DEVELOPMENT OF PRODUCTION TECHNOLOGY OF INTERMETALLIC COMPOUNDS ON BASE OF RARE-EARTH-Ni FOR HYDROGEN ACCUMULATORS

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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. In the present work the interaction of hydrogen with some alloys of the composition RT_5 (R—mischmetal and/or La, Ce; T—transition metals of iron triad) prepared by laboratory method was investigated and their production technology was worked out. The influence of the surplus mischmetal on the absorption–desorption characteristics was stated. The influence of carbon admixtures on the properties of alloys containing mischmetal was found and the possibility of its extraction in the form of titanium carbide was investigated. The technical characteristics of the typical hydrogen accumulator module are presented. Copyright © 1997 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 is 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.

In the present work the results of the fruitful cooperation of the two groups, from Moscow Polimetal Works and from Moscow State University, are presented which show the successful solving of the problem of hydrogen absorbing alloys and the hydrogen storage systems production.

EXPERIMENTAL PART

The following metals were used for the preparation of the starting alloys:

(1) Mischmetal (Mm) MC5OJ6, Technical Arrangement (TA) 48-4-280-91.
(2) Lanthanum La-0, TA 48-4-529-90.
(3) Cerium CeE-0, TA 48-4-529-90.
(4) Nickel N-0, N-1, N-1u, State Standard (SS) 123-78.
(5) Cobalt K-0, K-1, SS 123-78.
(6) Iron OO8JR, OO5JR, TA 14-1-2033-87.
(7) Aluminium, pure, TA 6-09-3742-87.
(8) Manganese Mr-0, SS 6008-90.

The laboratory fusions were performed in an arc furnace with tungsten nonspending electrode in an atmosphere of purified argon under normal pressure. Ingots were melted in a hole-type copper water-cooled crystallisor.

The mass of each ingot was 80–100 g. In order to achieve even bulk distribution of the components each ingot was remelted 4–5 times. The masses of industrial ingots were 40–50 kg and they were prepared in a universal introduction furnace UPPF-3M in a padded magnesite crucible in an argon atmosphere under a pressure of 0.5 atm. At first, the alloying mixture of nickel, cobalt and iron was melted. After that anthanum and cerium were added from the furnace loading apartment into the melting bath. The melt prepared in this way was poured off into the chink-type copper water-cooled hearth with a chink width of about 40 mm.

The chemical analysis of the chosen samples of the alloys was performed in order to control the alloy's cor-

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respondence to the pre-set composition and to find out the concentration of oxygen, nitrogen and carbon in it. 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. The testing of the metal-hydride accumulators was carried out at the control panel allowing measurement of the hydrogen desorption rate in the pre-set temperature mode and within a regulated pressure range.

RESULTS AND DISCUSSION

The first step of the work was to examine the influence of the preparation method of the alloy on its hydrogen absorption characteristics. 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.% correspondingly.

X-ray analysis showed that the main phase of all of the samples was the hexagonal one of 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$_2$Ni$_7$. Moreover, in sample III this second phase can be found in small quantities. On the contrary, in sample IV its presence is quite distinct.

The investigated alloys absorb hydrogen after the preliminary activation. The absorption is preceded by a induction period, the duration of which is dependent on the phase composition of the alloy. For sample I this period is about 24 h, for samples II and III—6–12 h and for 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, for samples 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 consequent 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
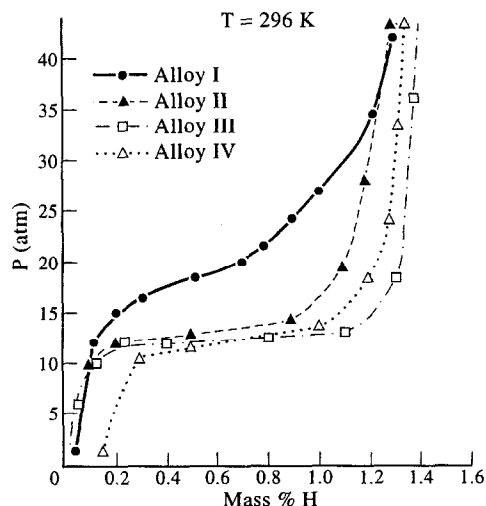

