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HYDRIDING BEHAVIORS OF $Zr(Fe_xMn_{1-x})_2$ ALLOYS

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The hydriding behaviors and crystallographic characteristics of $Zr(Fe_xMn_{1-x})_2$ alloys, wherein x is 0 to 1, vary depending on the x value. On substituting Mn of $ZrMn_2$ with Fe, the dissociation pressure of its hydride increases monotonously at temperatures around 400K.

In the future hydrogen economy, $LaNi_5$, Mg_2Ni and TiFe are well known candidates for energy storage media, however, they all have some difficulties for practical purposes. That is to say, $LaNi_5$ is rather expensive, the dissociation pressure of Mg_2Ni hydride is not so high as can be used influentially, and the activation process of TiFe prior to its hydriding reaction is fairly difficult.

About 0.1 to 1 MPa of hydrogen is usually required for many practical purposes. In the case where such hydrogen is provided using metal hydride beds, it is convenient to utilize any waste heats in order to heat and dissociate the hydrides employed in the beds. Thus those various alloy hydrides are required to have the dissociation pressures of 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 scarecely known. In our previous work, the dissociation isotherms for the $ZrMn_2$-H_2 system have been studied,$^{1)}$ and various modified systems such as $Zr(Ni_xMn_{1-x})_2$$^{2)}$ and $Zr_xTi_{1-x}(Fe_yMn_{1-y})_z$,$^{3)}$ wherein x and y are 0 to 1 and z is 1 to 2, are proposed for practical use particularly at such a middle temperature (around 400K).

In this paper, in order to clarify such modification effects on the dissociation pressure of $ZrMn_2$, Fe is chosen as the replacement element for Mn and the hydriding behaviors and crystallographic characteristics of $Zr(Fe_xMn_{1-x})_2$ alloys, wherein x is 0 to 1, are shown. In the Zr-Fe-Mn system, if the ratio of Mn plus Fe to Zr is 2, homogeneous Laves phase intermetallics are present at any ratio of Mn to Fe, as previously reported by Kanematsu.[4)]

$Zr(Fe_xMn_{1-x})_2$ alloy materials were prepared by mixing reagent grade zirconium, iron and manganese and arc-melting the mixture in an atmosphere of high purity argon. The procedure of measuring the hydrogen equilibrium pressures was as described in the literature.[1)] Heat treatments of alloys were performed by sealing the aluminum crucible having the alloy material in it into a quartz tube under argon, heating the tube to 1290 to 1295 K for 188 hours and rapidly cooling it.

$Zr(Fe_xMn_{1-x})_2$ alloys, wherein x is in the range of 0 to 0.8, readily occlude hydrogen at a pressure of lower than 0.1 MPa at room temperature provided that the air inside the reaction vessel is evacuated at room temperature. They easily desorb hydrogen at an elevated temperature. Any phase separations were not observed by the X-ray diffraction method after numerous hydrogen absorption-desorption cycles.

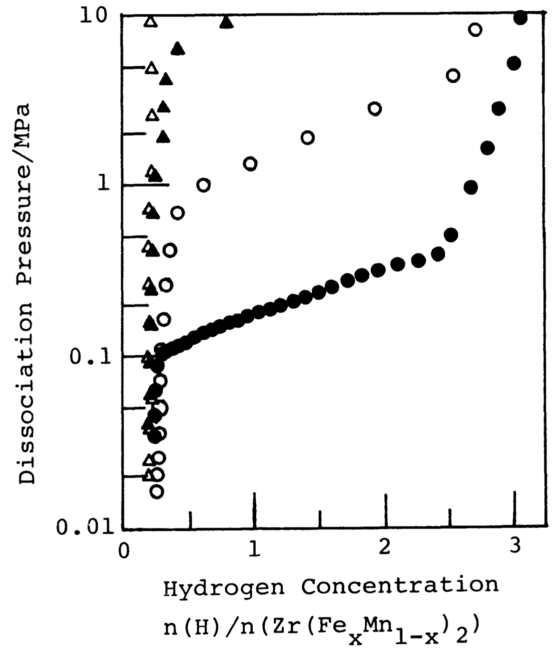

Fig. 1. Effect of Fe content on the 423K dissociation pressure of $Zr(Fe_xMn_{1-x})_2$

