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Study on the hydrogen solubility in UNiAl

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Abstract

The hydrogen solubility in UNiAl has been studied at a hydrogen pressure up to 2 MPa at temperatures ranging from 50 to 250°C. In the UNiAl–H system, there exist α (dilute solid solution), β (UNiAlH hydride), and γ (UNiAlH_2 hydride) phases. The enthalpy of solution of hydrogen into the α phase and the standard enthalpy of formation of the β phase were estimated from the equilibrium pressure–hydrogen concentration isotherms. The lattice parameters of the hydride were examined by X-ray diffraction analysis. The anisotropic lattice expansion was observed for the hydrogenation of UNiAl. It was found from DTA and TG analyses that the hydride of UNiAl showed no marked oxidation up to 300°C in air and appears to have excellent thermal stability in air. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen solubility; Thermodynamic properties; Uranium; Intermetallic compound

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1. Introduction

The industrial use of depleted uranium reduces the amounts of nuclear waste and improves the economics of nuclear fuel. Several non-nuclear applications for depleted uranium have been proposed [1,2]. One of the possible applications is a hydrogen storage material. It is well known that uranium metal can absorb a large amount of hydrogen and excellent kinetics of hydrogen absorption and desorption. However, uranium metal shows extremely low hydrogen equilibrium pressure around room temperature, which is not suitable for hydrogen storage materials.

A tailoring of the equilibrium pressure appears to be possible by use of uranium intermetallic compounds of transition metals with less hydrogen sorption properties. Although uranium compounds with Co, Zr and Ti were studied to elucidate their hydrogen sorption capability [3,4], these compounds have not yet been sufficient for hydrogen storage alloys. The uranium intermetallic compounds with Laves phase structure type such as UNi_2 and UAl_2 showed an inertness towards hydrogen absorption up to 10 MPa [5]. However, large hydrogen capacities were reported for the UMAl (M=Mn, Co, Ni) with the hexagonal Fe_2P-type structure [5,6]. Limited information on thermochemical properties is available for the UMAl–H systems.

In the present study, UNiAl has been selected as a uranium intermetallic compound, and its hydrogen absorption characteristics were studied to clarify the possibility of application of Fe_2P-type uranium compound as a hydrogen storage alloy. The hydrogen pressure–concentration isotherms were examined to estimate thermochemical properties of hydrides. The thermal stability of UNiAl hydride were also studied.

2. Experimental

The sample of UNiAl in the form of a button was prepared by high vacuum induction melting. The purities of starting materials are above 99.9%. The prepared button was annealed at 800°C for 10 hours in a vacuum below 10^{-5} Pa. The physico-chemical properties of the prepared UNiAl was characterized by several methods before hydrogen absorption experiments. The lattice parameters and thermal expansion coefficients were evaluated from high-temperature X-ray powder diffraction. The longitudinal and shear sound velocities were measured, which enabled us to estimate the elastic properties. The physico-chemical properties of the UNiAl prepared in the present study are shown in Table 1.

The UNiAl button was pulverized into fine particles with a diameter below 1 mm for hydrogen absorption experiments. Hydrogen gas (initial purity, 99.999%) was

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Table 1
Physico-chemical properties of UNiAl

Compounds	Prototype	Decomposition temperature T_d	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
		(K)	(nm)	(K^{-1})	(m/s)	(m/s)	(K)	(GPa)	(GPa)	(GPa)		(GPa)
UNiAl	Fe_2P	1373	$a=0.6768$ $c=0.4037$	3.44×10^{-5}	4425	2342	299	6.94	145	55.7	0.305	125

purified by passing through a liquid nitrogen trap and used for solubility measurement.

Hydrogen solubility in the UNiAl was measured by absorption process at temperatures between 50 and 250°C at a pressure below 2 MPa in a modified Sieverts UHV apparatus. The lattice parameters of the hydride were examined by X-ray diffraction analysis. Thermal stability of hydride was measured by thermogravimetric (TG) and differential thermal analysis (DTA) at a heating rate of 10°C/min in air.

