. Crystallography shows that the stacking faults in the area of the C15 phase can be regarded as an embryo for C14 phase with two atomic layers thick. The stacking faults bounded with two Shockley partial dislocations occur every two atom layer in the ⟨111⟩ direction. Thus in C15 phase stacking faults are the main defects which would affect the hydrogen absorbed/desorbed behavior during electrochemical process for hydride electrode alloys.

3.3. Crystalline characteristics of Zr–Ni binary compounds

From X-ray Rietveld analysis, Zr₉Ni₁₁ phase was identified in the given composition alloys with lattice constants a = 0.99 nm and c = 0.662 nm respectively. SAED pat-
terns recorded along various zone axis indicate that some weak reflections always appear in the middle of the main reflections. In order to characterize the structure of island-like Zr–Ni phase, systematically tilting the specimen relative to low index axes was carried out. All strong reflections in the obtained diffraction patterns (as shown in Fig. 4) can be indexed as a body centered tetragonal structure with lattice parameters are $a = 0.99$ nm and $c = 0.67$ nm. The lattice parameters is consistent well with the X-ray results. In fact, the weak reflections are absent spots which satisfies the condition $h + k + 0 = \text{odd}$.

The SAED patterns reveal that long range ordered structure occurred in the Zr$_8$Ni$_{11}$ phase along the $[010]$ and $[100]$ direction.

For Zr–Ni binary system, according to the phase diagram [5] the homogeneity region ranges from 978 to 1170°C. However, it is very difficult to synthesis Zr$_8$Ni$_{11}$ alloy with stoichiometry composition. The alloy prepared with the composition Zr$_8$Ni$_{11}$ shows that needle like ZrNi phase always appears in as-synthesized alloys [5]. The difficulties encountered in the synthesis of Zr$_8$Ni$_{11}$ can be explained by the peritectic formation of the Zr$_8$Ni$_{11}$ phase which comes from the melt and ZrNi phase. In the multicomponent ZrMn$_{0.8−x}$V$_x$Ni$_{0.2}$ ($x = 0.1–0.6$) alloys, the meta-stable Zr$_8$Ni$_{11}$ coexists with Laves phase without any other Zr–Ni binary compounds. According to our observations, the Zr$_8$Ni$_{11}$ phase was stabilized in the as-cast ingot in a long range ordered state. In the Laves phase matrix, Zr$_8$Ni$_{11}$ phase is almost surrounded by the C15 Laves phase as shown in Fig. 4. The $(111)_{ZrNi}$ is closely parallel to $(110)_{C15}$ and their orientation difference is only 2–3°.

3.4. Electrochemical properties of Zr–Mn–V–Ni system alloys

The hydrogen discharge capacity, the activation cycles, and the high rate dischargability (C200 mAh g$^{-1}$)/(C200

mAh/g + C50 mAh g⁻¹) with different phase abundance are shown in Fig. 6 as the composition of ZrMn₉₋ₓVₓNi₀₋ₓ varies from x = 0.2 to x = 0.6. The discharge capacity exceeds 340 mAh g⁻¹ after 12 cycles' activation when the abundance (wt%) of C15 Laves phase reached 70%. The discharge capacity and the high-rate dischargeability of alloys enhance with the increase of C15 Laves phase. On the other hand, cycles for activation decrease with the increase of C15 Laves phase and the alloys show better activation property.

4. Discussion

The capacity increases with the increment of C15 Laves phase as shown in Fig. 6. Thus, the capacity will decrease with the decrease of C14 phase. The above results reveal that the intrinsic electrocatalytic property or discharge efficiency of C15 phase is higher than that of C14 phase in the investigated Zr–Mn–V–Ni alloys. As to the intrinsic electrocatalytic property of C14 and C15 phases, investigations shown that the discharge capacity does not change significantly when the discharged current increased for single C14 Laves phase, and single C14 Laves phase shows a better electrocatalytic property than C15 phase in Zr based AB₂ type alloys such as Zr–Ni–Cr [4], Zr₁₋ₓTiₓM₂ [5], Zr–Ti–Mn–V–Ni [6]. It is reasonable to believe that the discharge efficiency of C15 phase is higher than that of C14 phase in ZrMn₉₋ₓVₓNi₀₋ₓ alloys.

