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SCREENING OF HYDROGEN STORAGE MEDIA APPLYING HIGH PRESSURE THERMOGRAVIMETRY

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Abstract

A number of commercially available hydride-forming alloys of the $MmNi_{5-x}Sn_x$ (*Mm*=mischmetal, a mixture of lanthanides) type were examined using a high pressure, high temperature microbalance, scanning electron microscopy and X-ray diffraction. Activation conditions, reversible storage capacity, working pressures and temperatures, sensitivity to impurities, and morphological changes were explored.

Keywords: high pressure gravimetry, high pressure microbalance, hydrogen absorption, hydrogen storage, metal hydride

Introduction

Several mobile hydrogen storage systems for fuelling vehicles are being tested today in various prototype and demonstration projects all over the world. The hydrogen may be stored in a tank either as a pressurised gas, a liquid gas or absorbed in a metal hydride [1–5]. The latter method is one of the safest as in case of an accident the hydrogen will be released only slowly from the tank. Furthermore, the storage efficiency is very high. The method is based on the reaction:

$$M+x/2H_2\leftrightarrow MH_x+Q$$

The reaction is a chemical equilibrium and for many hydride-forming metals or alloys, the equilibrium hydrogen pressure is suitable for practical applications at easily available temperatures, i.e. 0–5 MPa in the temperature range 0–100°C. In accordance with the Phase Rule the p-c isotherms of the above equation exhibit one or more plateaus, where the pressure is more or less constant, but a considerable hysteresis is often found for many real systems, meaning that there is a difference between the absorption and desorption pressure. As part of the Hydrogen Programme under the auspices of the Danish Energy Agency a collaborative project [6] was initiated between the company IRD A/S, the Technical University of Denmark, and Risø National Laboratory. The project was concerned with the development of a hydrogen storage tank based on metal hydrides for a passenger car with a hydrogen fuelled internal combustion engine. In order to characterise storage media that can operate at temperatures provided by the engine cooling system (80–90°C), a number of com-

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mercially available hydride-forming alloys were examined using a high pressure, high temperature microbalance, scanning electron microscopy (SEM) and X-ray diffraction (XRD). This provided knowledge of activation conditions, reversible storage capacity, working pressures and temperatures, hydriding and dehydriding kinetics, and sensitivity to impurities; all properties of crucial importance for the construction of a hydrogen storage tank. The present paper illustrates the characterisation performed at Risø National Laboratory.

Experimental

Literature [7–9] contains information on a range of hydride-forming alloys exhibiting a wide range of equilibrium pressures for the absorption/desorption of hydrogen. A working pressure range of 0.1–5 MPa and a max. temperature of 80°C was desired for the storage tank in question. Accordingly, a number of commercially available hydride-forming alloys were selected for investigation. They are listed in Table 1. They were crushed alloys; all in the form of more or less coarse powders (typical particle size ~100 μm and wide particle size distributions). Figure 4 shows Hydralloy E60/6834 as received.

Table 1 Investigated commercially available hydride-forming alloys. (*Mm*=mischmetal, a mixture of lanthanides)

Alloy type	Commercial code
$MmNi_{5-x}Sn_x$	Hydralloy E60/78*
$MmNi_{4.94}Sn_{0.15}$	Hydralloy E77*
$MmNi_{5-x}Sn_x$	Hydralloy E60/6834*

*From GfE Metalle und Materialien GmbH, Nürnberg, Germany

Activation behaviour, pressure–concentration isotherms, and reversible storage capacity between 0.1 and 5 MPa (in some cases 7 MPa) hydrogen were studied using a high pressure, high temperature ultra microbalance based on a Sartorius 4436MP8 beam type weighing unit; a modernised version of the equipment that has been described in detail previously [10–12]. The sensitivity of the balance was 1 μg in the applied measuring range (100 mg). The gas pressure could be varied between 0 and 7 MPa, controlled within 5 kPa. The total gas volume of the system was 0.4 l. The temperature was controlled from room temperature up to 500°C within 2°C. The stability of the weighing system was examined at room temperature over a period of 7 days during which gas pressure was varied several times between 0.1 and 5 MPa. A zero point drift of max. 2 μg at 0.1 MPa was found. During a heating cycle (room temperature–70°C–room temperature) over 4 days a zero point drift of max. 10 μg at 0.1 MPa was found. Approximately 100 mg samples of the investigated alloys, weighed to an accuracy of 10 μg, were placed in the stainless steel sample crucible (an equal amount of steel pieces in the reference crucible), and the system was evacuated to 13 Pa before the introduction of the hydrogen gas. The applied hydrogen was of 99.9997% purity (N57) supplied by l'air liquide. The main impurities were