3. Results and discussion

3.1. Equilibrium hydrogen pressure–hydrogen concentration isotherms

Fig. 1 shows the equilibrium hydrogen pressure P_{H_2} (Pa)–hydrogen concentration C_H (H/UNiAl) isotherms for the UNiAl. The P_{H_2}–C_H isotherms exhibit two plateau regions, suggesting the existence of different hydride phases. Jacob et al. [5] have reported the P_{H_2}–C_H isotherms for the UNiAl–H system at 246, 261 and 282°C and Drulis et al. [6] have performed the solubility measurement at lower temperatures of 150, 80, 60 and 40°C. Although there exist differences in equilibrium pressure or hydride composition between the results of Jacob et al., Drulis et al. and the present study, the isotherms for the UNiAl–H system revealed the existence of at least two hydride phases. The following phases appear to exist in the UNiAl–H system: α solid solution phase, β NiAlH hydride phase, and γ $UNiAlH_2$ hydride phase.

The hydrogen solubility in UNiAl appears to obey Sieverts' law in low hydrogen concentration region below 0.02 H/UNiAl, as shown in Fig. 1. The temperature dependence of Sieverts' constant K_H is indicated in Fig. 2. It is found from this figure that there holds a linear relationship between ln K_H and the reciprocal temperature $1/T$ (K) as follows:

$$\ln K_H = -15.25 + 3319/T.$$

From these results, the enthalpy of solution of hydrogen into UNiAl was estimated to be −27.6 kJ/mol.

The plateau pressure P_{H_2} for the α+β two-phase region is illustrated as a function of reciprocal temperature, as

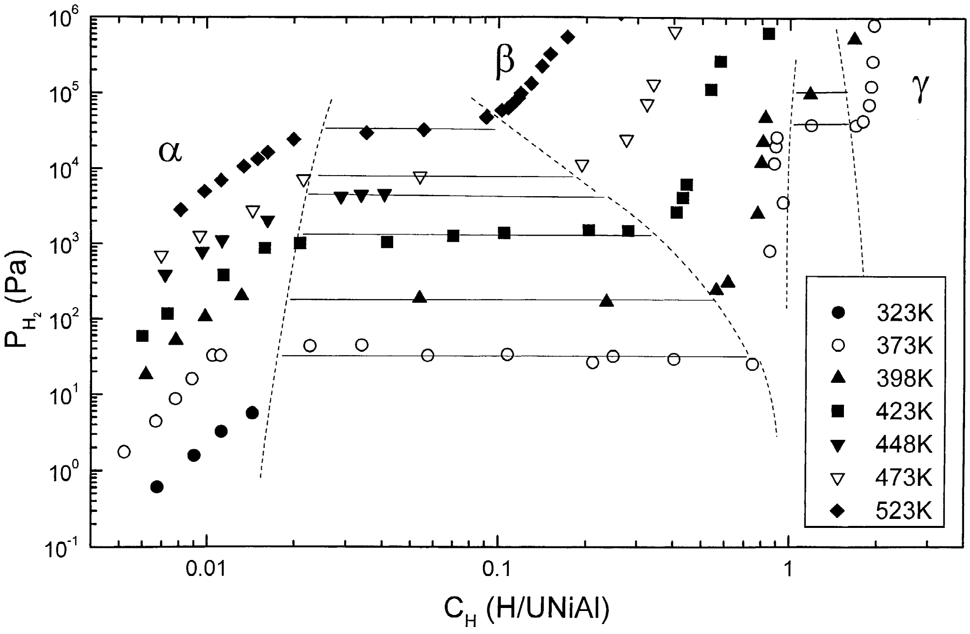

Fig. 1. Pressure–concentration isotherms for the UNiAl–H system.

