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## Synergistic effect between Laves phase and Zr-Ni phases in $\text{Zr}(\text{MnVNi})_2$ hydrogen storage alloys<sup>①</sup>

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**Abstract:** The effect of annealing treatment on the crystal structure and electrochemical properties of  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  and  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  hydrogen storage alloys was investigated by means of XRD analysis and electrochemical tests. The results of XRD analysis showed that the as-cast alloys consist of C15, C14 type Laves phase and  $\text{Zr}_9\text{Ni}_{11}$  and ZrNi phases. The composition of alloys homogenized after annealing treatment. The C15 type Laves phase is still stable while the  $\text{Zr}_9\text{Ni}_{11}$  and ZrNi phases decompose and C14 phase disappears partially. The final stable structure of the alloys was a mixture phase of C15 and C14 type Laves phases. The results of the electrochemical tests showed that the discharge capacity and the properties of activation as well as high-rate dischargeability are all decreased after annealing treatment. The exchange current density decreases in some degree too.

**Key words:** annealing treatment; hydrogen storage alloys; crystal structure; electrochemical properties; synergistic effect

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### 1 INTRODUCTION

The  $\text{AB}_2$ -type Zr-based Laves phase hydrogen storage alloys have been studied extensively due to their high capacity, long cycle lifetime and the potential to become a promising candidate for  $\text{AB}_5$ -type alloys in Ni-MH batteries<sup>[1,2]</sup>.

Unlike the common  $\text{AB}_5$ -type hydrogen storage alloys,  $\text{AB}_2$  type Zr-based hydrogen storage alloys commonly consists of multiphase structure. Besides the major Laves phases such as C15 and C14 structure occur in alloys, some other minor residual Zr-Ni phases in the forms of  $\text{Zr}_9\text{Ni}_{11}$ ,  $\text{Zr}_7\text{Ni}_{10}$  etc can also appear in alloys<sup>[3~5]</sup>. Ovshinsky *et al*<sup>[6]</sup> proposed that the electrochemical activity of the major phase exists in Zr-based alloys should be improved in the presence of the minor phases. As a consequence

of the multiphase structure, the improvement of electrochemical properties of Zr-based hydrogen storage alloys was also obtained too.

The different alloy phase structures can offer different effects on the electrochemical properties of the alloys. Huot *et al*<sup>[7,8]</sup> found that the C14 type phase with higher electrochemical activity is suitable for high rate discharge, while the C15 type phase shows poor rate dischargeability though it can absorb a large quantity of hydrogen. Ovshinsky *et al*<sup>[5]</sup> drew the similar conclusion, he also proposed that the phase structure of alloys can be adjusted by alloy designing.

The phase composition of Zr-based hydrogen storage alloys could be homogenized by annealing treatment. However, the effects of annealing treatment on the electrochemical proper-

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ties were not clarified yet. Moriwaki *et al*<sup>[9]</sup> found that the phase composition of  $\text{ZrMn}_{0.6}\text{Cr}_{0.2}\text{Ni}_{1.2}$  alloy was homogenized after annealing treatment, as a result, the hydrogen absorbing properties and electrochemical properties were improved. Sawa *et al*<sup>[10]</sup> also found that the Zr-based hydrogen storage alloys with a single Laves phase exhibits better electrochemical properties. However, the study of Yu *et al*<sup>[11]</sup> showed that the as-cast  $\text{ZrMn}_{0.6}\text{Cr}_{0.25}\text{V}_{0.05}\text{Ni}_{1.3}$  alloy consists of the major phases (i.e. Laves phases involving C14 and C15 structure) and the minor phases (Zr-Ni phases, such as  $\text{Zr}_7\text{Ni}_{10}$  and  $\text{Zr}_9\text{Ni}_{11}$ ). The C14 and  $\text{Zr}_9\text{Ni}_{10}$  phases decompose during annealing treatment, and the phase composition is homogenized gradually. However, the discharge capacity of the annealed alloy in the absence of  $\text{Zr}_7\text{Ni}_{10}$  phase decreases significantly as compared with the as-cast alloys. McCormack *et al*<sup>[12]</sup> also found the similar results for Zr-Cr-Ni hydrogen storage alloys. The as-cast Zr-Cr-Ni alloys consists of Laves phases and Zr-Ni phases. After annealing treatment, the Zr-Ni phase in alloys disappears and the phase structure of Zr-Cr-Ni alloys is homogenized. However, the annealing treatment reduces the electrochemical properties of Zr-Cr-Ni alloys. The discharge capacity of the as-cast alloy is 260 mAh/g and almost reaches to zero after annealing treatment. It indicates that the Zr-Ni phases have the relation with the electrochemical properties.

In this work, the  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  and  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloys were annealed at 1080 °C for various times, the effects of annealing treatment on the phase structure and the electrochemical properties were investigated.

