



ABSORPTION OF HYDROGEN BY $MmNi_5$ ALLOYS

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Abstract—In recent years much attention has been paid to the development of hydrogen absorbing alloys in which the pure rare-earth metals are substituted by a more accessible raw material—mischmetal, but the composition of mischmetal can vary widely. The properties of $MmNi_5H_x$ (hydrogen capacity, hydrogen desorption equilibrium pressure at given temperature) depend on the composition of mischmetal and the mode of preparation of the alloys. In this work the results of the investigation of the interaction of four alloys of $MmNi_{5\pm\delta}$ are presented. Copyright © 1996 International Association for Hydrogen Energy

INTRODUCTION

The successful development of hydrogen energetics is connected in considerable part with the elaboration of the production technology of the highly effective hydrogen absorbing alloys and the systems for storage and accumulation of hydrogen with high specific parameters. The main reason for restraining a wide application of metal-hydride systems is the high cost of the alloys of the $LaNi_5$ -type. Because of that, considerable attention has been paid in recent years to the development of alloys in which the pure rare-earth metals are substituted by a more accessible raw material—mischmetal.

EXPERIMENTAL PART

$MmNi_{5\pm\delta}$ alloys were prepared by using Mm (53%Ce, 2–5%Fe, $\Sigma RE = 42$ –45%). The laboratory fusions were performed in an arc furnace with tungsten nonspending electrode in an atmosphere of purified argon under a pressure of 2 atm. The set of $MmNi_5$ samples (I–IV) were prepared in which the surplus mischmetal concentration in schist was 1, 5, 10 and 15 mass %. The phase composition was controlled by X-ray and micro-X-ray structural analysis. The hydriding of the samples was performed in the standard apparatus.

RESULTS AND DISCUSSION

X-ray analysis showed that the main phase of all of the samples was the hexagonal one of the $CaCu_5$ -type.

According to the chemical analysis the fume of mischmetal while melting amounted to 2 mass %. Table 1 presents the results of the X-ray phase analysis. Besides the main phase there are some traces of pure nickel in sample I. In samples III and IV there is another phase present which was indexed as Mm_2Ni_7 . Moreover, in sample III this second phase can be found in small quantities, but in sample IV its presence is quite distinct.

The investigated alloys absorb hydrogen after the preliminary activation, and absorption is preceded by an induction period whose duration is dependent on the phase composition of the alloy. For sample I, this period is about 24 h; samples II and III—6–12 h, and sample IV—several minutes. After the beginning of the reaction, the equilibrium in the first absorption cycle is established for sample I after several days; for samples II and III after 6–7 h; and for sample IV—3 h. The quantity of hydrogen absorbed in the first cycle is dependent on the quantity of the surplus mischmetal and is about 0.18–0.23 mass % H_2 for sample I, 0.46–0.69 mass % H_2 for sample II, 1.39 mass % H_2 for sample III, and 1.43 mass % H_2 for sample IV. In subsequent cycles the duration of the induction period decreases and in the third or fourth cycle the reaction starts practically at once. About 80–90% of hydrogen is absorbed by all samples in 30–60 min, and equilibrium is established 2 h after the beginning of the reaction.

We carried out the investigation of the $MmNi_{5\pm\delta}-H_2$ system at 262, 273 and 296 K. The desorption isotherms at 296, 273 and 262 K are presented in Figs 1, 2 and 3 and the results of the determination of the desorbed hydrogen quantity and the equilibrium desorption pressure in different cycles are in Table 2. The quantity of desorbed hydrogen is practically the same for samples I–III and is about 1.34–1.39 mass % H_2 (see Table 1), sample

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Table 1. Phase composition $\text{MmNi}_{5\pm\delta}$ and absorption-desorption characteristics for the system $\text{MmNi}_{5\pm\delta}-\text{H}_2$ at $T = 296$ K

Sample No.	Surplus Mm in schist, mass %	Phase composition	P_{des} , atm, at 0.69 mass %H ₂	Mass %H ₂ under $P_{\text{abs}} = 50$ atm	Reversible hydrogen capacity, mass %
I	1	$\text{MmNi}_5 + (\text{traces}) \text{Ni}$	20.0	1.41	1.34
II	5	MmNi_5	13.5	1.36	1.34
III	10	$\text{MmNi}_5 + (\text{traces}) \text{Mm}_2\text{Ni}_7$	12.6	1.43	1.39
IV	15	$\text{MmNi}_5 + (\text{little}) \text{Mm}_2\text{Ni}_7$	13.0	1.43	1.25