Fig. 1. Desorption isotherms for the system MmNi$_{5\pm\delta}$-H$_2$ at $T = 296$ K.

in 30–60 min and the 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 and 273 K are presented in Figs 1 and 2 and the results of the determination of the desorbed hydrogen quantity and the equilibrium desorption pressure in different cycles 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 IV desorbs about 1.25 mass.%H$_2$. This can be connected with the fact that in the hydriding reaction of the second R$_2$Ni$_7$ phase, found in the samples III and IV, the product is X-ray amorphous which does not desorb hydrogen in the experimental conditions [1, 2]. This leads to the difference between the quantities of hydrogen absorbed in the first cycle and that 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

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

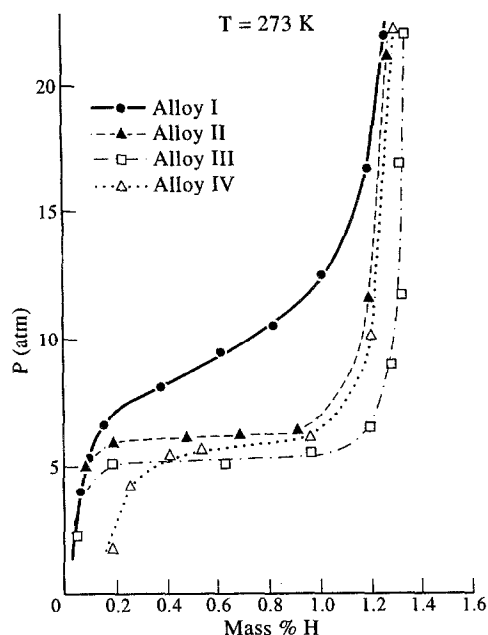| Sample no.	Surplus Mm in schist, mass.%	Phase composition	P_{des} atm, at 0.69 mass.%H$_2$	Mass.%H$_2$ under under $P_{abs} = 50$ atm	Reversible hydrogen capacity mass.%
I	1	MmNi$_5$ + (traces) Ni	20.0	1.41	1.34
II	5	MmNi$_5$	13.5	1.36	1.34
III	10	MmNi$_5$ + (traces) Mm$_2$Ni$_7$	12.6	1.43	1.39
IV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

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

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
	13	20.0	1.34
II	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

12.6 in the fourth cycle, for sample IV—from 11 to 13 atm in the fifth cycle (Table 2).

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 that 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 MmNi$_{5+\delta}$ and sample III, belonging to another boundary composition MmNi$_{5-\delta}$. Then, as it was for 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 practically change. Some alteration to this fact can be possibly explained by the presence of the second R$_2$Ni$_7$H$_x$ phase. The analogous dependence is calculated from the isothermal data thermodynamic parameters for the MmNi$_5$-H$_2$ system (Table 3). The absolute values of the reaction enthalpy ΔH increase in the row: sample III > sample II > sample I. It seems 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 better correspond to the results published in [4, 5].

So, our investigations showed that in the system MmNi$_{5\pm\delta}$-H$_2$ the deficiency in mischmetal leads to the deterioration of working parameters—the increase of the induction period, slow rate of first hydrogen absorption, the necessity of a large number of "absorption–desorption" cycles for the establishment of the constant desorption pressure in the "plateau" region. The optimal surplus quantity if mischmetal for the preparation of alloys is about 5 mass.% that corresponds to the final composition of MmNi$_{4.95}$. A larger amount of mischmetal leads to the appearance of the second phase and to a decrease of the reversible hydrogen capacity.

