CRYSTAL STRUCTURE AND PHASE ABUNDANCE

OF Zr-Mn-Ni LAVES PHASE HYDROGEN

STORAGE ALLOYS[①]

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ABSTRACT The crystal structure and phase abundance of $Zr(Mn_{1-x}Ni_x)_2$ ($x = 0.40 \sim 0.75$) Laves phase hydrogen storage alloys were investigated by means of X-ray powder diffraction Rietveld method. It was found that Mn site of $ZrMn_2$ alloy was partially substituted by Ni. The main phase structure of Zr-Mn-Ni alloy was of C15 type Laves phase. Ni element was considered to be a C15-stabilized element in $ZrMn_2$ alloy. Over the studied composition range, the alloys were composed of Laves phases and some residual phases ZrM_x. Laves phases including C15 and C14 type occurred over the studied composition range. The residual phases ZrM, Zr_9M_{11} and Zr_7M_{10} only appeared in a particular composition range. The lattice parameters and phase abundance of Laves phases changed with Ni concentration in alloys. The calculation of ANOE indicates that the occurrence of Laves phase in $Zr(Mn_{1-x}Ni_x)_2$ alloys is influenced by electron factors.

Key words Rietveld method Laves phase Zr-Mn-Ni alloy crystal structure phase abundance

1 INTRODUCTION

The hydrogen absorbing/desorbing properties of $ZrMn_2$ binary alloy with C14 phase structure were found in 1960s by Pebler *et al*[1,2]. Since then, the effect of alloying element on the crystal structure and hydrogen absorbing/desorbing properties of $ZrMn_2$-based alloys including ternary alloys Zr-Mn-M (M = Ni, Co, Cr, Al, Fe) has been studied extensively[3-5]. However, the crystal structure of Zr-Mn-Ni is not clarified yet. By means of XRD, Suzuki *et al*[6] found, with Ni substituting Mn in Zr $(Mn_xNi_{1-x})_2$ ($x = 0.2, 0.5, 0.8$) alloy, the crystal structure also remained C14 type. With contrast to the result of Suzuki *et al*, Cherkashin *et al*[6] and Hsu *et al*[7] found that the crystal structure of $Zr(Mn_xNi_{1-x})_2$ alloy converted to C15 type Laves phase.

Furthermore, the phase abundance of AB_2 type Laves phase alloys and their effects on the electrochemical performances have attracted extensive attention recently and many works were reported[8,9]. However, it is for ternary Zr-Mn-Ni hydrogen storage alloys that the phase abundance and its effect on the electrochemical performances are not reported yet.

X-ray powder diffraction Rietveld method was first put forward by Rietveld in 1967[10]. In recent years, it has become a new method to analyze the refined structure, phase abundance and microstructure of multiphase alloys. In the case of AB_2 type Laves phase alloys, it is generally a mixture of multiphases and very difficult to identify the phase abundance by conventional methods. Rietveld method has been proven by experiments to be effective in this field[11]. Therefore, in this paper, X-ray powder diffraction Rietveld method was adopted to determine the crystal

structure and phase abundance of Zr-Mn-Ni system hydrogen storage alloys.

2   EXPERIMENTAL DETAILS

The alloys $Zr(Mn_{1-x}Ni_x)_2$ ($x = 0.40 \sim 0.75$) were prepared by arc-melting under argon atmosphere. The purity of raw materials was all above 99%. The ingots were turned over and remelted three times to ensure homogeneity. As-cast samples were pulverized mechanically to pass through 300 mesh sieve for XRD study. X-ray powder diffraction studies were performed by a Rigaku D/Max IIIB diffractometer, using CuK_α radiation in the 2θ range from $20°$ to $120°$ with a 2θ scan rate of $0.02°$/step (10s/step). In order to identify the crystal structure and phase abundance of each phase that existed in Zr-Mn-Ni alloys, X-ray powder diffraction patterns except Zr $(Mn_{0.3}Ni_{0.7})_2$ alloy were analyzed by Rietveld method by using WYRIET software.