$H_2O<2$ ppm, $N_2<0.6$ ppm and $O_2<0.5$ ppm. After each absorption/desorption cycle new gas was introduced so a gradual build-up of contamination could be expected as every cycle introduced the equivalent of 41 μg oxygen. Activation at room temperature and increasing hydrogen pressure was attempted in all cases before activation at elevated temperatures. Though stored in an inert atmosphere prior to investigation the samples were exposed to the ambient during the initial weighing and transfer to the high temperature microbalance.

A JEOL 840 scanning electron microscope was applied to examine the morphological changes in the alloys due to repeated hydrogen absorption and desorption. X-ray diffraction (applying a STOE system) on some of the alloys before and after the cycling in hydrogen was performed in search of phase changes.

Results and discussion

Activation behaviour

Most hydride-forming alloys must be subjected to an activation procedure before a stable and reproducible hydrogen reaction is obtained. The conditions for this initial absorption of hydrogen depend on the alloy and can be very different from the possible working temperature of the storage tank. For some alloys temperatures up to 400°C may be needed. Therefore, knowledge of the activation conditions is very important for the choice of materials and the design of a hydrogen storage tank. From the observed activation behaviour of the investigated alloys, given in Table 2, it is evident that some of the $MmNi_{5-x}Sn_x$ alloys can be activated at room temperature, whereas others need elevated temperatures. According to the alloy supplier all of the selected alloys were to be activated at room temperature. It is possible, though, that this discrepancy was due to excessive passivation of the alloy surface during prolonged storage prior to this investigation.

Table 2 Conditions under which initial absorption of hydrogen occurred in the investigated samples

Alloy	Conditions
$MmNi_{5-x}Sn_x$/Hydralloy E60/78	70°C and 5 MPa H_2 resulted in absorption of 1.28 mass% H_2 in 30 min
$MmNi_{4.94}Sn_{0.15}$/Hydralloy E77	room temperature and 5 MPa H_2 resulted in absorption of 1.36 mass% H_2 in 6 h
$MmNi_{5-x}Sn_x$/Hydralloy E60/6834	at room temperature and 1.6 MPa H_2 absorption occurred after 6 h, but 5 MPa H_2 was necessary for a max. absorption of 1.47 mass%

Hydrogen storage capacity and sensitivity to impurities

The reversible hydrogen storage capacity for the investigated samples at different temperatures were studied by repeated cycling between 0.1 and 5 MPa H_2 (in some cases 7 MPa). The results are given in Table 3. The $MmNi_{5-x}Sn_x$/Hydralloy E60/78

Table 3 Reversible hydrogen storage capacity at different temperatures and permanent mass gains for the investigated samples cycled between 0.1 and 5 MPa H_2

Alloy	Reversible hydrogen storage capacity between 0.1 and 5 MPa hydrogen (N57) observed in the shown order, and permanent mass gain
$MmNi_{5-x}Sn_x$/Hydralloy E60/78	1.29 mass% at 74°C; 1.30 mass% at 56°C; 1.28 mass% at 28°C; 1.26 mass% at 92°C; and finally 1.19 mass% at 26°C after 22 cycles, 11 days at different temperatures and a permanent mass gain of 0.4%
$MmNi_{4.94}Sn_{0.15}$/Hydralloy E77	1.30 mass% at 27°C; 1.26 mass% at 78°C; 1.27 mass% at 72°C; 1.29 mass% at 27°C after 20 cycles, 9 days at different temperatures and a permanent mass gain of 0.2%
$MmNi_{5-x}Sn_x$/Hydralloy E60/6834 I	1.39 mass% at 27°C; <0.03 mass% at 157°C and permanent mass gain of 0.26% in 24 h; <0.04 mass% at 135°C; <0.08 mass% at 105°C; 0.48 mass% at 73°C; 1.02 mass% at 53°C; and finally 1.27 mass% at 25°C after 40 cycles, 20 days at different temperatures and a permanent mass gain of 0.63%
$MmNi_{5-x}Sn_x$/Hydralloy E60/6834 II	10 cycles over 4 days at 25°C caused a drop from 1.32 mass% to 1.28 mass%; 0.71 mass% at 70°C (1.03 mass% by 7 MPa); 0.83 mass% at 62°C (1.15 mass% by 7 MPa); and finally 1.23 mass% at 25°C (1.23 mass% by 7 MPa) after 16 cycles, 24 days at different temperatures and a permanent mass gain of 0.4%