In the course of the investigation we determined the set of alloys Mm–La(Ce)–Ni–(Fe,Mn,Al,Co) with altering values of equilibrium hydrogen desorption pressure. The analysis of the samples chosen from different parts of the industrially prepared ingots showed a high degree of equality of the bulk component distribution and the composition fully corresponded to the stoichiometric one. Simultaneously the analysis of the oxygen, nitrogen and carbon admixture presence was held. About 20 industrial ingots were analysed and it was stated that the concentration of oxygen in ingots changes from 0.02 to 0.07 mass.% and the concentration of nitrogen does not exceed 0.003 mass.%. On the contrary, quite unex-

Table 3. Thermodynamic parameters for the system MmNi$_{5\pm\delta}$-H$_2$ at the "plateau" region

Sample No.	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]

pectedly, we found a rather large scattering of carbon admixture concentration, which, as it has been revealed later, influences mostly the absorption parameters of intermetallics. The minimum concentration of carbon was about 0.03 mass.% and the maximum was about 0.23 mass.%. A detailed investigation of the starting alloys showed that the cause of the carbon soiling of intermetallics was mischmetal in which even in one lot the concentration of carbon in different ingots can differ from 0.07 to 0.7 mass.%. This content is not regulated by the technical arrangement.

As an example, in the present work we will discuss in more detail the properties of the alloys, for which a production technology was developed and which still are rarely described in literature, namely the alloys with high dissociation pressure.

Figure 3 shows the P-C-isotherms for the system $Mm_{0.8}La_{0.23}Ni_{4.75}Fe_{0.25}-H_2$ in the range of temperatures 273–323 K. As can be seen from Fig. 3 the equilibrium desorption pressure is about 7 atom at 295 K and the hydrogen concentration in the alloy reaches the value of $H/AB_5 = 6.4$ (1.47 mass.%) under a pressure of 40 atm. The desorption "plateau" slope corresponding to the change of the hydrogen concentration $\Delta(H/AB_5) = 5.8$ (1.33 mass.%) is about 1 atm. This alloy has a narrow α-region (about 0.1 H/AB_5) so the quantity of the reversibly accumulated hydrogen is about 6.2 H/AB_5 (1.4 mass.%) corresponding to the decrease of pressure down to 5 atm.

From isothermal data the dependence of $\ln P$ from reciprocal temperature was determined to be: $\ln P = -2912/T + 11.87$, where P is the equilibrium desorption pressure (atm), T—experimental temperature
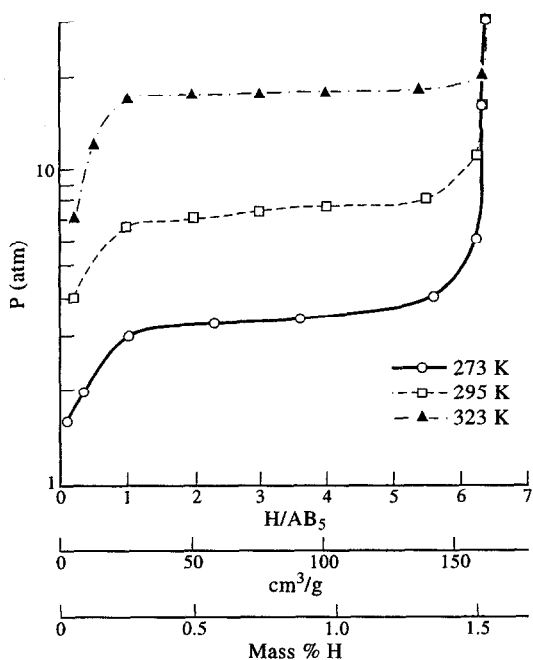
(K) and the thermodynamic functions for the hydrogen desorption in the region of $\alpha \Leftrightarrow \beta$ transition were calculated, $\Delta H = 24.1$ kJ/molH_2, $\Delta S = 98.3$ J/K $\cdot$ molH_2.