3   RESULTS AND DISCUSSION

3.1   Crystal structure and phase abundance

Fig. 1 shows the X-ray diffraction patterns of $Zr(Mn_{1-x}Ni_x)_2$ alloys. As shown in Fig. 1, the intensity, location and number of diffraction peaks change with the Ni concentration in al-

loys. It is indicated that the phases and their abundance all change with the alloy composition. Depending on the XRD patterns, the alloys are composed of Laves phases and residual phases. In comparison with the phase diagram of Zr-Ni binary alloy, the residual phases are assumed to be Zr_9M_{11}, Zr_7M_{10} and ZrM (where M = Mn, Ni, i.e. Mn site was partially replaced by Ni element). The results of Rietveld analysis showed that Laves phases including C15 and C14 occurred over the studied composition range, while the residual phases including Zr_9M_{11}, Zr_7M_{10} and ZrM phases only appeared in a particular composition range, i.e. ZrM phase appeared in $x = 0.40 \sim 0.50$, Zr_9M_{11} in $x = 0.45 \sim 0.60$ and Zr_7M_{10} in $x = 0.60 \sim 0.75$. The occurrence of Zr_9M_{11} and Zr_7M_{10} in pseudo-binary Laves phase alloy have already been reported by Liu et al[10] and Sawa et al[11,12], and the ZrM phase was first found to appear in $ZrMn_2$ based Laves phase alloys. The crystal structures of the residual phases Zr_9M_{11}, Zr_7M_{10} and ZrM are similar to those of Zr_9Ni_{11}, Zr_7Ni_{10} and ZrNi phases respectively. It is indicated that the above assumption is right. In case of the alloy of $x < 0.50$, a trace of the oxide ZrO_2 and ZrO was also found. It may be produced by oxidation during the alloy preparation.
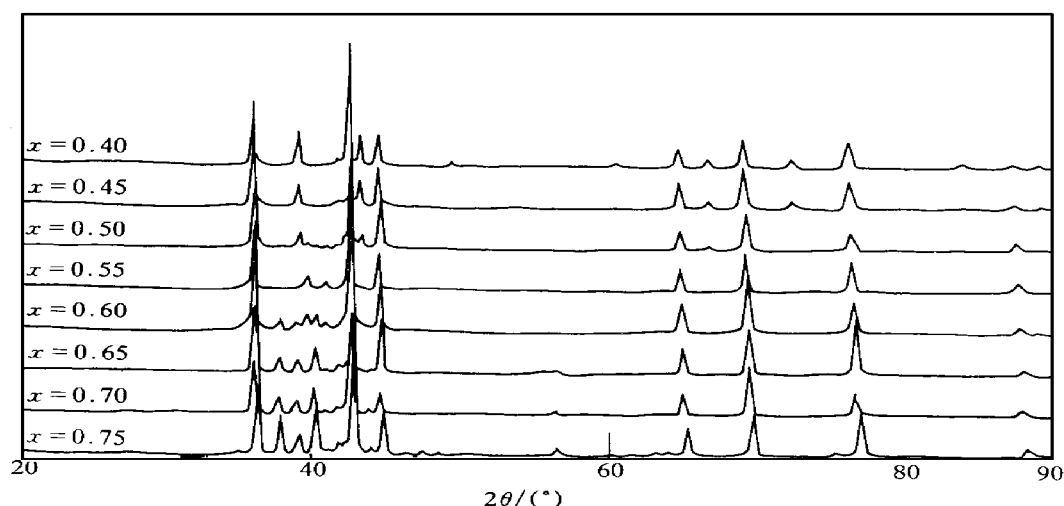
Fig. 2 shows the X-ray powder diffraction

Fig. 1   X-ray diffraction patterns of $Zr(Mn_{1-x}Ni_x)_2$ ($x = 0.40 \sim 0.75$) alloys

