Journal of Alloys and Compounds 271–273 (1998) 629–631

Hydrogen absorption properties of U_6Mn and U_6Ni

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Abstract

The hydrogen absorption properties of U, U_6Mn and U_6Ni were investigated at hydrogen pressures below 10^5 Pa. The pressure–composition (P–C) isotherms of U, U_6Mn and U_6Ni were obtained and the amounts of absorbed hydrogen for U, U_6Mn and U_6Ni were determined to be 3, 16.6 and 16.0 for x in MH_x, where M is U, U_6Mn and U_6Ni, respectively. The desorption plateau pressures at 573 K decreased in the order: U_6Mn–H>U_6Ni–H>U–H. In addition, the results for the amounts of absorbed hydrogen suggests the formation of ternary hydrides U_6MnH_{18} and U_6NiH_{14}. © 1998 Published by Elsevier Science S.A.

Keywords: Hydrogen; Intermetallic compound; Uranium

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1. Introduction

Uranium has attractive properties for hydrogen storage and some of its alloys have been investigated in this respect [1–4]. Although it readily absorbs hydrogen at 10^5 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. Further, uranium is easily powdered by hydrogenation, which is not covenient for its safe handling. It has been reported that the hydrides of U–Ti and U–Zr alloys have high resistances to powdering [5]. Owing to its low hydrogen desorption pressure, the uranium bed must be operated at a relatively high temperature for hydrogen to be recovered. In this paper, the hydrogen absorption properties of U–Mn and U–Ni intermetallic compounds are investigated in a search for a better hydrogen absorber with higher hydrogen desorption pressures.

2. Experimental details

Two intermetallic phases, U_6Mn and UMn_2, have been identified in the U–Mn phase diagram and five intermetallic compounds, U_6Ni, U_7Ni_9, U_5Ni_7, UNi_2 and UNi_5, in the U–Ni phase diagram. These compounds were prepared by arc melting in an argon atmosphere using uranium of 99.5% purity and manganese and nickel of 99.9% purity. The specimens obtained were annealed in silica tubes under 10^{-6} Pa. After annealing for around one day at 1000 K, the specimens were cooled slowly. A small fraction of each sample was used for the hydrogen absorption/desorption measurement. The apparatus employed to anneal the specimens as well as to examine their hydrogen absorption–desorption properties is shown schematically in Fig. 1. The connecting tubes and reservoir were made of stainless steel, while the reactor vessel was a silica tube. This device allowed the specimens to be hydrided under a hydrogen pressure of up to 0.1 MPa and

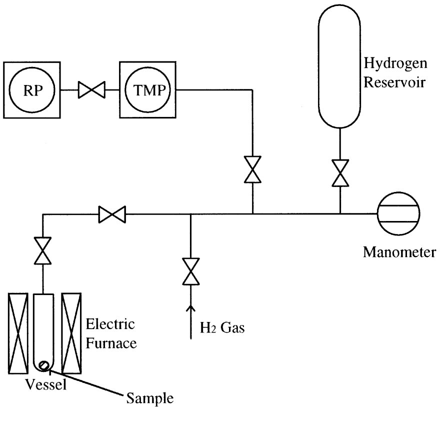

Fig. 1. Schematic diagram of the hydrogen absorption–desorption apparatus (TMP, turbo molecular pump; RP, rotary pump).

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0925-8388/98/$19.00
PII: S0925-8388(98)00174-1

at a temperature up to 1273 K. The volume of the reactor vessel was about 40 cm^3, while that of the reservoir was about 1000 cm^3. The high purity hydrogen gas used in the experiments was admitted through a hydrogen purifier installed with a thin Pd–Ag alloy film. Each sample was first pre-activated in hydrogen at about 0.1 MPa in the temperature range 300–873 K and subjected to several hydriding–dehydriding cycles before the pressure–composition–temperature readings were taken. The isotherms were measured during the dehydriding phase of the cycle, where hydrogen was extracted in small decrements from the hydrogen saturated sample, by determining the H_2 pressure above the sample after equilibrium had been established. The measurements were performed at 573 and 673 K. In the case of UMn_2, U_7Ni_9, U_5Ni_7, UNi_2 and UNi_5, another experiment was carried out at a temperature lower than 573 K and a pressure of about 5.0 MPa because hydrogen absorption did not occur in these specimens at 0.1 MPa of hydrogen.