Figure 4 shows the kinetic curve for the interaction of hydrogen with $Mm_{0.8}La_{0.23}Ni_{4.75}Fe_{0.25}$ under a pressure of 30–40 atm. It is clearly seen that about 90% of hydrogen is absorbed during the first 10 minutes. In the case of additional cooling, the rate of absorption can be increased several times.

The isotherms of desorption for other investigated alloys are shown in Figs 5 and 6.

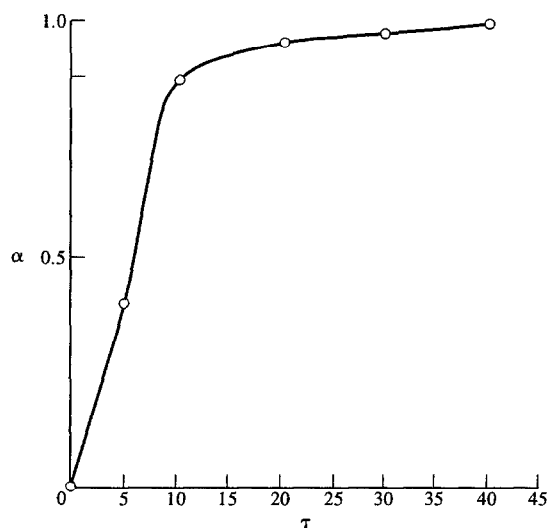In the course of the work it appeared that some alloys

Fig. 4. Kinetic curve of hydrogen interaction with $Mm_{0.8}La_{0.23}Ni_{4.75}Fe_{0.25}$.

Fig. 3. Desorption isotherms for the system $Mm_{0.8}La_{0.23}Ni_{4.75}Fe_{0.25}-H_2$ at 1–273 K, 2–295 K, 3–323 K.
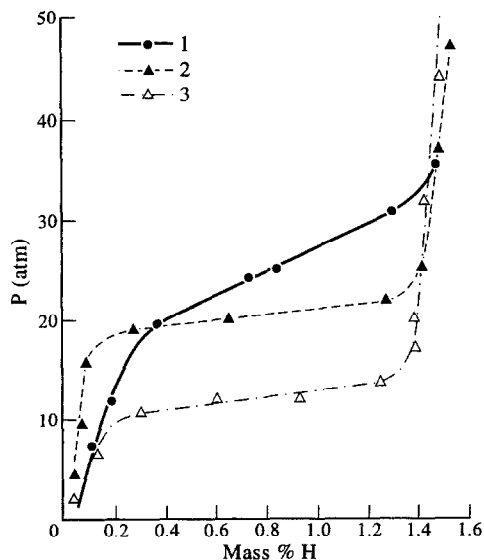

