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Research on compressor utilizing hydrogen storage materials for application in heat treatment facilities

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ABSTRACT

The design of hydrogen compressor utilizing hydrogen storage alloys for application in heat treatment facilities is presented. This compressor working between 0.02 and 3.3 MPa could be an alternative for a mechanical compressor. In laboratory experiments, a model of the hydride compressor was used (scale 1:13). The compressor model uses $LaNi_{4.8}Sn_{0.2}$ (45 kg) and $LaNi_{4.25}Al_{0.75}$ (3.5 kg) alloys closed in two separate containers equipped with heat exchangers. The alloys were being heated and cooled by oil flowing through the containers. It was noticed that penetration of hydrogen to the alloy bed situated in the lower part of the containers was not sufficient. The experiments have shown a high efficiency of heat exchangers mounted in the container with $LaNi_{4.8}Sn_{0.2}$ (finned tubes) and too small efficiency of heat exchangers mounted in the container with $LaNi_{4.25}Al_{0.75}$ (smooth tubes). The initial research of the stability of alloys subjected to many hydrogen absorption-desorption cycles (207 cycles) was carried out for 0.3–3.3 MPa pressure range ($LaNi_{4.8}Sn_{0.2}$ at 310–450 K) and 0.02–0.3 MPa ($LaNi_{4.25}Al_{0.75}$ at 315–410 K). The desorption isotherm for $LaNi_{4.8}Sn_{0.2}$ at 293 K was also determined.

The experiments revealed that energy losses were too high to use the hydride compressor instead of a mechanical compressor in an industrial application. Reducing energy loss would be the most important point of further research.

1. Introduction

In the literature related to metal hydrides, various materials are proposed for hydrogen storage with possible application for hydrogen compression [1–5]. By using two or more metal hydrides working in a different pressure range, it is possible to compress hydrogen from a very low pressure (e.g. 0.00013 MPa—ZrNi alloy [2]) to a high pressure (40 MPa—hydrides of $MmNi_5$, $LaNi_5$ (AB_5), TiFe [1,3]). During absorption and desorption of hydrogen, it is necessary to cool or heat alloys to reach and sustain temperature of these alloys corresponding to the required equilibrium pressure. From a practical point of view, a metal hydride compressor should use minimal number of alloys of different types working in a similar range of temperature (possibly slightly higher than the ambient temperature). It is also important to achieve fast kinetics of absorption and desorption and to have a possibility of carrying out many absorption–desorption cycles without significant changes in work parameters of the compressor.

In most of applications involving in hydrogen compression or hydrogen storage, the alloys absorbing hydrogen are in the form of powder with particle size about several μm. The alloys in the form of such fine powders are characterized by a low value of heat transfer coefficient [6]. In case of $LaNi_5$ type alloys, the kinetics of hydrogen absorption and desorption in practical applications are indeed determined by the velocity of heat transfer [6]. If fast kinetics are required we have to assure effective heat transfer between the alloy and a heat transfer medium. The literature related to hydrogen storage applications describes usually a solution where the heat transfer fluid flows through tubes [7,8] or fluid mantel [9] situated in the container with a storage alloy. Aluminum foams [7,10], meshes, fins [11] and binders [9] (e.g. graphite binder) are used to enhance the heat transfer.

The aim of our investigations was to verify if it is possible to build an industrial compressor based on metal hydrides which could be used in the hydrogen recycling system connected to the hardening furnace. The technology using gas as a quenching medium is rapidly developing in recent years. Gas quenching under high pressure is an alternative for quenching methods based on liquids, e.g. oils, liquid polymers, water, water solutions and fluid beds. The use of gas instead of liquid as a quenchant has many advantages and the most important of these are environmental and product quality benefits (distortion reduction). The evolution of gas quenching technology is also connected with the development of vacuum carburizing and an easy combination of both technologies.