3. Results and discussion

3.1. Hydrogen absorption properties of U_6Mn and U_6Ni

The crystal structure of U_6Mn, U_6Ni, U_6Fe and U_6Co is of the U_6Mn-type. Drulis [6] reported that U_6Fe was hydrogenated not to form UH_3 but the ternary hydride U_6FeH_{15}. For this reason U_6Mn and U_6Ni were expected to form a similar ternary mixed hydride. The pressure–composition isotherms for the U–H, U_6Mn–H and U_6Ni–H systems are shown in Fig. 2. As can be seen from this figure, the composition corresponding to the maximum hydrogen absorption of each specimen was determined to be H/M=3.0, 16.6 and 16.0 for H–U, H–U_6Mn and H–U_6Ni, respectively (M=U, U_6Mn or U_6Ni). As for U_6Mn and U_6Ni, the amount of absorbed hydrogen per mole of U was slightly reduced compared to that of UH_3. The isotherms of the U_6Mn–H and U_6Ni–H systems were similar to that of the U–H system for H/M ratios up to 2.5 and 2.2, respectively, where the different H_2 desorption pressures over UH_3 are attributable to the different activities of U in each alloy and pure uranium. For H/M ratios larger than those values, the characteristics of the isotherms were clearly different from those of the U–H system. Fig. 3 shows the X-ray diffraction pattern for $U_6MnH_{16.6}$ (nominal composition) after several hydriding–dehydriding cycles. The many unknown peaks observed seem to be attributable to U–Mn–H ternary hydride which most probably increased the H_2 desorption pressure. This figure also reveals partial decomposition of $U_6MnH_{16.6}$ (n.c.) to UH_3 and UMn_2 upon hydrogenation. The reaction is considered to be

$$U_6Mn + \tfrac{33}{4}H_2 \rightarrow \tfrac{11}{2}UH_3 + \tfrac{1}{2}UMn_2$$

Taking into account the X-ray results and the similarity of the desorption isotherms for U_6Mn and U_6Ni, the two pressure plateaus for the U_6Mn–H and U_6Ni–H systems of Fig. 2 were assigned to UH_3 (the lower pressure plateau)–U_6MnH_x (the higher pressure plateau) and UH_3 (the lower plateau)–U_6NiH_y (the higher plateau), respectively. Based on the amount of absorbed hydrogen (calculated from the length of the plateau pressure), the formulae for the reaction of U_6Mn and U_6Ni with hydrogen can be estimated. These are

$$U_6Mn + 9H_2 \rightarrow U_6MnH_{18}$$

$$U_6Ni + 7H_2 \rightarrow U_6NiH_{14}$$

The hydrogen desorption pressures of the two compounds were higher than those of the U–H system at each measured temperature. The amounts of absorbed hydrogen and the desorption plateau pressures of the H–U_6Mn, H–U_6Ni and H–U systems at 573 K are shown in Table 1. From this table, it can be seen that the U_6MnH_x compound has a higher H_2 desorption pressure, i.e. less stability than

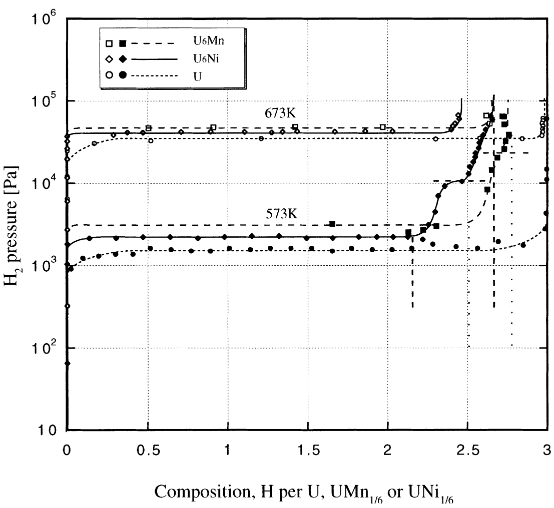

Fig. 2. Desorption isotherms for U, U_6Mn and U_6Ni.