Fig. 5. Desorption isotherms at 296 K for the systems: (1) $Mm_{0.8}Ce_{0.2}Ni_{4.48}fe_{0.4}Co_{0.3}-H_2$; (2) $Mm_{0.9}Ce_{0.2}Ni_{4.7}Co_{0.3}-H_2$; (3) $Mm_{0.9}Ce_{0.2}Ni_{4.8}Fe_{0.2}-H_2$.
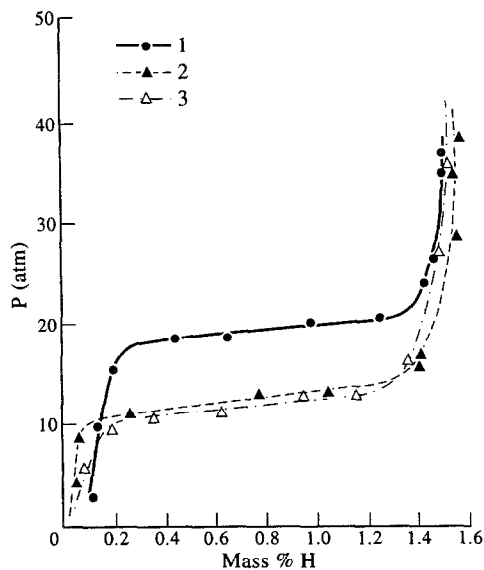
Fig. 6. Desorption isotherms at 296 K for the systems: (1) $Mm_{0.9}Ce_{0.2}Ni_{4.44}Fe_{0.06}Co_{0.5}$-$H_2$; (2) $Mm_{1.1}Ni_{4.9}Fe_{0.1}$-H_2; (3) $Mm_{0.8}Ce_{0.3}Ni_{4.85}Cr_{0.15}$-$H_2$.
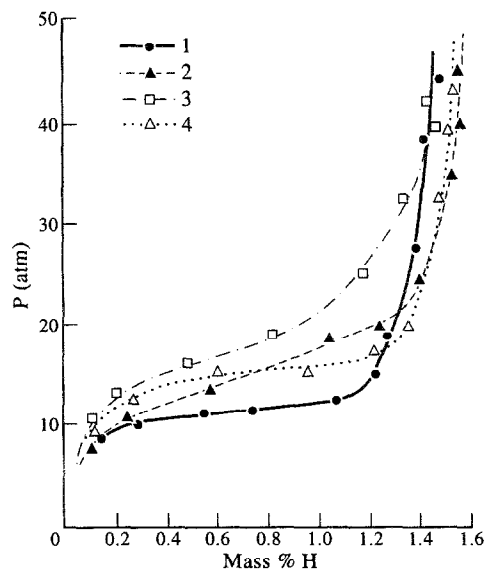

Fig. 7. Desorption isotherms for industrial alloys at 296 K: (1) alloy no. 3; (2) alloy no. 4; (3) alloy no. 5; (4) alloy no. 6.

of the same composition which were prepared at different times to obtain some statistical data do not behave equally. Some of them became activated only under rather high pressure and possessed different hydrogen capacity and different equilibrium hydrogen desorption pressure. The chemical analysis of these alloys showed that the concentration of carbon in them is considerably higher compared to other alloys. As it was stated earlier in this work, it appeared that carbon is drawn in the alloy from mischmetal in some lots of which the carbon concentration reached the value of 0.7 mass.%. Because of that, we carried out an additional investigation to determine the degree of influence of carbon and the possibility of its extraction from alloys in the form of titanium carbide. We prepared the set of Mm–Ce–Ni–Fe alloys with additions of cobalt and titanium. The desorption isotherms for some of the studied alloys are shown in Fig. 7.

All alloys (Fig. 7) have a large hydrogen capacity and are characterised by high dissociation pressures in the "plateau" region. The experiments showed also that small additions of cobalt help to conclude the activation process of mischmetal alloys with low carbon content quicker and under lower P,T-conditions. The characteristics of these alloys are presented in Table 4. The data in Table 4 allows one to see that with the increase in carbon content in mischmetal (and in alloy correspondingly) the pressure at the "plateau" region and the pressure needed for the activation process also increase. So, one can draw a conclusion that sufficiently low P,T-conditions of activation process can be guaranteed only for those alloys in which carbon concentration does not exceed 0.1 mass.%. It is possible that carbon

contained in mischmetal introduces into the interstitial sites of the crystal cell and blocks the centres of activation of the molecular hydrogen dissociation. Such a conclusion was drawn also in Ref. [6] where the authors stressed that hydrogen atoms occupy tetrahedral sites and the addition of oxygen, nitrogen and carbon placed in the octahedral sites of the hydride lattice begin to block the placement of hydrogen in the nearest neighbour tetrahedral sites. Yet, it is hard to simply conclude on the influence of titanium on the properties of carbon-containing alloys. As can be seen from the data in Fig. 7 and Table 4, at a concentration of carbon in mischmetal of about 0.1 mass.%, titanium expresses a considerable influence on the properties of alloys, the activation parameters soften and the equilibrium dissociation pressure in the "plateau" region decreases. At a concentration of carbon in mischmetal of about 0.7 mass.%, small additions of titanium do not show a profound influence, the hydriding reaction begins under pressures of 70–80 atm and the equilibrium dissociation pressure in the "plateau" region also stays rather high. Possibly at such high concentrations of carbon one must add larger quantities of titanium.