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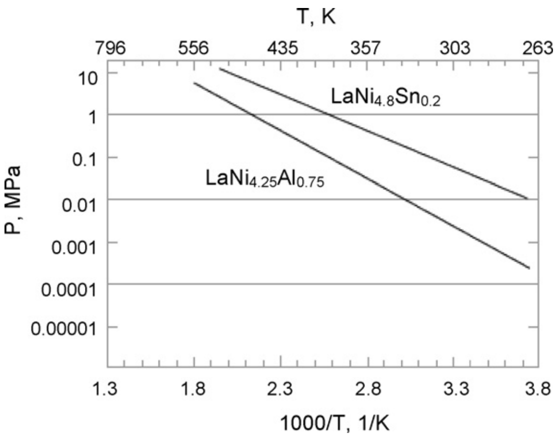

Fig. 1. Van't Hoff plots for $LaNi_{4.8}Sn_{0.2}$ and $LaNi_{4.25}Al_{0.75}$ [17,18].

The gas with the highest cooling capacity is hydrogen (quenching in hydrogen is approximately two times more effective than in nitrogen—mostly used today). However, due to high flammability of hydrogen, its storage and release to the atmosphere can be dangerous. Therefore, the application of hydrogen would require cost-effective use of gas recycling system and appropriate safety measures.

Metal hydride compressors which are characterized by simple construction, require very little maintenance and can operate almost unattended, seem to be a very good solution for safety use of hydrogen for quenching.

For testing purpose, we designed the installation simulating the work of an industrial hydride compressor. The scale of this installation in comparison with a compressor needed for hardening furnace is 1:13.

The hydrogen compressor, the main elements of which would be alloys reversibly absorbing hydrogen should be characterized by parameters (velocity of gas compression, life time) and the cost of exploitation comparable with or better than those of mechanical compressors. The initial estimation shows that the price of the hydride compressor needed for a hydrogen recycling system would be lower than the price of an adequate mechanical compressor (the price of hydrogen storage alloys is about three or four times lower than the price of mechanical compressors). From the economical point of view, the most critical parameter of employing hydrides in the aforementioned application is the energy consumption of the hydride compressor.

2. Experimental details

2.1. Hydride compressor model

The model of an industrial compressor uses two alloys: $LaNi_{4.8}Sn_{0.2}$ (45 kg) and $LaNi_{4.25}Al_{0.75}$ (3.5 kg) manufactured by Treibacher Industrie AG, Austria. These alloys, similar to $LaNi_5$ are characterized by very fast kinetics of absorption and desorption [12–15], a moderate value of reaction enthalpy (32.8 kJ/mol for $LaNi_{4.8}Sn_{0.2}$ [16] and 44.1 kJ/mol for $LaNi_{4.25}Al_{0.75}$ [17]) and temperatures of ab- and desorption convenient from the technological point of view. Fig. 1 shows pressure–temperature characteristics (Van't Hoff plots) of $LaNi_{4.8}Sn_{0.2}$–H_2 and $LaNi_{4.25}Al_{0.75}$–H_2 systems.

The main elements of the experimental installation are two alloy containers, an oil container equipped with heating elements, six cylinders for hydrogen (40 l each), an oil pump, a heat exchanger (water–oil) and temperature, pressure and oil flow sensors. Inside alloy containers, eleven tubes through which the oil (hot or cold) was flowing were mounted. The container no. 1 with $LaNi_{4.8}Sn_{0.2}$ (45 kg of alloy) was supplied with finned tubes, while the container no. 2 with $LaNi_{4.25}Al_{0.75}$ (3.5 kg) was equipped with plain, smooth-walled tubes. Heat exchange was conducted also by means of an oil mantle along the walls of the containers.

During the absorption process, oil was flowing through the water–oil heat exchanger where it was cooled by water whose temperature was 288–298 K (15–25). During desorption, oil was heated in the oil container. A schematic view of the experimental installation is presented in Fig. 2. Hydrogen gets inside the containers through a porous filter tube (pore size ≤0.5 μm). The construction of the container with $LaNi_{4.8}Sn_{0.2}$ alloy is shown schematically in Fig. 3.