## 2 EXPERIMENTAL DETAILS

The alloys  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  and  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  were prepared by mixing appropriate amounts of constituent elements whose purity were all above 99.9% and by arc melting under argon atmosphere. The ingots were turned over and remelted three times to ensure homogeneity. The prepared as-cast samples

were divided into two parts. One part was crushed to pass through 300-mesh sieve for XRD analysis and electrochemical tests.

The other was put into a quartz glass tube, then evacuated to 0.1 Pa. After this procedure, the samples were annealed in a furnace at 1080 °C for 4 and 8 h, respectively. After annealing treatment, the annealed alloy samples were crushed mechanically in air to pass through 300-mesh sieve for XRD analysis and electrochemical measurements. X-ray diffraction studies were performed by a Rigaku D/Max IIIB diffractometer with  $\text{Cu K}\alpha$  radiation.

The preparation of metal hydride electrodes and their electrochemical performance measurements were carried out according to Ref.13.

## 3 RESULTS AND DISCUSSION

### 3.1 Phase analysis

Fig.1 shows the XRD patterns of the as-cast and annealed  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  and  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloys. As shown in Fig. 1, the major phases that occurred in the as-cast alloys were of C15 and C14 Laves phases with some minor Zr-Ni phases such as  $\text{Zr}_9\text{Ni}_{11}$  and ZrNi coexisting. After 4 h annealing treatment, most of  $\text{Zr}_9\text{Ni}_{11}$  and all the ZrNi phase disappeared. The intensity of diffraction peak of C14 phase had a little decrease and that of C15 phase strengthened, indicating that the abundance of C15 phase increases and that of C14 phase decreases. With time of annealing treatment increasing to 8 h, only C15 and C14 phase existed in alloys without the coexistence of Zr-Ni phases. The Zr-Ni phases have decomposed completely after 8 h annealing treatment. It indicates that the C15 phase is a thermodynamically stable phase and the C14 phase comes second in above alloys. In the contrary, the Zr-Ni phases are the thermodynamically unstable intermetallic phases. According to the XRD patterns, the main diffraction peaks for C15 or C14 phase became sharper after annealing treatment, indicating that the homogeneity and crystalline of the alloys are improved after annealing treatment.

Table 1 presents the changes of lattice parameters of C15 and C14 phase before and after

**Fig. 1** XRD patterns of as-cast and annealed  $\text{Zr}(\text{MnVNi})_2$  alloys

- (a) —  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$ ;  
(b) —  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$

annealing treatment in  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  and  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloys. Compared with that of the as-cast alloys, with increase of annealing time, the lattice parameters as well as the volume of the unit cell of C15 had a tendency to increase. However, the lattice parameters in  $a$ -axis and  $c$ -axis direction decreased with the increase of the annealing time for C14 phase. As

a result, the volume of unit cell of C14 phase reduced, too. The changes in lattice parameters indicate that a homogeneity phenomenon has taken place during the annealing treatment.

### 3.2 Electrochemical properties

Fig. 2 shows the electrochemical activation properties of the as-cast and annealed alloys. As shown in Fig. 2, in the case of  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  alloy, the charging-discharging cycle numbers for activating increased with increase of annealing times, indicating that the activation property of the annealed alloys decreases. The electrochemical discharge capacity also decreased markedly with the annealing time increasing. For example, the highest discharge capacity is 342 mAh/g for the as-cast  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  alloy; however, the discharge capacity reduced to 226 mAh/g and 163 mAh/g after 4 and 8 h annealing treatment, respectively. The loss of the discharge capacity increased with increase of annealing times. The similar tendency was observed for  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloy.

Fig. 3 depicts the linear polarization curves of Zr-Mn-V-Ni alloy electrodes in the full-charged state. As shown in Fig. 3, the slopes of the polarization curves increase gradually with increase of annealing time, meaning that the value of exchange current decreases with annealing time increasing. Table 2 presents the electrochemical capacity, high-rate dischargeability as well as exchange current of the above alloys. As shown in Table 2, for  $\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$  alloy, with increase of the annealing treatment times, the high-rate dischargeability decreased from 75.1 % to 68.5 % and 63.2 %, and from 52.7 % to 50.2 % and 45.7 % for  $\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloy.

**Table 1** Changes in lattice parameters of C15 and C14 Laves phases before and after annealing treatment(Å)

Alloy composition	Treatment procedure	Phase component	Lattice parameters
$\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$	As-cast	(1) C15 ; (2) C14	(1) $a = 7.0831$ ; (2) $a = 5.0200$ ; $c = 8.1989$
	4 h annealing	(1) C15 ; (2) C14	(1) $a = 7.0983$ ; (2) $a = 5.0187$ ; $c = 8.1973$
	8 h annealing	(1) C15 ; (2) C14	(1) $a = 7.0942$ ; (2) $a = 5.0148$ ; $c = 8.1902$
$\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$	As-cast	(1) C15 ; (2) C14	(1) $a = 7.0106$ ; (2) $a = 5.0482$ ; $c = 8.2542$
	4 h annealing	(1) C15 ; (2) C14	(1) $a = 7.1282$ ; (2) $a = 5.0393$ ; $c = 8.2453$
	8 h annealing	(1) C15 ; (2) C14	(1) $a = 7.1294$ ; (2) $a = 5.0374$ ; $c = 8.2416$

**Fig.2** Activation curves of as-cast and annealed  $\text{Zr}(\text{MnVNi})_2$  alloys

- (a)  $\text{—Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$ ;  
(b)  $\text{—Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$

$\text{V}_{0.40}\text{Ni}_{0.55})_2$  alloy. Moreover, with increase of the annealing times, the discharge capacity as well as the exchange current also decreased gradually compared to that of the as-cast alloys. This indicates that the annealing treatment results in the deterioration of the electrochemical performances.