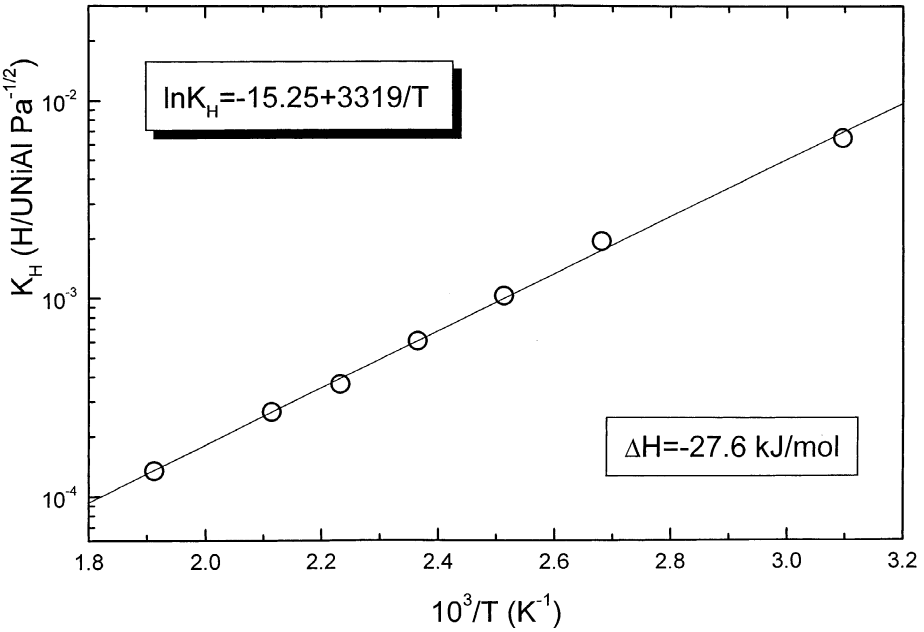

Fig. 2. Temperature dependence of Sieverts' constant K_H for UNiAl.

shown in Fig. 3. The relationship between plateau pressure and temperature can be expressed by

$$\ln P_{H_2} = 27.9 - 8970/T.$$

The standard enthalpy of formation of β UNiAlH hydride $\Delta H°$ was evaluated to be −74.6 kJ/mol, which is slightly higher than the reported values of Jacob et al. [5].

3.2. Lattice parameters and thermal stability of hydride

UNiAl and UNiAl hydride were characterized by the X-ray powder diffraction method. The X-ray diffraction pattern indicated that UNiAl had Fe_2P type structure. The lattice parameters of UNiAl were estimated as $a = 0.6768$ and $c = 0.4037$ nm. The γ $UNiAlH_{1.9}$ hydride showed almost the same pattern indexed to hexagonal unit cell. Its

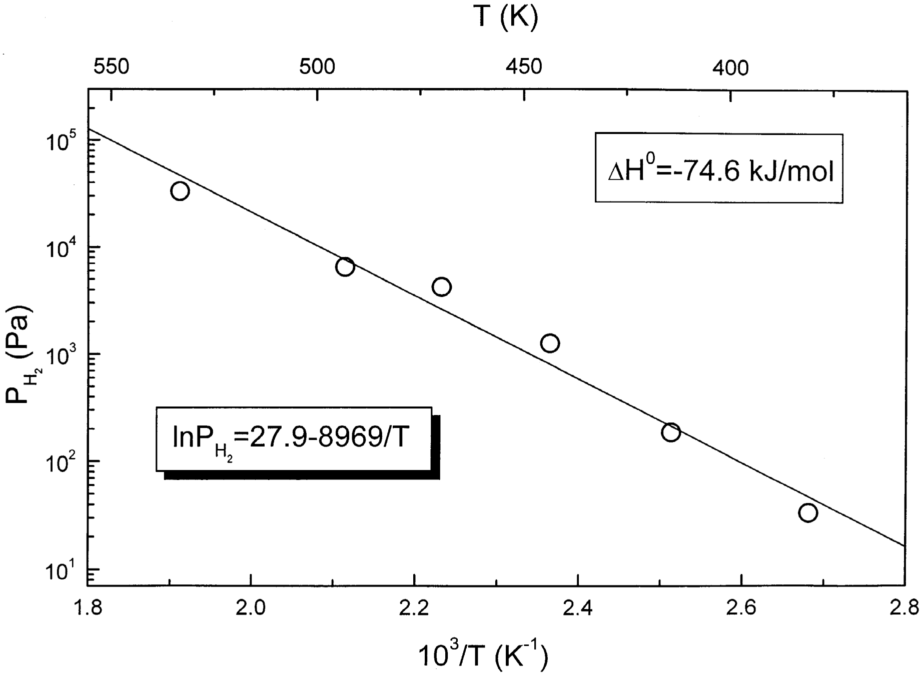

Fig. 3. Temperature dependence of plateau pressure for the two-phase region of α+β.

hexagonal lattice parameters $a=0.7175$ and $c=0.3989$ nm were markedly changed with hydrogenation resulting in the contraction of the c-axis by 1.2% and the expansion of the a-axis by 6.5%. This lattice distortion corresponded to the relative increase of volume of 12%. Yamamoto et al. [7] have reported that the lattice parameters of β $UNiAlH_{0.8}$ are $a=0.697$ nm and $c=0.399$ nm. Although the changes in the lattice parameters are smaller for the β phase than for the γ phase, the anisotropic lattice expansion occurs for both hydride phases.