Using the thermodynamic data obtained for the investigated systems and the measured rates of absorption and desorption, we constructed several pilot metal-hydride accumulators and performed tests. On the base of results obtained in these tests a serial sample of the module type hydrogen accumulator was worked out and the design and technological documentation was prepared.

The technical parameters of the typical module type metal-hydride accumulator are presented in Table 5 and Fig. 8 shows its general plan.

This module is designed as a hermetic multisectional

Table 4. The characteristics of the industrially produced alloys

| No. | Mm | Ce | Alloy composition, mass.% | | | Ti | Carbon in Mm, mass.% | Carbon in alloy, mass.% | Initial hydriding pressure, atm |
			Ni	Co	Fe				
1	30.52	3.24	60.96	5.45	0.71	—	0.35	0.12	90
2	30.0	3.24	61.1	4.5	0.8	0.8	0.7	0.21	70–80
3	30.0	3.24	61.1	4.5	0.8	0.8	0.075	0.05	35
4	30.0	3.24	61.1	4.5	0.71	—	0.15	C–0.05 O_2–0.02 N_2–0.001	50
5	30.55	3.24	60.88	4.09	2.13	—	—	0.03–0.04	40
6	30.52	3.24	60.96	5.45	0.71	—	0.15	0.06	50
7	30.52	3.24	60.96	5.45	0.71	—	0.2	0.08	50
8	30.52	3.24	60.96	5.45	0.71	—	0.7	0.2	70–80
9	30.52	3.24	61.1	4.5	0.71	0.17	0.15	< 0.15	50

Table 5. Technical characteristics of the typical metal-hydride accumulator module

|	
Hydrogen outlet pressure in discharge mode (MPa)	0.5–5.5
Module working hydrogen capacity	
—absolute (STPm^3)	9.4
—specific mass (%)	1.13
—specific volume (STPm^3/m^3)	620
Purity of discharged hydrogen (%)	⩾ 99.999
Maximum stationary flow rate in discharge mode (1/s)	⩾ 20
Working temperature range (°C)	0–32
Hydrogen pressure in charge mode (MPa)	35
Charging time (h)	⩽ 3
Guaranteed number of chargings (without loss of capacity)	⩾ 150
Module mass (kg)	74
Alloy mass in module (kg)	58
Alloy type	Mm–Ce(La)–Ni–Fe
Module dimensions (mm)	
—diameter	75
—length	3870
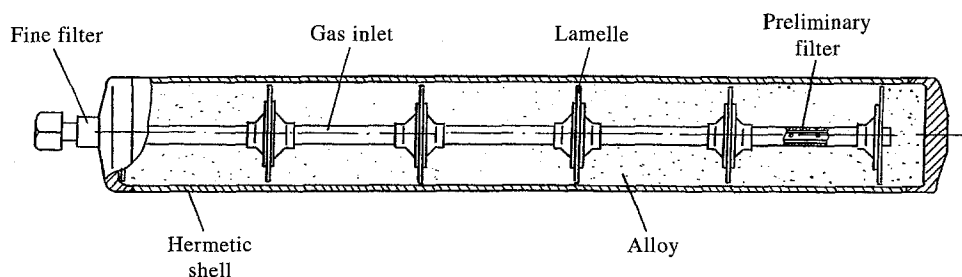
Fig. 8. Module of the hydrogen accumulator.

shell filled with hydrogen absorbing alloy powder. The module is placed in an outer shell with water inlet and outlet. The heating and cooling of the module is controlled by the change of the circulating water tempera-ture. On the basis of the typical hydrogen accumulator one can work out different kinds of accumulators with altering hydrogen capacity, apparatus for molecular puri-fication of hydrogen and for hydrogen utilisation in elec-

trolytic devices, hydrogen compressors without moving parts and hydride refrigerators.

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