Rietveld refinement pattern of $Zr(Mn_{0.4}Ni_{0.6})_2$ alloy. The upper curve and dots are the calculated and experimental powder diffraction data respectively. The middle tick marks indicate the centers of Bragg reflections. The lower curve is the difference between the measured and calculated profiles. The refined structure parameters and Bragg factors of each phase occurring in $Zr(Mn_{0.40}Ni_{0.60})_2$ alloy are listed in Table 1. As shown in Table 1, in the case of C15 and C14 Laves phase, R_B was all less than 10%, however, that of Zr_9M_{11} was above 10%, which may be ascribed to the low amount of Zr_9M_{11} phase in the alloys. In the case of $Zr(Mn_{0.4}Ni_{0.6})_2$ alloy, the final refinement parameters were as follows: $R_{wp}= 7.88\%$, $R_p= 5.98\%$, S (the goodness of fit) = 1.83, indicating that the refinement result is reliable.

Since the radius of Mn is larger than that of Ni ($r_{Mn}= 1.35$ Å> $r_{Ni}= 1.25$ Å[13]), Ni element substituting for Mn element will lead to a change in lattice parameters of various phases in $Zr-M_{11}-Ni$ alloys. As shown in Fig. 3, the lattice

parameters of the main C15 Laves phase have a tendency to decrease gradually with increasing Ni concentration, which is consistent with the result found in Zr-Ti based Laves phase alloys[9]. In the case of the residual phases ZrM_x, the tendency is opposite. This indicates that the lattice parameters are in relation to the atomic size factor.

3.2　Phase abundance analysis

By using Rietveld method, crystal lattice parameters and phase abundance can be determined[10]. Depending on the scale factor S given by Rietveld analysis, the abundance by mass of each phase can be calculated as follows[11]:

$$W_p = \frac{S_p(ZMV)_p}{\Sigma S_j(ZMV)_j} \qquad (1)$$

where S is the scale factor, Z is the AB_2 molecule number in a unit cell, M is the molecular mass and V is the volume of a cell of p th phase, respectively. The results are shown in Fig. 4.