△ : x = 0.8 ▲ : x = 0.7

○ : x = 0.5 ● : x = 0.2

The dissociation pressure of this system monotonously increases depending on the Fe content as shown in Fig. 1. Each dissociation pressure of the alloys having high x values, is too high to occlude substantial amounts of hydrogen. When Fe content is not large, the dissociation pressure is in the range of 0.1 to 1 MPa at temperatures around 400K and the amount of absorbed hydrogen is generally about 150 ml per one gram alloy. Typical isotherms for $Zr(Fe_xMn_{1-x})_2$-H_2 systems are shown in Fig. 2 and Fig. 3.

$ZrMn_2$ occludes hydrogen to a hydrogen concentration (defined as $n(H)/n(Zr(Fe_xMn_{1-x})_2)$, wherein n denotes mols of the parenthesized species) of 3.46,[1)] in other words, $ZrMn_2H_{3.46}$ is formed, while $ZrFe_2$ are found to be scarecely active to hydrogen. In the Zr-Fe system there exist three intermetallic compounds other than $ZrFe_2$, namely, Zr_4Fe, Zr_2Fe and $ZrFe_3$.[5)] Of these Zr-Fe alloys the former two intermetallic compounds occlude hydrogen, but they are not applicable as the hydrogen storage media, because they form the ZrH_2 phase, which does not release hydrogen at moderate temperatures below 1000K. The $ZrFe_3$ phase is inactive to hydrogen. Generally, the dissociation pressures of stable binary metal hydrides increase by replacing a component metal with a second element which does not form any stable hydrides. The fact that the dissociation pressure of $Zr(Fe_xMn_{1-x})_2$ increases by a successive replacement of Mn with Fe is clearly understood by considering this modification as replacing $ZrMn_2$ with $ZrFe_2$. Thus $ZrFe_2$ could be considerd as the "second element" and $ZrMn_2$ as the "component metal" of the stable hydride.

The dissociation pressure of $ZrMn_2$ also increases by replacing a part of Mn with Ni.$^{2)}$ The modification effect of Fe on the dissociation pressure of $ZrMn_2$ is larger than that of Ni. Numerically, the relative partial molal enthalpy for the $ZrMn_2H_{1.5}$-H_2 system is -39 kJ/mol H_2 and those for the $Zr(Ni_{0.5}Mn_{0.5})_2H_{1.5}$-$H_2$ system and the $Zr(Fe_{0.5}Mn_{0.5})_2H_{1.5}$-$H_2$ system are -34 kJ/mol H_2 and -31 kJ/mol H_2, respectively.

Isotherms for the heat treated $Zr(Fe_{0.5}Mn_{0.5})_2$ alloy-H_2 system and for the untreated alloy-H_2 system at 423 K are shown in Fig. 4. The flatness of the