The anisotropic lattice expansion was also observed for the hydrogenation of ZrNiAl and RENiAl with Fe_2P type structure [8,9] and $ZrBe_2$ with the AlB_2 type structure [10]. Yoshida et al. [8] have reported that hydrogen at the trigonal-bipyramidal site, surrounded by three Zr and two metal atoms, strongly causes the anisotropic lattice expansion. The attraction between Zr and D decreases the Zr–Zr distance and the repulsion between Ni and D increases the Ni–Ni distance. They concluded that the deformation of the trigonal bipyramid by hydrogenation can be attributed to the anisotropic lattice expansion in ZrNiAl [8]. Neutron diffraction of β $UNiAlD_{0.7}$ [7] revealed occupation of deuterium at a 3U–2Ni site. A similar explanation to Zr NiAl [8] can be applied to the anisotropic expansion of UNiAl hydride.

Fig. 4 reveals the results for TG and DTA analyses of the hydride of UNiAl in air, together with the results of UNiAl before hydrogenation. For the UNiAl powder before hydrogenation, the DTA curve has two exothermic peaks at 500 and 700°C and the TG curve indicates the mass increase above 400°C. These results show that the oxidation of UNiAl occurred with two stages and the final reaction products were U_3O_8, NiO and Al_2O_3. The results of the γ $UNiAlH_{1.9}$ hydride indicates a drastic mass change in the TG curve and a sharp exothermic peak above 300°C in the DTA curve. The reaction is considered to involve the oxidation and hydrogen desorption, and the reaction rate is higher than that of UNiAl. The final products were the same as those observed for the oxidation of UNiAl. The UNiAl hydride appears to be oxidized in air more easily than UNiAl. The UNiAl hydride has better thermal stability in air than UH_3 or hydrides of uranium alloys such as UZr_2 and U_2Ti [4].

3.3. Comparison of plateau pressure of UNiAl hydride with various hydrides

For hydrogen storage alloys, the plateau pressure is required to range from 0.1 to 20 MPa from room temperature to 100°C, as indicated by solid rectangle shown in Fig. 5. The standard enthalpies of 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. The plateau pressures of UNiAl hydrides are lower than those of hydrogen storage alloys such as $LaNi_5$ and TiM_2. For practical application of uranium intermetallic compound with Fe_2P-type structure to hydrogen storage materials, it is required to increase the plateau pressure by one order of magnitude.

4. Conclusions

The hydrogen solubility in UNiAl has been studied at a hydrogen pressure up to 2 MPa at temperatures ranging from 50 to 250°C in a modified Sieverts apparatus. In the