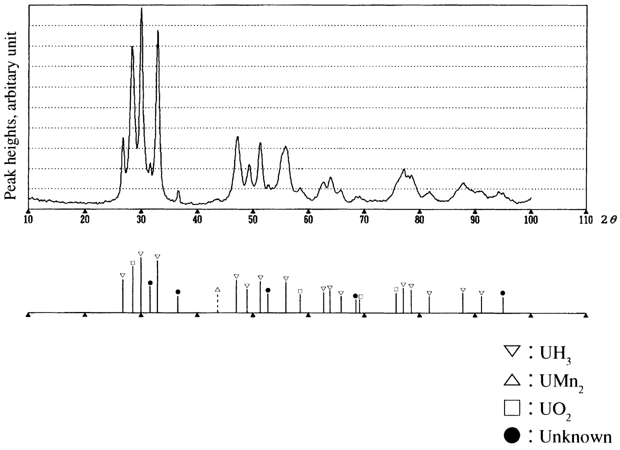

Fig. 3. XRD pattern for $U_6MnH_{16.8}$.

Table 1
Hydrogen absorption characteristics for U, U_6Mn and U_6Ni

Specimen	Maximum H_2 absorption capacity [H]/[M]	H_2 desorption pressure (Pa) 573 K
U	3.0	1.58×10^3
U_6Mn	16.6	2.30×10^4
U_6Ni	16.0	1.03×10^4

Table 2
Correlation between unit volume and H_2 desorption pressure at 573 K

Specimen	Lattice parameter (Å) Ref. [8]		Unit volume a^2c (Å)	H_2 desorption pressure (Pa)
	a	*c*		
U_6Mn	10.29	5.24	554.83	2.30×10^4
U_6Ni	10.37	5.21	560.27	1.03×10^4

the isostructural compound U_6NiH_y. This result agrees with Lundin's correlation [7] between the stability of the hydride and the size of the interstitial hole in the original intermetallic compound: the stability of the hydride increases with the size of the interstitial hole in the original intermetallic compound. Since U_6Mn and U_6Ni are isostructural compounds, the change of the hole size affects the change of the volume of the compound. The correlation between the unit volume and the H_2 desorption pressure is shown in Table 2. The volume of U_6Mn is smaller than that of U_6Ni, therefore U_6NiH_x is more stable (i.e. the desorption pressure is lower) than U_6MnH_y.

3.2. UMn_2, U_7Ni_9, U_5Ni_7, UNi_2, and UNi_5

The pressure change due to temperature for the U_7Ni_9–H system is shown in Fig. 4. This shows no hydrogen absorption. The other four U-poor compounds showed the same trend. This is in striking contrast to the fact that considerable absorption was observed in the case of U_6Mn and U_6Ni even at room temperature and the relatively low pressure of 0.1 MPa.

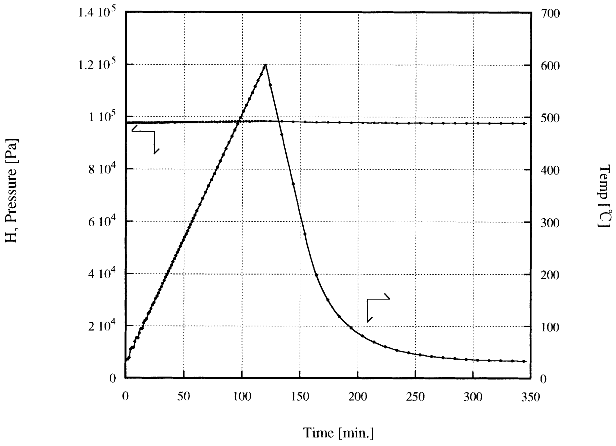

Fig. 4. H_2 pressure change for the U_7Ni_9–H system.

4. Conclusion

The hydrogen absorption–desorption properties of U–Mn and U–Ni intermetallic compounds were examined over the temperature range 300 to 673 K at hydrogen pressures below 10^5 Pa. U_6Mn and U_6Ni absorbed hydrogen up to 16.6 and 16.0 per gram mole of metal, respectively. The two pressure plateau observed on the desorption isotherms of U_6Mn and U_6Ni at 573 K were assigned to UH_3 (the lower pressure plateau)–U_6MnH_x (the higher pressure plateau) and UH_3 (the lower plateau)–U_6NiH_y (the higher plateau), respectively. The hydrogen desorption pressures of these compounds at 573 K were higher than that of pure uranium, where the order of the desorption pressures of U_6MnH_x and U_6NiH_y is in agreement with the correlation between the stability of hydrides and the size of holes in the original intermetallic compounds. The other five intermetallic compounds, UMn_2, U_7Ni_9, U_5Ni_7, UNi_2 and UNi_5, showed no detectable hydrogen absorption.

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