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HYDRIDING BEHAVIORS OF $Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$ ALLOYS

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$Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$ alloys, where x and y are 0 to 1 and z is 1 to 2, are found to have practically promising characteristics that their hydrogen equilibrium pressures can be adjusted to 0.1 to 1 MPa at about 400K by varying the three parameters.

In the future hydrogen economy, $LaNi_5$, Mg_2Ni and TiFe are well known candidates for energy storage media, but they all have some difficulties in practical uses. That is to say $LaNi_5$ is rather expensive and the dissociation pressure of Mg_2Ni hydride is not so high as can be used influentially and the activation processes of TiFe prior to its hydriding reaction is fairly difficult. $TiMn_{1.5}$, recently discovered by Yamashita and co-workers,1) is a promising alloy and a number of modified alloys are suggested to be useful in many applications.

For the automotive use are required those various alloy hydrides the dissociation pressures of which reach 0.1 to 1 MPa at temperatures of several levels of waste heats. However, those hydrides having plateau pressures of 0.1 to 1 MPa at about 400K are scarcely known. In our previous work, the dissociation isotherms for the $ZrMn_2$-H_2 system have been studied,2) and various modified systems such as $Zr(Ni_xMn_{1-x})_2$3) and $Zr(Fe_xMn_{1-x})_2$4) are proposed for practical uses particularly in such a middle temperature range.

In this report the hydriding behaviors and crystallographic characteristics of $Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$ alloys are investigated, wherein x and y are 0 to 1 and z is 1 to 2. These alloys can be regarded as developed systems of the above mentioned $TiMn_{1.5}$ or $ZrMn_2$.

Alloy materials were prepared by blending the pure Ti, Zr, Mn and Fe metals in the calculated amounts and arc-melting the mixture in an atmosphere of argon for six times. All these alloys were easy to be crushed. The alloys $Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$ are monophasic provided that the x, y and z parameters are within the following specified ranges;

$$x = 0.2 \text{ to } 0.8,\ y = 0.2 \text{ to } 0.8, \text{ and } Z = 1.5 \text{ and } 2.0.$$

Neither pure metallic phases nor binary to ternary alloy phases are present in these ranges. The structures of the present alloys belong to the hexagonal crystal group. Table 1 shows the crystal parameters, a_0, c_0 and axial ratio c, for each alloy having the z value of 1.5. As x (Zr content) increases both a_0 and c_0 axes expand and as y (Fe content) increases both a_0 and c_0 axes contract, as is expected according to the simple atomic radius concept. Such is also the case for the z=2.0 hexagonal alloys, except that both axes are slightly shorter.

Hydriding reactions were conducted in the conventional manners.[2)] The alloy samples were used in the form of lumps as crushed in a mortar made of tungsten carbide. Table 2 shows the comparative behaviors of the alloys on hydriding in the case where z equals to 1.5 or 2.0. The listed alloys were reacted with 4 to 10 MPa of hydrogen at room temperature for 10 days after the indicated activation processes.

The alloys having the z value of 1.5 readily react with hydrogen at room temperature under a pressure of 0.01 to 4 MPa, after being evacuated at room temperature, to form pseudo-binary hydrides. The induction periods before the initial absorption are substantially zero to several minutes. After some absorption-desorption cycles, the alloys are in finely divided forms in the order of microns. The resulting hydrides release hydrogen at a temperature slightly higher than room temperature and restore the initial alloy phases. No structural change of the dehydrided samples was observed and no binary hydride such as TiH_2

Table 1. Crystallographic data for the z=1.5 hexagonal alloys

Alloy	a_0/A	c_0/A	c
$Zr_{0.5}Ti_{0.5}(Fe_{0.8}Mn_{0.2})_{1.5}$	4.965+0.002	8.103+0.006	1.632
$Zr_{0.5}Ti_{0.5}(Fe_{0.2}Mn_{0.8})_{1.5}$	4.997+0.001	8.194+0.005	1.640
$Zr_{0.5}Ti_{0.5}(Fe_{0.5}Mn_{0.5})_{1.5}$	4.979+0.003	8.149+0.009	1.637
$Zr_{0.8}Ti_{0.2}(Fe_{0.5}Mn_{0.5})_{1.5}$	5.037+0.006	8.244+0.020	1.637
$Zr_{0.2}Ti_{0.8}(Fe_{0.5}Mn_{0.5})_{1.5}$	4.895+0.001	8.001+0.004	1.635

or ZrH_2 was detected in these samples as measured by the X-ray diffraction method. The reversibilities of the reactions of these alloys with hydrogen are essentially complete.

Some alloys having the z value of 2 hardly react with hydrogen as can be seen from Table 2. Those alloys having relatively large amounts of manganese and/or zirconium can store much hydrogen regardless of the z value. Where the manganese content and/or zirconium content are not so large, particularly in the case of $Zr_{0.5}Ti_{0.5}(Fe_{0.5}Mn_{0.5})_2$ and $Zr_{0.2}Ti_{0.8}(Fe_{0.5}Mn_{0.5})_2$, the hydriding reaction does not proceed to a significant extent, but by varying the z parameter from 2 to 1.5, the reaction can substantially proceed. Generally, where x is less than 0.2 and/or y is more than 0.8, the hydrogen contents are so small.