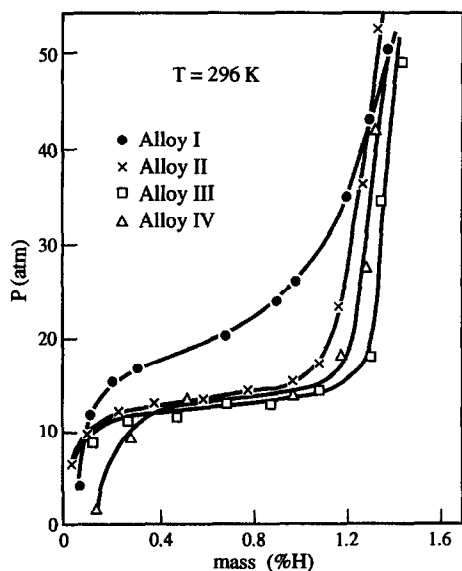
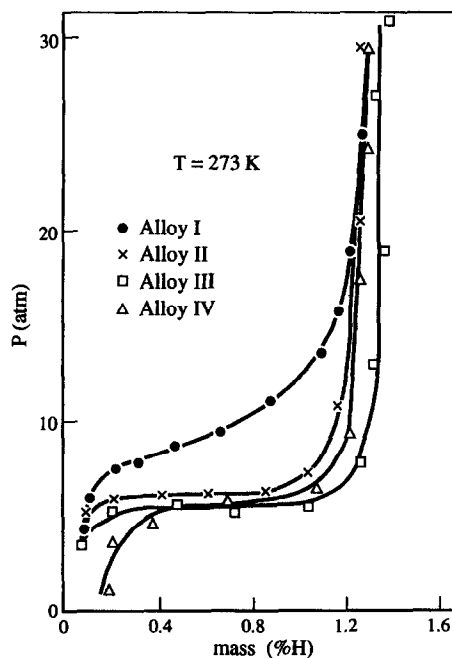
IV desorbs about 1.25 mass %H₂. This can be connected with the fact that in the hydriding reaction of the second R_2Ni_7 phase, found in the samples III and IV, the product is X-ray amorphous which does not desorb hydrogen in experimental conditions [1, 2]. This leads to the difference between the quantities of hydrogen absorbed in the first cycle and that of desorbed while heating.

In repeated "absorption-desorption" cycles the desorption pressure is increased with increasing number of cycles. So, for the hydride phase of sample I the equilibrium desorption pressure rises from 16 atm in the first cycle to 20 atm in the ninth. For other hydrides this change is not so profound: for sample II—from 12.5 to 13.5 atm in the fifth cycle; for sample III—from 11 to 12.6 in the fourth cycle; for sample IV—from 11 to 13 atm in the fifth cycle (Table 2). The change of the equilibrium desorption pressure in "plateau region" with the number of hydrogen absorption-desorption cycles for sample I is presented in Fig. 4.

From the data in Figs 1 and 2 and Tables 1 and 2, one can see that the equilibrium hydrogen desorption

pressure for sample I is higher than for all other samples at all studied temperatures. This regularity is preserved for sample II—the desorption pressure is higher than that of sample III. But for sample IV it is slightly higher than for sample III.

The results can possibly be accounted for as follows. In resemblance to LaNi_5 [3] the MmNi_5 also has some homogeneity region. Sample I can be considered as belonging to the boundary composition $\text{MmNi}_{5+\delta}$ and sample III—belonging to another boundary composition $\text{MmNi}_{5-\delta}$. Then, as it was for $\text{LaNi}_{5\pm\delta}$ the increase in rare-earth metal content decreases the desorption pressure in the "plateau" region. Sample IV is distinctly a two-phase one and the desorption pressure in the "plateau" region should not change significantly. Some alteration to this fact can possibly be achieved by the presence of the second $\text{R}_2\text{Ni}_7\text{H}_x$ phase. The analogous dependence is calculated from the isothermal data thermodynamic

Fig. 1. Desorption isotherms for the system $\text{MmNi}_{5\pm\delta}-\text{H}_2$ at $T = 296$ K.Fig. 2. Desorption isotherms for the system $\text{MmNi}_{5\pm\delta}-\text{H}_2$ at $T = 273$ K.