**Fig.3** Linear polarization curves of  $\text{Zr}(\text{MnVNi})_2$  alloy electrodes

- (a)  $\text{—Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$ , equilibrium potential:  
(1)  $\text{—} -0.9478\text{ V}$ , (2)  $\text{—} -0.9442\text{ V}$ ,  
(3)  $\text{—} -0.9421\text{ V}$ ;  
(b)  $\text{—Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$ , equilibrium potential:  
(1)  $\text{—} -0.9465\text{ V}$ , (2)  $\text{—} -0.9432\text{ V}$ ,  
(3)  $\text{—} -0.9405\text{ V}$ , Scan rate =  $5\text{ mV/s}$

### 3.3 Discussion

In the previous studies, some authors<sup>[13,14]</sup> have found that some Zr-Ni alloy phases can

**Table 2** High rate-dischargeability and exchange current  $J^0$  for as-cast and annealed alloys

Alloy composition	Treatment procedure	Discharge capacity $/(\text{mAh}\cdot\text{g}^{-1})$	High-rate dischargeability $[C_{200}/(C_{200} + C_{50})]/\%$	Exchange current $J^0/(\text{mA}\cdot\text{g}^{-1})$
$\text{Zr}(\text{Mn}_{0.25}\text{V}_{0.20}\text{Ni}_{0.55})_2$ alloy	As-cast	342	75.1	49.9
	$1\ 080\ ^\circ\text{C}$ , 4 h annealing	226	68.5	32.4
	$1\ 080\ ^\circ\text{C}$ , 8 h annealing	163	63.2	29.6
$\text{Zr}(\text{Mn}_{0.05}\text{V}_{0.40}\text{Ni}_{0.55})_2$ alloy	As-cast	245	52.7	38.2
	$1\ 080\ ^\circ\text{C}$ , 4 h annealing	177	50.2	25.1
	$1\ 080\ ^\circ\text{C}$ , 8 h annealing	150	45.7	22.4

absorb a large quantity of hydrogen. For example, the hydrogen absorbed by ZrNi, Zr<sub>9</sub>Ni<sub>11</sub> and Zr<sub>7</sub>Ni<sub>10</sub> phases corresponded to 460 mAh/g, 340 mAh/g and 370 mAh/g, respectively. Unfortunately, the hydrides of these alloys are too stable to desorb in normal temperature, the absorbing-desorbing hydrogen plateau pressure is very low and the reversibility of hydrogen is very bad. As a result, the electrochemical capacity of these alloys was very low. However, the activation property of these Zr-Ni phases was very easy. In addition, the rates of the electrochemical capacity degradation were also very slow. This indicates that the Zr-Ni alloy phase can offer a better surface catalytic activity and corrosion-resistance performances. Joubert *et al.*<sup>[15]</sup> found that there was a synergistic effect between the Laves phases and the Zr-Ni phases on the electrochemical properties of Zr-Cr-Ni alloys. By precipitation of Zr-Ni phases in Zr-Cr-Ni alloys, the electrochemical properties of Zr-Cr-Ni alloys can be improved considerably. Notten *et al.*<sup>[16]</sup> also found that the electrochemical properties of AB<sub>5</sub>-based hydrogen storage alloys can be improved significantly in the presence of the minor secondary alloy phase with higher electrocatalytic activity, i. e. a synergistic effect existed between the major phase and the minor residual phases.

In this study, it can be found that the overall electrochemical properties are dependent of the existence of the Zr-Ni phases in Zr(MnVNi)<sub>2</sub> alloys. For the as-cast alloys containing some Zr-Ni phases, they can exhibit a better overall electrochemical property. However, on annealing treatment, the Zr-Ni phases existed in the as-cast alloys decomposed gradually with the increase of annealing time, the correspondingly electrochemical performances deteriorated significantly. In the case of the alloys after 4 h annealing treatment, a little residual Zr<sub>9</sub>Ni<sub>11</sub> phase still existed. However, after 8 h annealing treatment, all the Zr-Ni phases decomposed com-

pletely in alloys. In regard to the electrochemical properties, the alloys after 4 h annealing treatment was better than that annealed for 8 h. The results indicate that a synergistic effect exists between the Zr-Ni phases and the Laves phases. Therefore, the decrease of the overall electrochemical properties of the annealed alloys should be attributed to the disappearance of Zr-Ni phases.

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