Our research model was used for simulation of the work of the compressor connected to the industrial furnace. Starting from the situation after quenching where the hydrogen pressure inside the furnace chamber is 1.6 MPa, the industrial hydride compressor should be working according to the following scheme:

- absorption of hydrogen from the chamber by $LaNi_{4.8}Sn_{0.2}$;
- absorption of remaining hydrogen from the furnace by $LaNi_{4.25}Al_{0.75}$;
- transfer of hydrogen from $LaNi_{4.25}Al_{0.75}$ to $LaNi_{4.8}Sn_{0.2}$ (desorption from $LaNi_{4.25}Al_{0.75}$ and absorption by $LaNi_{4.8}Sn_{0.2}$);
- hydrogen desorption from $LaNi_{4.8}Sn_{0.2}$ to the buffer container to obtain 3.3 MPa.

The above steps will be repeated after every quenching. It is particularly important to achieve a short time of hydrogen absorption from the furnace.

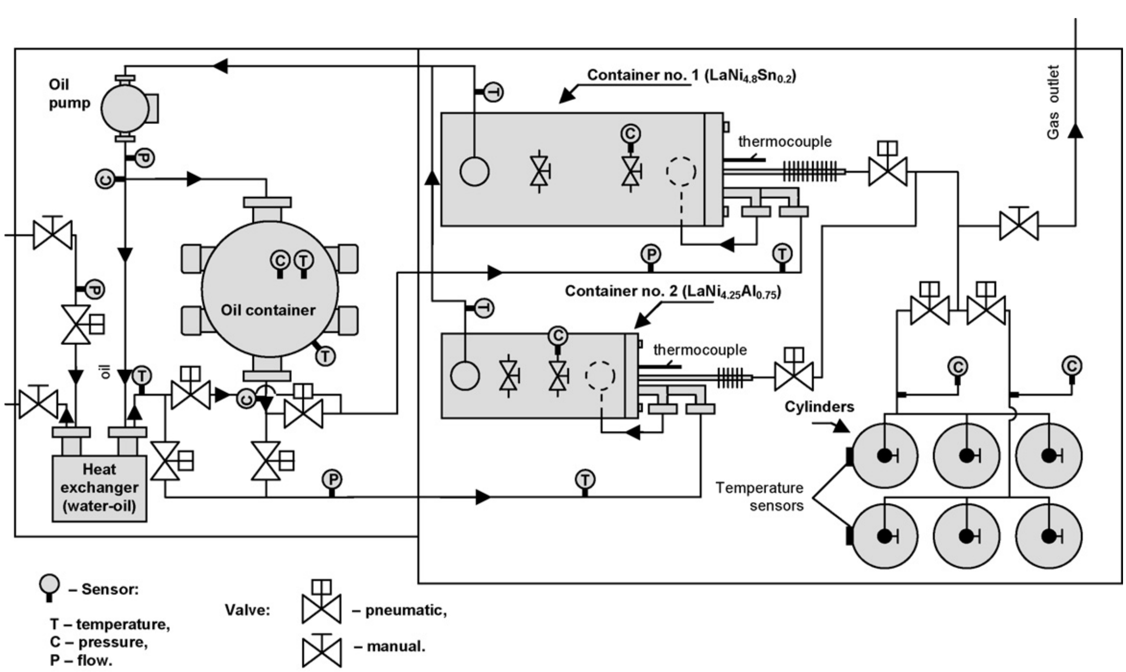

Fig. 2. Schematic view of experimental installation.