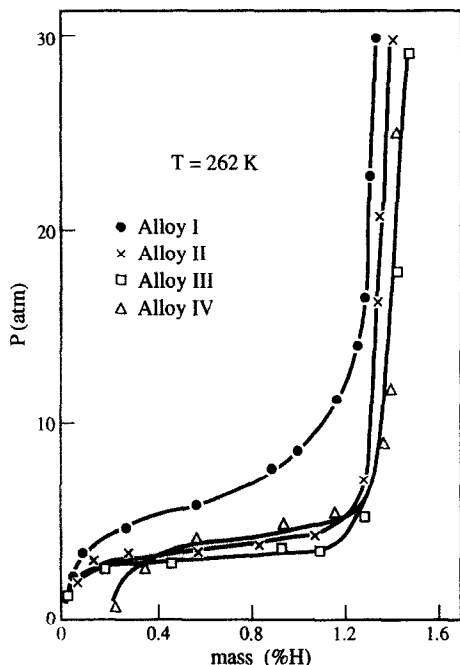


Fig. 3. Desorption isotherms for the system MmNi_{5±δ}-H₂ at T = 262 K.

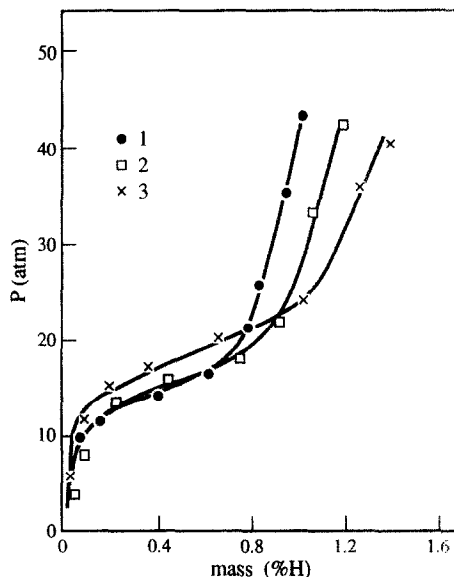


Fig. 4. Effect of repeating of absorption-desorption cycles on the equilibrium desorption pressure for sample 1 (T ≈ 296 K): 1—second cycle, 2—fifth cycle, 3—twelfth cycle.

parameters for the MmNi₅-H₂ system (Table 3). The absolute values of the reaction enthalpy, ΔH, increase in the order: sample III > sample II > sample I. It seems

Table 2. Change of "plateau" region P_{des} in repeated cycles absorption-desorption (T = 296 K)

Sample No.	Cycle No.	P _{des} atm, at 0.69 mass %H ₂	Reversible hydrogen capacity, mass %
I	2	16.4	0.97
	3	16.0	1.15
	4	17.0	1.20
	5	17.0	1.22
	9	19.5	1.34
	11	20.0	1.34
	12	19.5	1.34
II	13	20.0	1.34
	2	12.5	1.18
	3	13.0	1.20
	4	13.4	1.34
	5	13.5	1.34
III	1	11.0	1.34
	2	12.6	1.39
	3	12.4	1.39
	4	12.6	1.39
IV	1	11.0	1.25
	3	12.5	1.25
	5	13.0	1.25
	7	13.0	1.25

not quite correct to compare the values for sample IV, which consists of two phases. The obtained values of pressure and the desorption enthalpy and entropy changes correspond better to the results published in [4, 5].

So, our investigations showed that in the system MmNi_{5±δ}-H₂ the deficiency in mischmetal leads to the deterioration of working parameters: the increase of the induction period, slow rate of first hydrogen absorption, and the necessity for many "absorption-desorption" cycles for the establishment of the constant desorption pressure in the "plateau" region. The optimal surplus quantity of mischmetal for the preparation of alloys is about 5 mass %, which corresponds to the final composition of MmNi_{4.95}. A larger amount of mischmetal leads to the appearance of the second phase and to decrease of the reversible hydrogen capacity.

Table 3. Thermodynamic parameters for the system MmNi_{5±δ}-H₂ at the "plateau" region

Sample	ΔH, kJ/molH ₂	ΔS, J/K · molH ₂	Ref.
I	22.2 ± 0.4	100 ± 1.5	This work
II	23.7 ± 0.4	102 ± 1.4	
III	25.1 ± 0.3	106 ± 0.6	
IV	22.0 ± 1.4	93 ± 5.0	
MmNi ₅	26.4	111.3	[4]
MmNi ₅	-25.9; 27.6		[5]

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