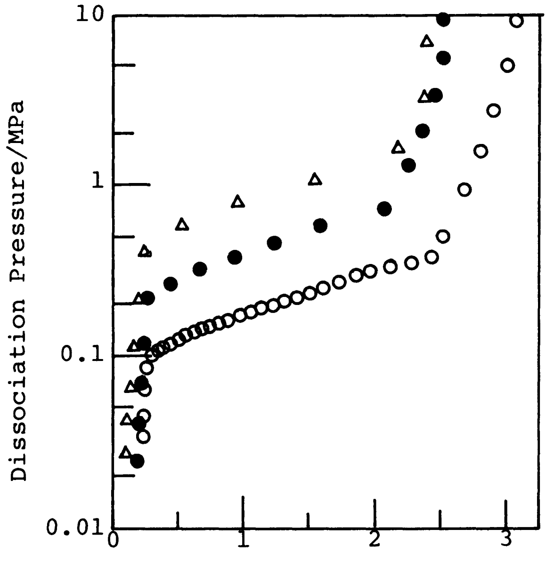

Fig. 2. Dissociation isotherms for $Zr(Fe_{0.2}Mn_{0.8})_2$-H_2 system

△: 483K, ●: 453K, ○: 423K

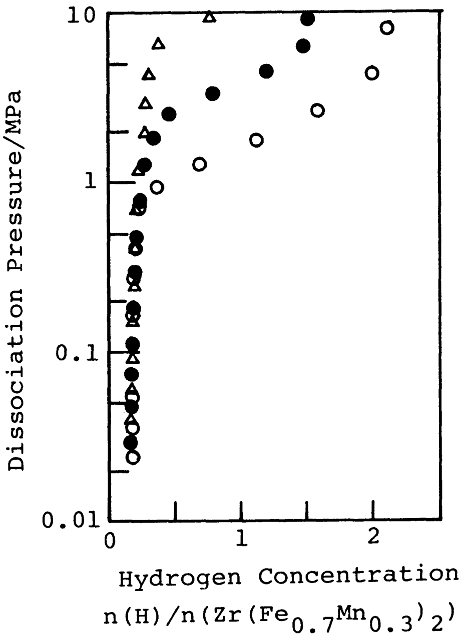

Fig. 3. Dissociation isotherms for $Zr(Fe_{0.7}Mn_{0.3})_2$-H_2 system

△: 423K, ●: 373K, ○: 333K

plateau region of the heat treated alloy hydride was a little better than that of untreated one. The region of the alpha-phase of the treated sample was narrower than that of untreated one. But these changes were not drastic.

The present alloys have a $MgZn_2$ type hexagonal structure where x is less than 0.7 and have a $MgCu_2$ type cubic structure where x is above 0.7. The lattice parameters of hexagonal $Zr(Fe_xMn_{1-x})_2$ decrease on increasing the x parameter, as already described by Kanematsu.[4] No transformation occurs on hydriding whene x is over 0.7, except for the lattice expansion. When x is 0.5 or 0.2, the second phase (hydrogen-rich phase) is also hexagonal.

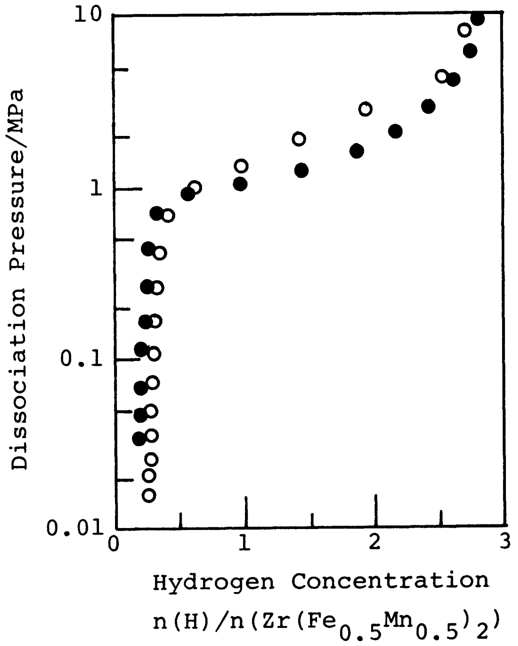

Fig. 4. Effect of heat treatment on the 423K dissociation pressure of $Zr(Fe_{0.5}Mn_{0.5})_2$

○ : as grown

● : after heat treatment

The relation between the hydrogen dissociation pressures and the lattice parameters of $Zr(Fe_xMn_{1-x})_2$ alloys is similar to that for Ti-Zr-Fe-Mn alloys,[3] that is to say, when the lattice parameters of the alloys decrease, the dissociation pressure of their hydride increases.

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