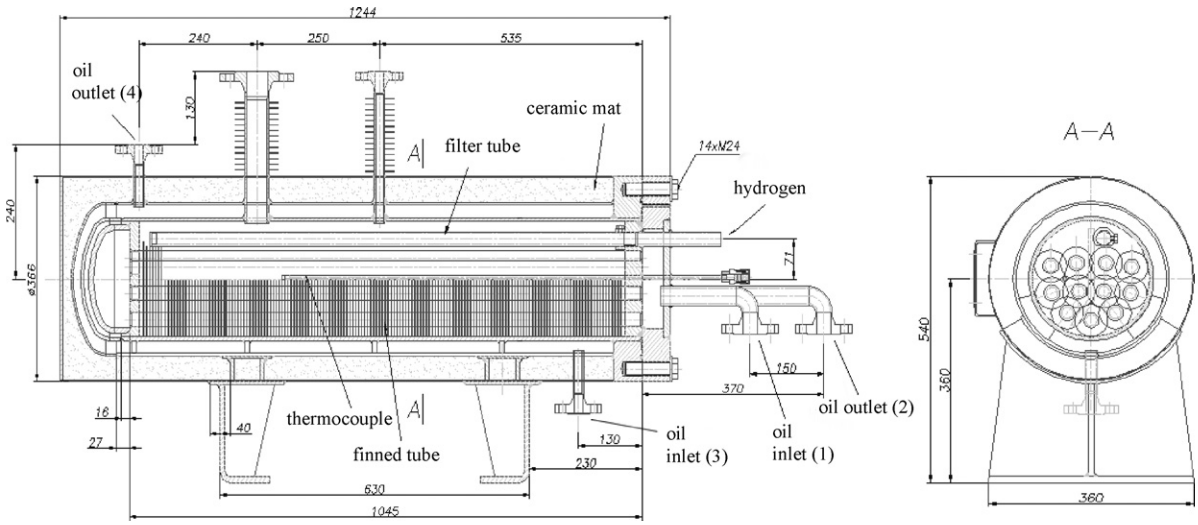

Fig. 3. Schematic view of container 1 (for $LaNi_{4.8}Sn_{0.2}$).

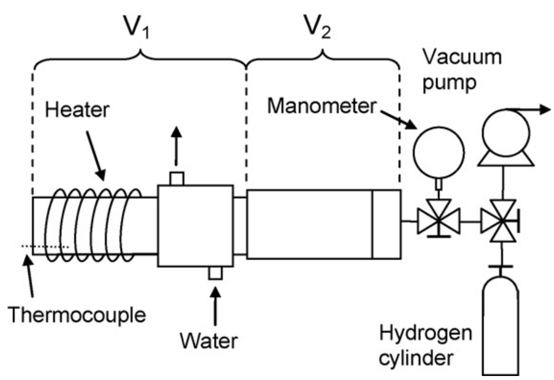

Fig. 4. Alloy cycling installation.

2.2. Cycling the alloys

For both alloys used in the compressor model, we carried out 207 cycles of absorption and desorption of hydrogen the purity of which was 99.99% H_2. The device which was used for cycling the alloys is presented in Fig. 4. The experiments were conducted for 10 g of each alloy (the samples were placed in V_1 volume). The alloys were working under pressure and temperature conditions similar to those used in the compressor model. However, in this case the alloys were being saturated in the higher degree. Saturation of $LaNi_{4.8}Sn_{0.2}$ after every absorption reached approximately 75% of the maximum load (4.77 H/$LaNi_{4.8}Sn_{0.2}$). During desorption, the alloy was heated to 453.90 K and the pressure increased to 3.15 MPa. The $LaNi_{4.25}Al_{0.75}$ alloy was saturated in 81% (3.75 H/$LaNi_{4.25}Al_{0.75}$) and the highest desorption temperature reached 413.15 K.

Table 2
Hydrogen storage capacity of $LaNi_{4.8}Sn_{0.2}$ and $LaNi_{4.25}Al_{0.75}$ effectively used in the experiments.

	H/M[a]	% max.	wt.%
$LaNi_{4.8}Sn_{0.2}$	2.91	45.7	0.66
$LaNi_{4.25}Al_{0.75}$	2.73	59.2	0.67

[a] M—$LaNi_{4.8}Sn_{0.2}$ or $LaNi_{4.25}Al_{0.75}$.

