EQUILIBRIUM DEUTERIUM PRESSURES OVER $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) ALLOYS

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Introduction

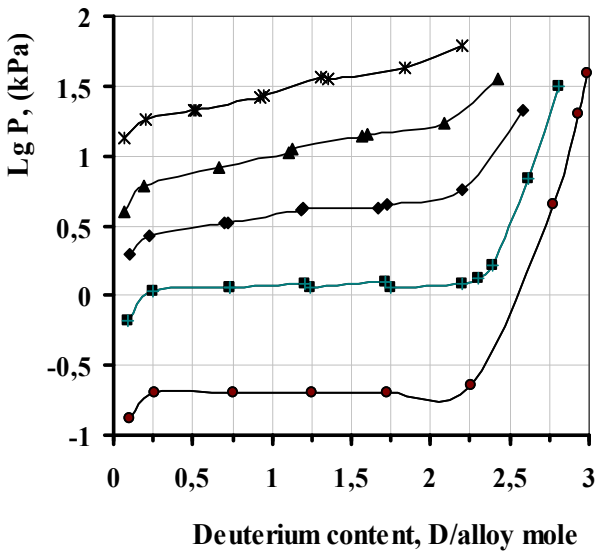
Transition metal intermetallic compounds, forming hydride phases rich in hydrogen, are often used for hydrogen isotope accumulation. The hydrides of intermetallic compound $ZrMn_2$ are of relatively high stability and can be used to accumulate hydrogen [1, 2]. It is known that alloyed additive small amounts in intermetallic compounds change the thermodynamical characteristics of the corresponding hydrides approximately linearly [3]. The substitution of other elements for manganese allows to increase dissociation pressure of $ZrMn_2$ hydrides by several orders of magnitude up to the values acceptable for practical using [3, 4]. The investigation of $ZrMn_2$ hydrides alloyed with cerium was carried out in paper [4]. Equilibrium pressure isotherms over $Zr_{1-x}Ce_xMn_2$ (x=0,2-0,3) alloy hydrides were obtained there in the temperature range from 100 to 160^{0}C.

The aim of this work is equilibrium desorption pressure measurements in the $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) – D_2, H_2 systems at the temperature range from 22 to 130^{0}C, and also the evaluation of equilibrium pressure isotopic effect over the corresponding alloy hydrides and deuterides.

Results and Discussion

As a result of the work, the equilibrium pressures have been measured in the $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) – D_2. systems. The isotherms of all investigated alloy deuterides are characterized by equilibrium pressure plateau. The desorption isotherms of $Zr_{0,9}Ce_{0,1}Mn_2$ alloy deuteride are given in Fig. 1 in the temperature range from 22^{0}C to 130^{0}C. The desorption isotherms analogous in form have been also obtained for $Zr_{1-x}Ce_xMn_2$ (x=0,2; 0,3) alloys. As cerium is substituted for zirconium, alloy sorption capacity decreases. Plateau length region decreases respectively. Deuterium sorption capacity at the end of the plateau for $Zr_{0,9}Ce_{0,1}Mn_2$ is ≈ 122 cm^3/g at room temperature. The above mentioned magnitude is ≈32% less for $Zr_{0,7}Ce_{0,3}Mn_2$.

The values of equilibrium pressures over the alloy deuterides increase in plateau region as cerium content increases in the initial alloy. The value of equilibrium pressure in the middle of plateau is ≈ 0,2kPa (≈ 1,5 mm Hg) for $Zr_{0,9}Ce_{0,1}Mn_2$ at room temperature. This is ≈6 times lower than that for $Zr_{0,7}Ce_{0,3}Mn_2$.

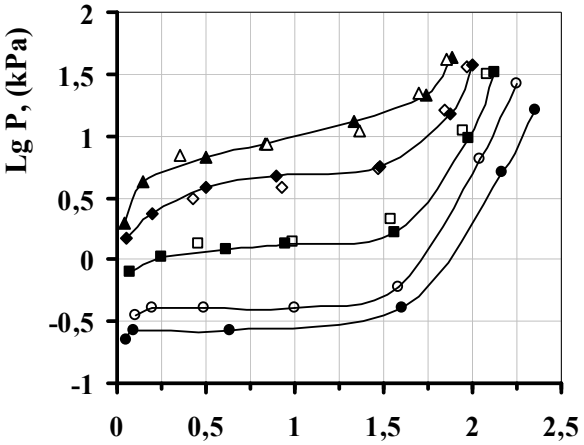


● – 22^{0}C; ■ – 50^{0}C; ♦ - 77^{0}C; ▲ – 100^{0}C; ∗ - 130^{0}C

Fig.1 Equilibrium desorption pressure isotherms in the $Zr_{0,9}Ce_{0,1}Mn_2$ — D_2 system

Equilibrium desorption pressure isotherms are measured over $Zr_{0,8}Ce_{0,2}Mn_2$ hydride and deuteride. The obtained isotherms are given in Fig. 2. It is seen from the presented isotherms that the isotopic effect in the investigated system is characterized by a negligible magnitude. The differences in equilibrium pressure values over alloy hydrides and deuterides are within experimental data scattering for elevated temperatures.

