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Hydrogen solubility in uranium intermetallic compounds with Fe_2P type structure

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Hydrogen absorption properties of UMAl (M = Ni, Co) intermetallic compounds with a Fe_2P type structure were examined in the temperature range from 298 K to 523 K and at the hydrogen pressures up to about 2 MPa by using a modified Sieverts apparatus. UNiAl had great capacities for hydrogen absorption per formula unit, but UCoAl didn't have. The crystal structures and lattice parameters of the compounds were examined by X-ray diffraction analysis. In UNiAl-H system, there exists α (dilute solid solution), β (UNiAlH hydride), and γ ($UNiAlH_2$ hydride) phases. The standard enthalpy changes of formation of the hydrides were estimated from the equilibrium pressure-composition isotherms.

KEYWORDS: uranium, hydrogen absorption, intermetallic compound

I. Introduction

The industrial use of depleted uranium has been investigated in our laboratory, and one of those is hydrogen storage. Uranium has attractive properties for hydrogen storage and some of its alloys have been investigated in this respect[1-4]. Although uranium readily absorbs hydrogen at 5-10 Pa and below 500 K to form UH_3, the desorption pressure of UH_3 is too low for its convenient use in a hydrogen absorption–desorption system. So it is difficult to use uranium for hydrogen storage alloys.

However some of uranium intermetallic compounds show the higher desorption pressure than uranium metal[5]. Especially large hydrogen capacities were reported for the UMAl (M = Mn, Co, Ni) with a hexagonal Fe_2P type structure[5-7].

In the present study UMAl (M = Ni, Co) has been selected, and its hydrogen absorption and desorption properties were studied.

II. Experimental

The samples of UMAl (M=Ni, Co) in the form of buttons were prepared by high vacuum melting. The purities of starting materials are above 99.9 %. The prepared buttons were annealed at 1073 K for 10 hours in a vacuum below 10^{-5} Pa. The physicochemical properties of the prepared UMAl were characterized by several methods before hydrogen absorption experiments[7,9]. The lattice parameters were evaluated from X-ray powder diffraction. The physicochemical properties of the prepared UMAl are shown in **Table 1**[9].

The UMAl buttons were pulverized into fine particles with a diameter below 1 mm for hydrogen absorption-desorption experiments. Hydrogen gas (initial purity, 99.999 %) was purified by passing through a liquid nitrogen trap and used for solubility measurements.

The hydrogen solubility in UMAl was measured by absorption and desorption processes at temperatures between 298 K and 523 K at pressures below 2 MPa in a modified

Table 1 Physicochemical properties of UMAl (M = Ni, Co)[7,9].

Compounds	Prototype	Lattice parameters	Thermal expansion coefficient α	Longitudinal sound velocity V_l	Shear sound velocity V_s	Debye temperature θ_D	Micro-hardness H_V	Young's modulus E	Shear modulus G	Poisson's ratio ν	Bulk modulus K
		(nm)	(K^{-1})	(m/s)	(m/s)	(K)	(GPa)	(GPa)	(GPa)		(GPa)
UNiAl	Fe_2P	a=0.6768 c=0.4037	$3.44x10^{-5}$	4425	2342	299	6.94	145	55.7	0.305	125
UCoAl	Fe_2P	a=0.6682 c=0.3966	$4.47x10^{-5}$	4056	2219	286	6.92	133	51.8	0.286	104

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Sieverts UHV apparatus.

III. Results and discussions

Figure 1 shows X-ray diffraction patterns of UMAl (M = Ni, Co) compounds with a literature data[8]. The structure type and lattice parameters of these compounds are shown in **Table 1**[7,9].

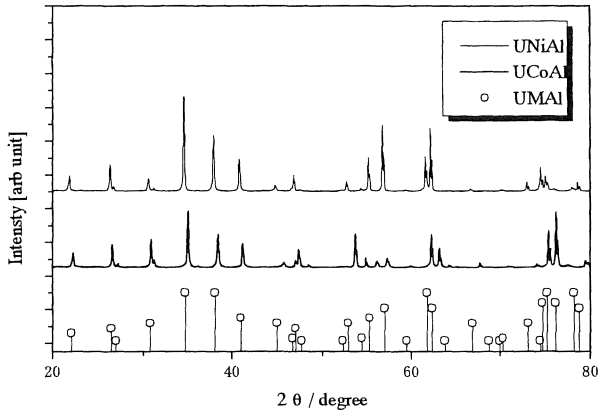

Fig.1 X-ray diffraction patterns of UMAl (M = Ni, Co).