3. Results

3.1. Hydride compressor model performance

Using the compressor model, simulation of the industrial compressor performance was carried out. Table 1 shows average results (except pressure values for absorption which are exact) obtained during simulation.

The results confirm that the reduction of hydrogen pressure from 1.65 MPa (value required for quenching) to 0.02 MPa due to hydrogen absorption will last no longer than 30 min. Since in container 2 plain smooth tubes were mounted, the heating and cooling of $LaNi_{4.25}Al_{0.75}$ proceeded significantly slower than in case of $LaNi_{4.8}Sn_{0.2}$. Influence of insufficiently effective heat exchangers in container 2 was particularly noticeable at stage 4 whose average duration was 111 min (Table 1). The absorption pressure values (for both alloys) given in Table 1 are the minimal values reached during the simulation of the industrial compressor. In every subsequent process, the end pressure for absorption was higher and higher. It was probably caused by particle decay and tamping down

Table 1
Pressures and times of processes obtained for the compressor model.

Nr	Stage	Time (min)	Container no. 1		Container no. 2		Buffer container[a]		Furnace	
			P (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)
1	After quenching								1.65	296.52
2	Absorption for $LaNi_{4.8}Sn_{0.2}$–H	15	0.25	311.85					0.25	299.95
3	Absorption for $LaNi_{4.25}Al_{0.75}$–H	15			0.02	324.45			0.02	299.65
4	Desorption for $LaNi_{4.25}Al_{0.75}$–H; absorption for $LaNi_{4.8}Sn_{0.2}$	111	0.26	300.58	0.26	409.95				
5	Desorption for $LaNi_{4.8}Sn_{0.2}$	63.5	3.30	447.30			3.30	300.05		
6	Cooling of $LaNi_{4.8}Sn_{0.2}$	16.5		308.15						
	Whole cycle	221								

[a] Buffer container and furnace denote cylinders simulating volumes of buffer container and furnace.

Table 3
Energy input and output for the container 1 ($LaNi_{4.8}Sn_{0.2}$)—the comparison of results obtained by different methods of calculation.

Calculation method		Absorption			Desorption		
		$(T_{end} - T_{start})$ (K)	Energy (kJ)	V_{H_2} [a] (m^3)	$(T_{end} - T_{start})$ (K)	Energy (kJ)	V_{H_2} (m^3)
1 Calculations based on pressure and temperature of hydrogen and temperature of alloy		−0.5	−5515.5	3.48	158.2	29504.8	3.58
2 Calculations based on flow and temperature of oil			−7993.5			35008.5	
3 Work performed by heat elements and oil pump	Pump		3206.5			5786	
	Heat elements		0			45270	

[a] V_{H_2}: volume of hydrogen absorbed/desorbed (normal conditions).

Table 4
Energy input and output for the container 2 ($LaNi_{4.25}Al_{0.75}$)—the comparison of results obtained by different methods of calculating.

Calculation method		Absorption			Desorption		
		$(T_{end} - T_{start})$ (K)	Energy (kJ)	V_{H_2} (Nm^3)	$(T_{end} - T_{start})$ (K)	Energy (kJ)	V_{H_2} (Nm^3)
1 Calculations based on pressure and temperature of hydrogen and temperature of alloy		11.2	−98.58 (−507.04)	0.26	111	4533.39	0.25
2 Calculations based on flow and temperature of oil			−570.06			30933.7	
3 Work performed by heat elements and oil pump	Pump		3065.7			7360.1	
	Heat elements		0			34488	

of the alloy. This resulted in more and more difficult saturation of the alloy placed in the lower part of the containers. The pressure value requested in the buffer container (stage 5) was reached in 63.5 min. The whole cycle lasted 3 h and 40 min.