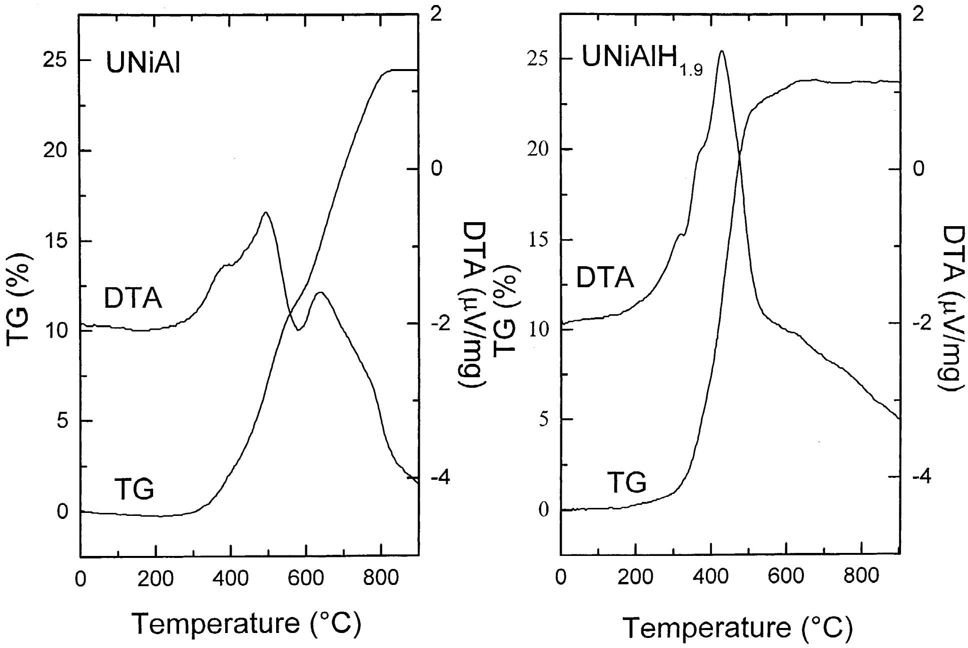

Fig. 4. TG and DTA curves for UNiAl and $UNiAlH_{1.9}$ (10°C/min, in air).

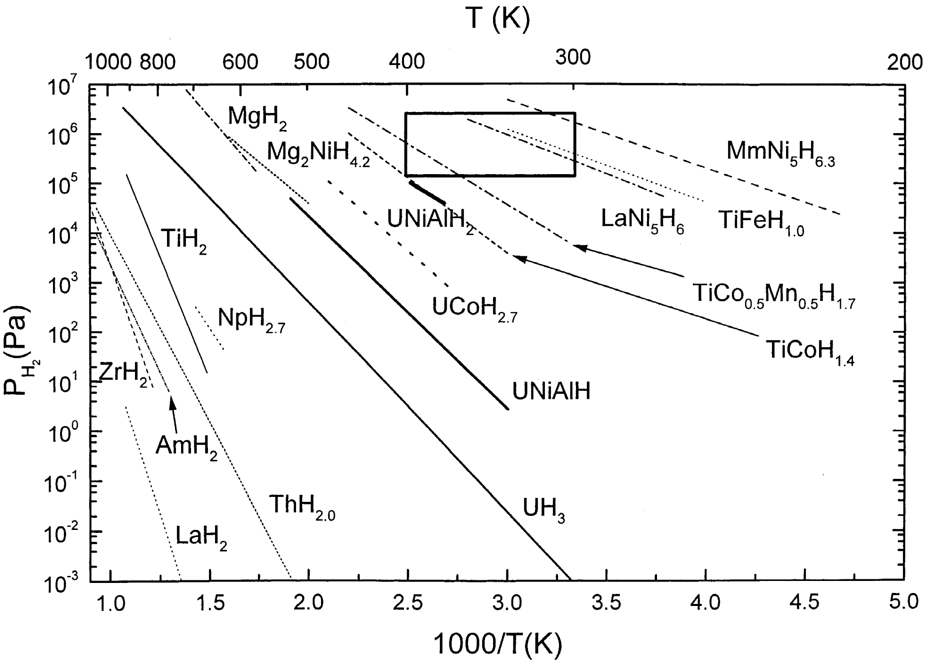

Fig. 5. Temperature dependence of plateau pressure for various hydrides.

UNiAl–H system, there exist α (dilute solid solution), β (UNiAlH hydride), and γ ($UNiAlH_2$ hydride) phases. The enthalpy of solution of hydrogen into the α phase was estimated to be −27.6 kJ/mol. The standard enthalpy of formation of the β hydride phase was estimated from the isotherms to be −74.6 kJ/mol.

The crystal structure and the lattice parameters of the γ $UNiAlH_{1.9}$ hydride was in good agreement with the literature data. The hydrogen absorption into UNiAl brought about anisotropic lattice expansion. The TG and DTA analyses indicated that the hydride of UNiAl showed no marked oxidation up to 300°C in air. This suggests that the hydride of UNiAl has excellent thermal stability in air. Further improvements of hydrogen sorption characteristics appear to be needed for practical uses of UNiAl as a hydrogen storage alloy in nuclear power plants.

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