Figure 2 shows the P_{H_2}-C_H isotherms for the UNiAl in desorption process. UNiAl absorbs hydrogen up to C_H (H/UNiAl) = 2.66[7]. The P_{H_2}-C_H isotherms exhibit two plateau regions, suggesting the existence of different hydride phases. The following phases appear to exist in the UNiAl-H system: α solid solution phase, β UNiAlH hydride phase, and γ $UNiAlH_2$ hydride phase.

The plateau pressure P_{H_2} for the α + β two–phase region is illustrated as a function of reciprocal temperature, as shown in **Fig.3**. The relationship between the plateau pressure and temperature can be expressed by the following equation (1).

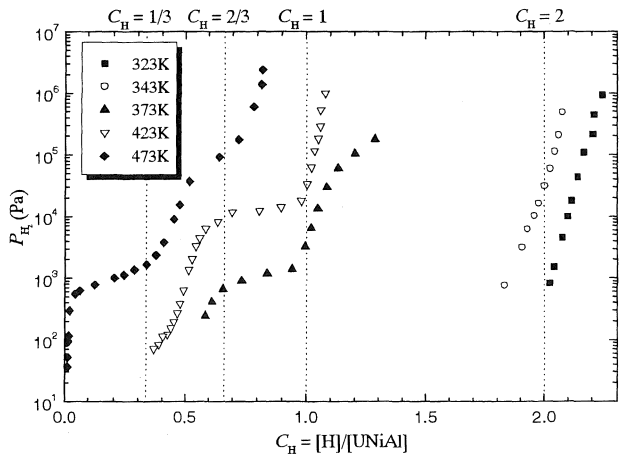

Fig.2 P_{H_2}-C_H isotherms of UNiAl in desorption process.

$$\ln P_{H_2} = 19.5 - 9159/T \quad \text{(in desorption process)} \qquad (1)$$

From these results, the standard enthalpy change of formation of β UNiAlH hydride ΔH° is evaluated to be -76.2 kJ/mol in desorption process. It is slightly higher than the reported value in absorption process[7].

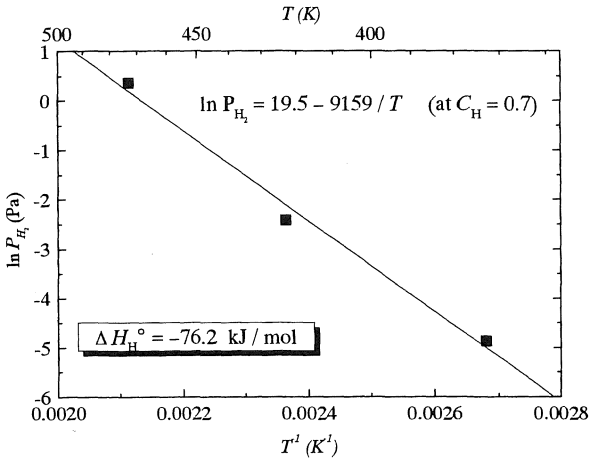

Fig.3 Van't Hoff plots for $UNiAlH_{0.7}$ in desorption process.

Figure 4 shows the P_{H_2}-C_H isotherms for UNiAl in absorption and desorption process at 473 K. In this figure, the hysteresis exsists between absorption and desorption pressure in UNiAl-H system. The hysteresis effect is represented by a hysteresis factor ($\mathbf{H_f}$), which is estimated by the following equation (2).

$$H_f = \ln(P_{abs} / P_{des}) \quad \text{(at } C_H = \text{(H/UNiAl)} = 0.2) \qquad (2)$$

In UNiAl-H system the value of $\mathbf{H_f}$ is calculated to be 1.64, which is too large to use as a hydrogen storage alloy in a heat pomp system.

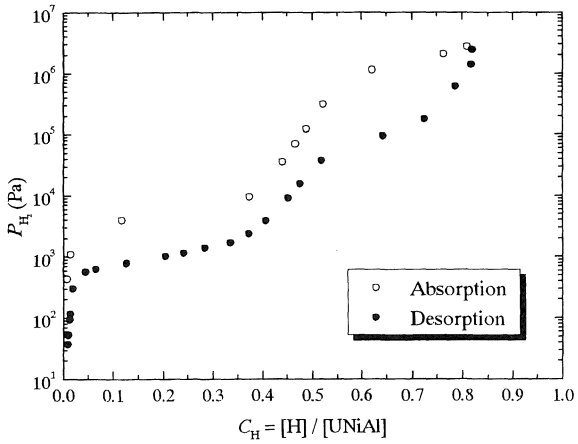

Fig.4 Hysteresis characteristics of UNiAl at 473 K.