An important issue from a practical point of view is effective usage of the hydrogen storage capacity for both alloys (Table 2). Since lower parts of the $LaNi_{4.8}Sn_{0.2}$ alloy remained unsaturated, the average saturation of $LaNi_{4.8}Sn_{0.2}$ was lower than it was assumed during the planning stage (the highest saturation after 30 min of absorption was 62.6% max., 0.90 wt.%). As a result $LaNi_{4.25}Al_{0.75}$ was being saturated in the higher degree than it was assumed (58.2% max.; 0.66 wt.%; 35 min) (after absorption by $LaNi_{4.8}Sn_{0.2}$ the hydrogen pressure was higher than it was anticipated).

The loss of hydrogen in the cycle described in Table 1 (the percentage of hydrogen which would remain in the furnace chamber and would be released to the atmosphere) was below 1.5% of the total amount of hydrogen in the installation.

3.1.1. Energy consumption

To determine the amount of the energy necessary for the compressor operation, three methods of calculation were used. The results are shown in Tables 3 and 4. Calculations were carried out by the following methods:

(1) Calculations of the energy based on the quantity of hydrogen absorbed. Temperature changes of alloys and container nos. 1 and 2 were taken into account.
(2) Estimations of the heat exchanged between oil and the alloy containers.
(3) Calculations of the work done by the oil pump and heating elements.

From the results obtained for the compressor model, the energy necessary for the use of the industrial compressor can be estimated. We assume that the industrial compressor requires approximately 720 kg of $LaNi_{4.8}Sn_{0.2}$ and 105 kg of $LaNi_{4.25}Al_{0.75}$. The energy required solely for desorption for the industrial compressor would amount approximately to 560 MJ. This value is very high in comparison with energy consumption of a mechanical compressor working in a similar range of pressures. The significant part of the 560 MJ value required for desorption is the energy needed for heating the container with the alloy and the heat released by oil to the ambience. The energy of reaction and the energy necessary for heating $LaNi_{4.8}Sn_{0.2}$ to the desired temperature amount only to 137 MJ. After estimations based on values shown in Tables 3 and 4, we assumed that the whole energy required to conduct a cycle of hydride compressor work would be at least 270 MJ (the energy of desorption, heating of alloys and the work of the oil pump). This value is still high but to minimize energy consumption of hydride compressor it is possible to utilize the heat whose great amount is lost in heat treatment plants.

3.2. PCT isotherm for $LaNi_{4.8}Sn_{0.2}$–H_2

Before testing the compressor model, we measured the isotherm for the $LaNi_{4.8}Sn_{0.2}$ alloy manufactured by Treibacher Indusrie AG. The isotherm was determined for activated alloy. The isotherm measured for $LaNi_{4.8}Sn_{0.2}$ (Fig. 5) was slightly more sloping in the

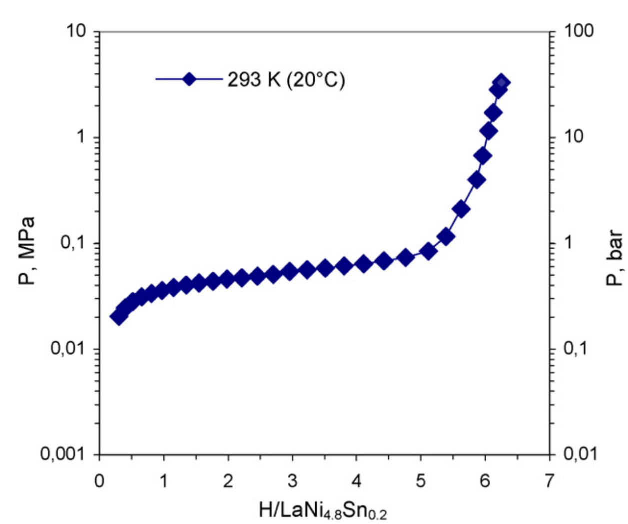

Fig. 5. Desorption isotherm for $LaNi_{4.8}Sn_{0.2}$ measured at 293 K.

Table 5
Results obtained during thermal cycling of $LaNi_{4.8}Sn_{0.2}$ (207 cycles).