Based on the measured isotherms, we have plotted the curves of equilibrium desorption pressures as a function of reciprocal temperature.



● – 22^{0}C; ■ – 50^{0}C; ♦ - 77^{0}C; ▲ – 100^{0}C

Fig. 2 Equilibrium desorption pressure isotherms in the systems: $Zr_{0,8}Ce_{0,2}Mn_2$—D_2(closed symbols); $Zr_{0,8}Ce_{0,2}Mn_2$— H_2(opened symbols).

Fig. 3 presents the equilibrium desorption pressures as a function of reciprocal temperature for $Zr_{0,9}Ce_{0,1}Mn_2$ at the ratio D/alloy mole ≈ 1,25 (plateau middle).

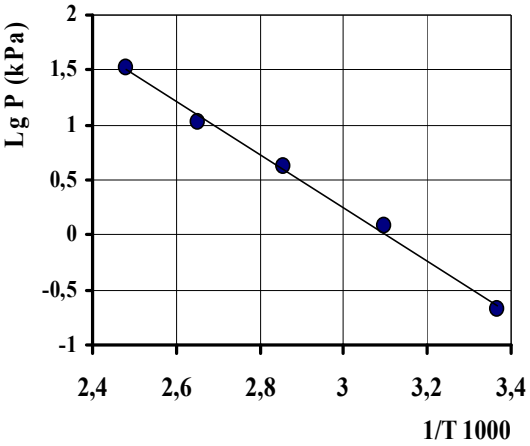


Fig. 3 Equilibrium deuterium pressure over $Zr_{0,9}Ce_{0,1}Mn_2$ vs. temperature.

The equilibrium desorption pressures for $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) alloys versus temperature are as follows:

lgP (kPa)=7,51-2418,5/T, for x=0,1;
lgP(kPa)=7,09-2267,4/T, for x=0,2;
lgP(kPa)=5,86-1713,9/T, for x=0,3.

The variations of enthalpy, ΔH, and entropy, ΔS, of decomposition processes for $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) alloy deuterides have been calculated from the obtained dependences. Decomposition enthalpy values are given in Table 1.

In accordance with paper [4], the enthalpy value of $Zr_{0,8}Ce_{0,2}Mn_2$ alloy hydride decomposition is 43,8 kJ/mole, which agrees with the value in the Table 1.

Table-1 Enthalpy variation for $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) alloy deuteride decomposition

System	ΔH, kJ/mole
$Zr_{0,9}Ce_{0,1}Mn_2$ - D_2	46,3
$Zr_{0,8}Ce_{0,2}Mn_2$ - D_2	43,4
$Zr_{0,7}Ce_{0,3}$ Mn_2 - D_2	32.8

The equilibrium pressures measured in this work at 100 and 130^{0}C are 2 times lower the values obtained by the authors of paper [4]. The differences in the values could occur as a result of using the different methods of carrying out measurements and the ways of alloy preparation.

Conclusions

1. The isotherms of equilibrium deuterium pressures over $Zr_{1-x}Ce_xMn_2$(x=0,1-0,3) alloys have been plotted in the temperature range (21-130)^{0}C. The isotherms of all the investigated systems are characterized by the existence of plateau. The plateau region length is (83-122) cm^3/g at room temperature. The equilibrium desorption pressure values for alloy deuterides are in the range 0,27-1,33 kPa (2-10 mm Hg) in the middle of plateau at room temperature,

2. Enthalpy values of $Zr_{1-x}Ce_xMn_2$ (x=0,1-0,3) alloy deuteride decomposition are in the range (46,3-32,8) kJ/mole.

3. The differences in the equilibrium pressure values of hydrogen isotopes are within the limits of pressure measurement accuracy for the temperature range (21 - 130)^{0}C at the interaction of deuterium and protium with $Zr_{0,8}Ce_{0,2}Mn_2$.

References

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