Fig. 1 shows the pressure-composition isotherms of the studied alloy systems at 423K. The equilibrium dissociation pressures of these systems are dependent on the compositions of the alloys. At y = 0.5, the pressure decreases as x increases. At x = 0.5, the pressure increases as y increases. Where the hydrogen concentration (defined as $n(H)/n(Zr_xTi_{1-x}(Fe_yMn_{1-y})_z)$, wherein n denotes mols of the parenthesized species) is less than about 2, the dissociation pressures of the pseudo-binary hydrides at 423K decrease on increasing the lattice parameters by

Table 2. Comparative hydriding behaviors of $Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$ alloys

x	0.5	0.5	0.5	0.8	0.2	0.5	0.5	0.5	0.8	0.2
y	0.8	0.2	0.5	0.5	0.5	0.8	0.2	0.5	0.5	0.5
z	2	2	2	2	2	1.5	1.5	1.5	1.5	1.5
Activating Condition	A	B	C	A	C	B	A	A	A	B
Hydrogen Concentration	0.81	2.88	0.13	2.88	0.04	1.23	2.54	2.26	2.74	1.11

A; Admitting and removing low pressure (less than 0.1MPa) hydrogen after evacuating at room temperature.

B; Admitting and removing moderate pressure (2 to 4 MPa) hydrogen after evacuating at room temperature.

C; Admitting and removing high pressure (more than 8MPa) hydrogen at an elevated temperature (about 600K) after evacuating at that temperature.

replacing the composite elements.

In conclusion, as the present alloy systems are characterized in that they include a number of alloys that can be hydrided and dehydrided at moderate temperatures without severe activation processes and that the equilibrium pressures thereof can be adjusted to any desired ones by varying the x, y and/or z parameters, or varying the lattice parameters, they can be used to various applications where a wide variety of equilibrium pressures are required.

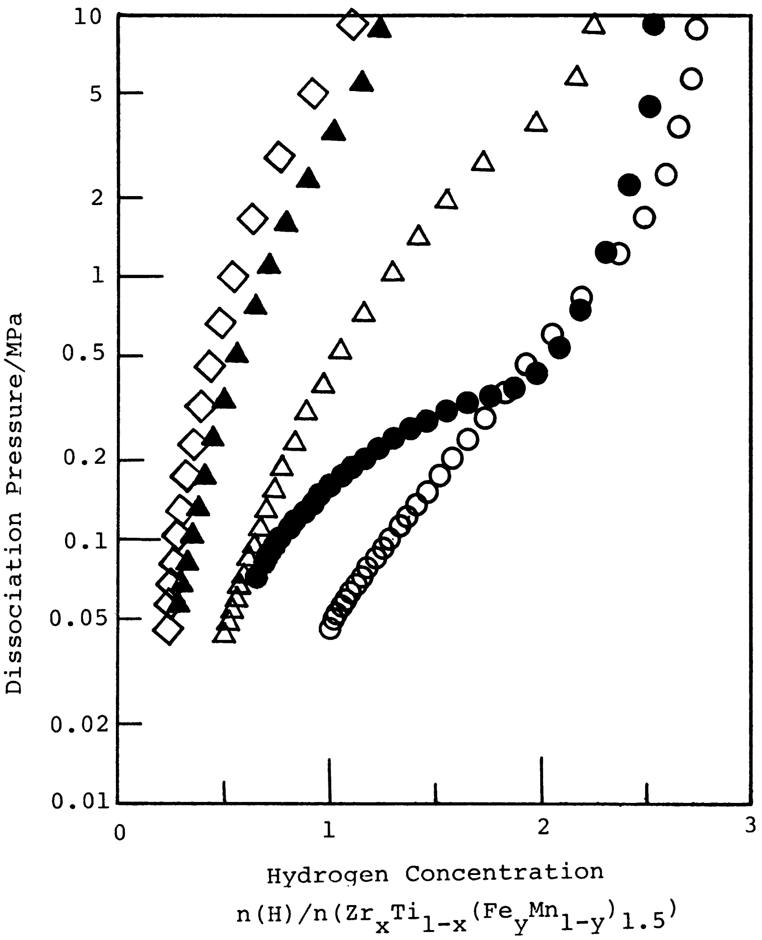

Fig. 1. Dissociation isotherms for the pseudo-binary hydrides at 423K

◇ ; $Zr_{0.2}Ti_{0.8}(Fe_{0.5}Mn_{0.5})_{1.5}$

▲ ; $Zr_{0.5}Ti_{0.5}(Fe_{0.8}Mn_{0.2})_{1.5}$

△ ; $Zr_{0.5}Ti_{0.5}(Fe_{0.5}Mn_{0.5})_{1.5}$

● ; $Zr_{0.5}Ti_{0.5}(Fe_{0.2}Mn_{0.8})_{1.5}$

○ ; $Zr_{0.8}Ti_{0.2}(Fe_{0.5}Mn_{0.5})_{1.5}$

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