Cycle number		*P* (MPa)	*T* (K)	$H/LaNi_{4.8}Sn_{0.2}$	% max.
1	Abs.	0.3	311.35	4.73	74.4
	Des.	3.3	454.15	1.6	25.2
2	Abs.	0.3	311.15	4.73	74.4
	Des.	3.3	454.15	1.63	25.6
205	Abs.	0.3	296.05	4.71	74.1
	Des.	2.9	451.65	2.04	32.1
206	Abs.	0.25	310.05	4.81	75.6
	Des.	2.9	453.25	2.05	32.2
207	Abs.	0.26	310.45	4.8	75.5
	Des.	2.8	454.05	2.09	32.9

Table 6
Results obtained during thermal cycling of $LaNi_{4.25}Al_{0.75}$ (207 cycles).

Cycle number		*P* (MPa)	*T* (K)	$H/LaNi_{4.25}Al_{0.75}$	% max.
1	Abs.	0.04	313.15	3.87	83.8
	Des.	0.28	414.35	2.33	50.4
2	Abs.	0.03	315.85	3.91	84.6
	Des.	0.27	413.35	2.39	51.7
205	Abs.	0.02	293.15	4.01	86.8
	Des.	0.26	412.55	2.45	53
206	Abs.	0.06	315.15	3.67	79.4
	Des.	0.25	409.65	2.51	54.3
207	Abs.	0.06	314.05	3.67	79.4
	Des.	0.29	416.35	2.27	49.1

plateau region than the isotherms reported in the literature [5,19]. More sloping plateau is probably caused by a higher composition inhomogeneity of the alloy—the alloy that we used was manufactured in an industrial furnace in the quantity of 45 kg.

3.3. Cycling the alloys

After carrying out 207 cycles of absorption–desorption for $LaNi_{4.8}Sn_{0.2}$, no changes in the hydrogen storage capacity of the alloy were detected. In the final cycles of $LaNi_{4.25}Al_{0.75}$, the absorption pressure was slightly higher than in the initial cycles whereas the pressure of desorption was lower at the end. These results may indicate that a small degradation of $LaNi_{4.25}Al_{0.75}$ occurred. Tables 5 and 6 show the results obtained in the initial and in the final cycles carried out for both alloys.

The degradation in the hydrogen storage capacity connected with formation of the LaH_x and Ni phases is typical of $LaNi_5$ type alloys subjected to many absorption–desorption cycles [20,21]. The X-ray diffraction patterns measured for $LaNi_{4.8}Sn_{0.2}$ and $LaNi_{4.25}Al_{0.75}$ samples after 207 cycles did not reveal any new diffraction peaks or peaks displacement. In the patterns there are no detectable peaks from the LaH_x or Ni phases.

4. Summary and conclusions

This paper presents the test results of the metal hydride compressor model (scale 1:13) to be used in heat treatment facility. The compressor model using $LaNi_{4.8}Sn_{0.2}$ and $LaNi_{4.25}Al_{0.75}$ alloys was used for verifying if the hydride compressor could be employed in a hydrogen recycling system connected to a heat treatment furnace. The results of experiments allow to conclude that hydrogen compression in required for considered application pressure and temperature range is possible and the process is sufficiently fast. The loss of hydrogen in a single cycle of the compressor work was less than 1.5%. The results indicate that the containers for hydrides need further improvements which should take into account modifications ensuring easy access of hydrogen to the whole alloy. Moreover, more effective heat exchangers should be mounted in the containers (especially in case of $LaNi_{4.25}Al_{0.75}$).

In order to reduce energy loss during desorption, some improvements of the heating installation are also required. The waste of energy in case of the compressor model was too high. The energy consumption for the industrial compressor estimated from the test results was significantly higher than the energy consumption of mechanical compressors and must be reduced to make the hydride compressor competitive.

The initial research of the stability of both alloys (207 cycles; 99.99 H_2) revealed practically no changes in the work parameters (pressures, temperatures), in hydrogen storage capacity and in alloy structure.

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