The discharge efficiency is believed to be related to the diffusion ability of hydrogen, nucleation and growth of alloy in hydride bulk. The formation of the hydride requires cooperative motion between H atoms by diffusion and the metal atoms by shear. In most systems the precipitation of hydride is accompanied by a large volume change and the deformation of matrix. For example, while exposing LaNi₅ to hydrogen, with the volume expansion of 24%, polycrystalline aggregates are decrystallization into particles of the size 4–20 μm [7]. Both the surface state and bulk defects of alloy particles change a lot after hydride formation [9]. Hydride nucleation does not necessarily require the presence of dislocations. However, the hydride precipitates do nucleate preferentially on the dislocations when present [8]. For AB₃ alloy, the structural defects formed during hydrogen activation process accelerate the hydrogen diffusion rate in the alloy and reduce the hydrogen absorbing pressure hysteresis [9]. For Zr-based AB₂ type alloys, structure defects exist in

Fig. 6. Relation between the electrochemical properties and Laves phase abundance.
the as cast alloy before hydride formation. These defects could also be considered as an important reason for the observed electrochemical differences between C14 and C15 Laves phases. Thus, the high density of defects in C15 Laves phase lead to the high diffusion speed of hydrogen in this phase and finally enhance the dischargeability of the alloy. This is also proved by the strengthened tendency of activation of the alloy while increasing C15 abundance as we mentioned above in section 3.4. The activation of an electrode alloy depends on the nucleation and growth of the alloy in hydride bulk and the diffusion of H atoms through oxide film on the particle surface. Easy nucleation and growth of hydride in high density defects alloy matrix will accelerate the activation process as well as the high rate discharge capacity. The preferential precipitation of hydride at stacking faults also increases the discharge capacity.

The effect of non-Laves phase on the hydrogen absorption-desorption has attracted much attention in recent years [5, 10]. As discussed in section 3.3, the orientation difference of Zr$_8$Ni$_{11}$ with respect to the neighbouring C15 Laves phase is about 2–3°. Free surface, grain boundaries and incoherent intermetallic particles may act as hydride precipitation sites. The misfit interface between C15 and Zr$_8$Ni$_{11}$ phases will enhance hydrogen diffusion in the alloy just as that between C14 and C15. The electrochemical discharge capacity of Zr$_8$Ni$_{11}$ is reported to be 95 mAh g$^{-1}$[5], which is extremely poor in comparison with the value of C15 Laves phase [1]. Strains caused by the difference of volume expansion between Zr$_8$Ni$_{11}$ and C15 Laves phase will be formed in the Zr–Mn–V–Ni alloys during the electrochemical process. Microstrain and microcracks will also occur at the boundaries between Laves phase and Zr–Ni binary [10]. The tendency of hydride precipitation and hydrogen diffusion were then further enhanced due to the formation of microstrain and microcracks [8]. When the content of vanadium substitution of Mn by V reaches the value $x = 0.7$, the additional precipitation of ZrNi phase will occur. This additional precipitation results in further changes of lattice parameters and the electrochemical properties of the Laves phases.

5. Conclusions

1. C14, C15 Laves phases and Zr$_8$Ni$_{11}$ coexist in the ZrMn$_{0.9-x}$V$_x$Ni$_{11}$ ($x = 0.1$–0.8) hydrogen absorbed alloys in the composition range from $x = 0.1$ to $x = 0.6$. Following orientation relationship is obtained between C14 and C15 Laves phases, namely (0001)$_{C14}$/|[111]$_{C15}$ and $\langle1-210\rangle_{C14}$/|$\langle110\rangle_{C15}$. In the Zr–Ni binary system, the homogeneity region ranges from 978 to 1170°C. Metastable Zr$_8$Ni$_{11}$ are stabilized at room temperature by a long range ordered structure along the [100] and [010] directions of body centered tetragonal crystallography structure.

2. The proportion of the C15 and C14 Laves phases varies with the amount of substitution of Mn by V. The capacity, hydrogen activation and the high rate discharge capacity increase with the increment of C15 phase. The high diffusion rate of hydrogen atoms in the alloy bulk with high density of defects and preferential precipitation of hydride at stacking faults lead to the electrochemical differences between C14 and C15 Laves phase.

3. Zr–Ni binaries can enhance the hydrogen desorption rate and capacity of the alloy ZrMn$_{0.9-x}$V$_x$Ni$_{11}$ ($x = 0.1$–0.8) in the composition range from $x = 0$ to $x = 0.6$.

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References