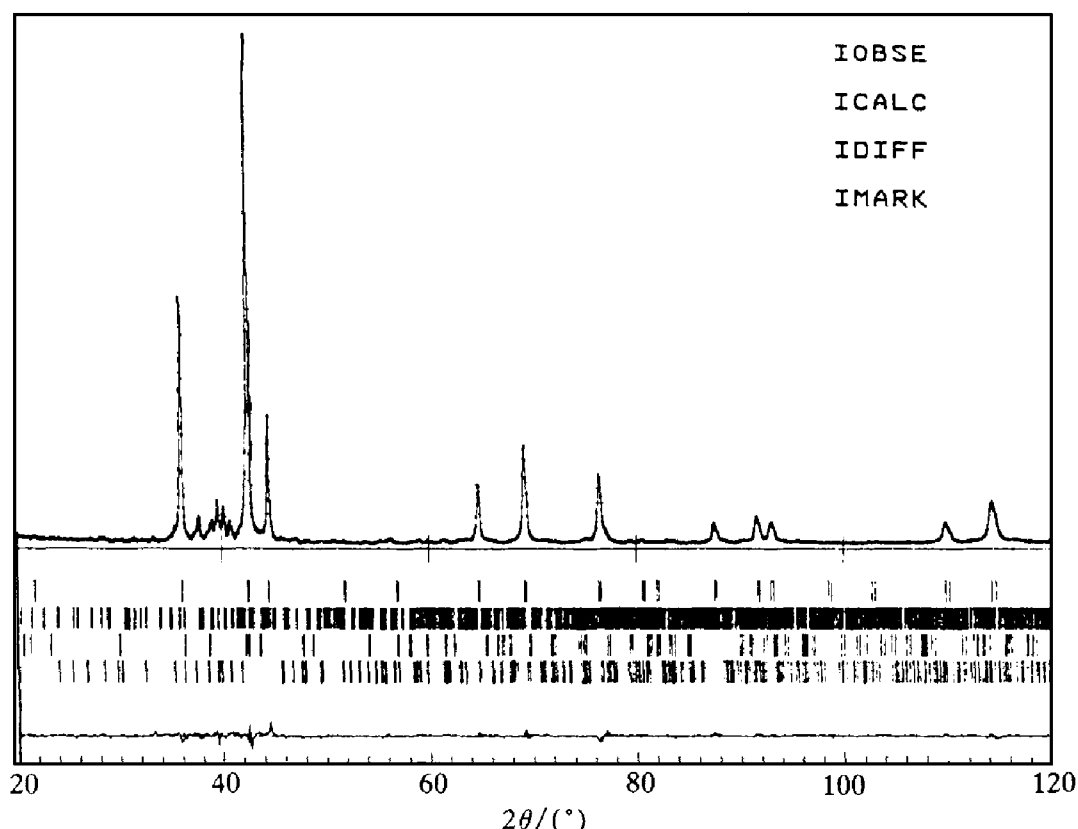As shown in Fig. 4, C15 type Laves phase

Fig. 2　X-ray powder diffraction pattern fitting by rietveld refinement of $Zr(Mn_{0.40}Ni_{0.60})_2$
(short vertical bars representing C15, Zr_7M_{10}, C14 and Zr_9M_{11} phase respectively)

Table 1   Structure parameters and Bragg factors
for Zr($Mn_{0.40}Ni_{0.60}$)$_2$

Phase	Space group	Lattice parameters/ Å	Atom	Wykoff symbol	R_B/ %
C15	Fd3m	a= 7.0386(1)	Zr M	8 a 16 d	2.60
C14	P6$_3$/ mmc	a= 4.9311(23), c= 8.1998(59)	Zr M$_1$, M$_2$	4 f 2 a, 6 h	8.99
Zr$_9$M$_{11}$	I4/ m	a= 9.8797(31) c= 6.6265(9)	Zr$_1$ Zr$_2$, Zr$_3$ M$_1$, M$_2$, M$_3$	2 a 8 h 2 b, 4 d, 16 i	10.77
Zr$_7$M$_{10}$	C$_{2v}^{17}$– Aba2	a= 12.3403(20) b= 9.2000(13) c= 9.2483(11)	Zr$_0$, Zr$_{1a}$, Zr$_{1b}$, Zr$_2$, Zr$_3$ M$_1$, M$_2$, M$_3$, M$_4$, M$_5$	4 a 8 b 8 b	9.38

*   The number in parentheses was deviation.
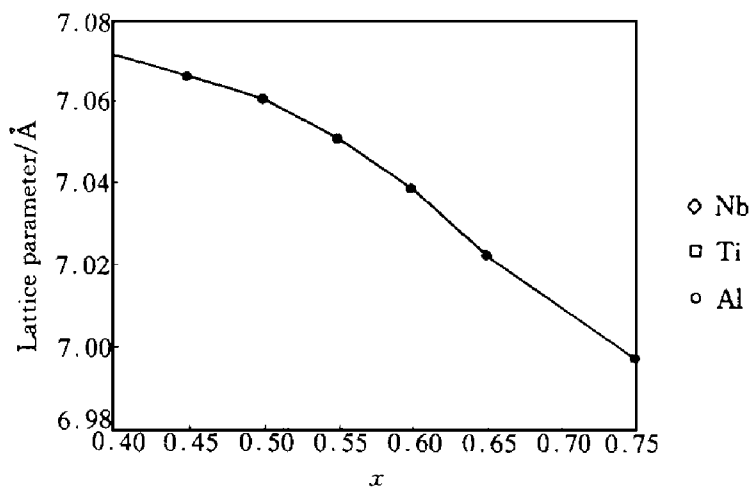
Fig. 3   Variation of lattice parameter of C15 Laves phase as a function of x