Figure 5 shows the P_{H_2}-C_H isotherms for UCoAl in absorption process. Although Drulis et al. reported that UCoAl absorbed hydrogen up to C_H (H/UCoAl) = 1.2 at hydrogen pressure of 4 MPa[6], in the present study, it absorbs hydrogen up to C_H (H/UCoAl) = 0.39 at about 2 MPa at 298 K. Compared with UNiAl, this value is very small[7].

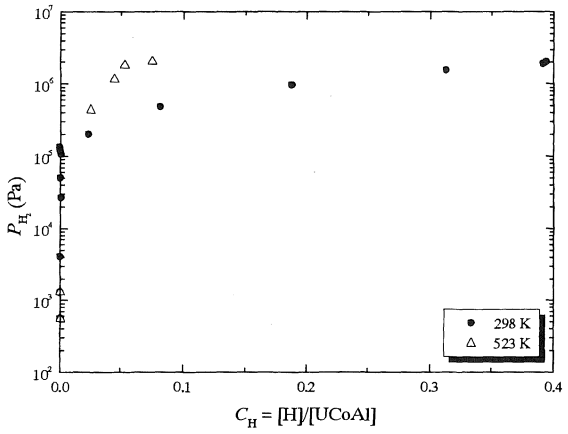

Fig.5 P_{H_2}-C_H isotherms of UCoAl in absorption process.

Figure 6 shows the temperature dependence of plateau pressures for various hydrides. For hydrogen storage alloys, the plateau pressure is required to range from 0.1 to 2 MPa from room temperature to 373 K, as indicated by solid rectangle shown in **Fig.6**. The standard enthalpy changes of

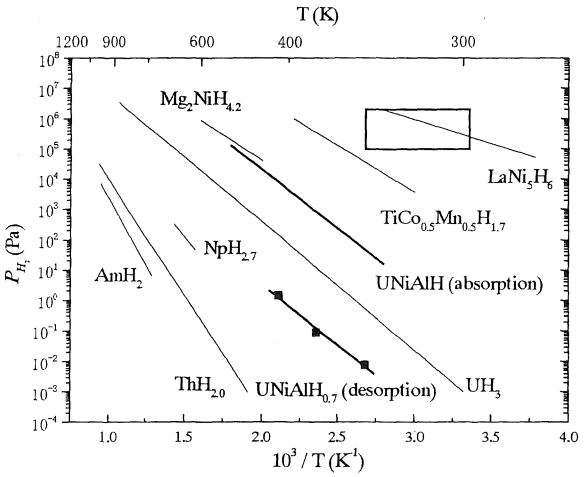

Fig.6 Temperature dependence of plateau pressure for various hydrides[7].

formation of the hydrides are from -30 to -50 kJ/mol. The hydrides of UNiAl show higher plateau pressures than UH_3 or hydrides of actinide metals such as Th, Np and Am. However, the plateau pressures of UNiAl hydrides are lower than those of other hydrogen storage alloys such as $LaNi_5$ and TiFe. For practical application of uranium intermetallic compounds to hydrogen storage materials, it is required to increase the plateau pressure.

IV. Conclusion

The hydrogen absorption and desorption properties in UMAl (M = Ni, Co) has been studied at hydrogen pressure up to 2 MPa at temperature ranging from 298 K to 523 K in a modified Sieverts apparatus. In the UNiAl-H system, there exist α (dilute solid solution), β (UNiAlH hydride), and γ ($UNiAlH_2$ hydride) phases. From the P_{H_2}-C_H isotherms the standard enthalpy change of formation of the β hydride phase is estimated to be –76.2 kJ/mol in desorption process. The hydrogen capacity of UCoAl is much smaller than that of UNiAl.

UNiAl absorbs a large amount of hydrogen, but has poor hysteresis characteristics at 473 K.

To use the UMAl (M = Ni, Co) as a hydrogen storage alloy in nuclear power plants, we must improve the hydrogen sorption characteristics drastically.

Acknowledgment

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