Fig. 4   Percentage of each phase in Zr($Mn_{1-x}Ni_x$)$_2$(x= 0.40~ 0.75) alloys

occurred as a main phase over the studied composition range. It is indicated that Ni element is a C15-stabilizing element in ZrMn$_2$ alloy. This result is in agreement with those of Yoshida et al[9] and Hsu et al[7], however, different with that of Suzuki et al[6]. In x= 0.40~ 0.55, the abundance of C15 phase increased gradually with increasing Ni concentration, and reached a maximum value (85.98 ±0.89%) at x= 0.55, then decreased gradually. In the case of C14 Laves phase, with contrast to C15 phase, the phase abundance decreased gradually with increasing Ni concentration when x< 0.55. After x ⩾
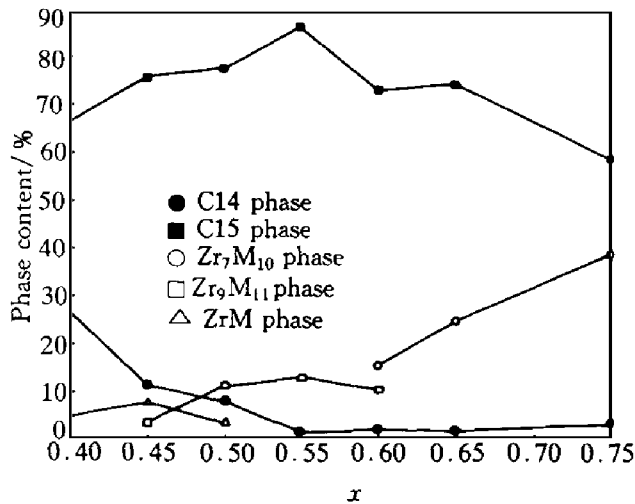
0.55, there existed a trace of C 1 4 alloys. The alloy with smallest concentration of Ni contained highest content of C14 type Laves phase (26.38 ±0.49%).

3.3   Effect of electron factor on occurrence of Laves phase

The main phase of Laves phase alloys is mainly controlled by the atomic size factor, i. e. the ratio of A side atom and B side atom. In 1950s, Elliot and Rostocker et al[14] proposed that there was a correlation between the averaged number of outer electrons (ANOE) and the

structure type for Ti- and Zr-based alloys. If the ANOE was less than 4. 67, no Laves phase was formed. If the ANOE was between 4. 67 and 5. 40, Zr-based AB_2 type alloys usually had a C15-type structure but no Laves phase for the Ti-based alloys. The C14 type structure appeared to occur in Zr- and Ti-based alloys if the ANOE was between 5. 4 and 7. 0. When the ANOE was larger than 7. 0, both of them formed the C15 type structure again.

Assuming that the ANOEs of Zr, Mn and Ni are 4. 0, 7. 0, 10. 0, the ANOE of $Zr(Mn_{1-x}Ni_x)_2$ alloys can be calculated by

$$(ANOE)_x = \frac{1 \times 4 + 2 \times (1-x) \times 7 + 2x \times 10}{3}$$

$$= 6 + 2x \qquad (2)$$

If $x < 0.5$, $(ANOE)_x$ is less than 7. 0. Depending on the Elliot's theory, the main phase may be of C14 type Laves phase. However, the experimental results showed that the main phase of all alloys was of C15 type. This means that the Elliot's theory has some deviation for multicomponent Zr-based Laves phase alloys. However, for the alloys of $x \geqslant 0.5$, the abundance of C14 phase increased. It is indicated that the abundance of C14 phase was also affected by the electron factor.

4　CONCLUSIONS

In this paper, the crystal structure and phase abundance of $Zr(Mn_{1-x}Ni_x)_2$ Laves phase hydrogen storage alloys were studied by using Rietveld method and concluded as follows:

(1) Ni element partially substitutes Mn sites and is a C15-stabilizing element in $ZrMn_2$ alloy. The main phase of $Zr(Mn_{1-x}Ni_x)_2$ ($x = 0.40 \sim 0.75$) alloys was of C15 type Laves phase, while C14 only appeared obviously when Ni concentration is less than 0. 50. The residual phases only appeared in a particular composition range, i. e. Zr_7M_{10} appeared in $x = 0.60 \sim 0.75$, Zr_9M_{11} in $x = 0.45 \sim 0.60$ and ZrM in $x = 0.40 \sim 0.50$. The phase abundance and lattice parameters of Laves phases had correlation with Ni concentration.

(2) The occurrence and phase abundance of Laves phase were not only affected by size factor, but also by electron factor.

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(Edited by Peng Chaoqun)