and $MmNi_{4.94}Sn_{0.15}$/Hydralloy E77 alloys exhibited a reversible hydrogen storage capacity of ~1.3 mass% in the temperature range of interest (up to 90°C), whereas the 0.1–5MPa H_2 capacity of $MmNi_{5-x}Sn_x$/Hydralloy E60/6834 was considerably lower at temperatures higher than 50°C. At 0.1 MPa H_2 most alloys contain a small amount of hydrogen as illustrated by the observation of an initial 1.47 mass% H_2 absorption for $MmNi_{5-x}Sn_x$/Hydralloy E60/6834, sample II, at room temperature of which only 1.32 mass% could be cycled between 0.1 and 5 MPa. For all of the investigated samples some loss of hydrogen storage capacity and permanent mass gain during prolonged cycling was noted (Table 3). This was attributed to reaction with impurities (H_2O and O_2) in the applied gas, forming oxides and thereby inactivating part of the alloy. The $MmNi_{5-x}Sn_x$/Hydralloy E60/6834, sample I, exhibited an 8.6% drop in capacity at room temperature from 1.39 mass% at the beginning to 1.27 mass% at the end of the experiment after 40 cycles and 20 days at different temperatures. This was accompanied by a permanent mass gain of 0.63% which could be consistent with the oxidation of ~8% of the Mm content by formation of an MmO_2-type compound. Likewise, for the $MmNi_{5-x}Sn_x$/Hydralloy E60/6834, sample II, showing a capacity decrease at room temperature of 6.8% and a permanent mass gain of 0.4%. Roughly, the permanent mass gains corresponded to reaction with half of the oxygen introduced into the system. This indicated that the alloys readily reacted with impurities.

In every cycle the ratio of hydrogen gas to alloy in our experimental set-up were ~1000 times larger than would be the case in a storage tank. Thus, the investigations applying the microbalance are well suited to do accelerated impurity sensitivity tests.

In an attempt to identify any phase changes XRD was applied to some samples before and after the cycling in hydrogen. The raw alloys consisted of $LaNi_5$ type phase mainly. After cycling in hydrogen some of the samples exhibited traces of new phases. However, these were too minute to be identified with certainty.

Pressure–concentration isotherms

The hydrogen pressure-concentration relationship during absorption and desorption at various temperatures was established for the selected alloys via the high pressure gravimetry. An example is given in Fig. 1 showing the hydrogen content of the alloy

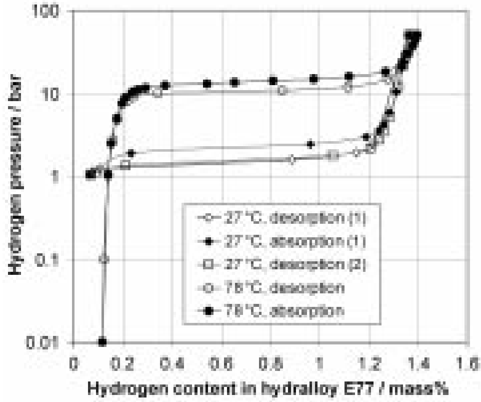

Fig. 1 Hydrogen pressure-concentration relationship for $MmNi_{4.94}Sn_{0.15}$/Hydralloy E77 at 27 and 78°C during absorption and desorption

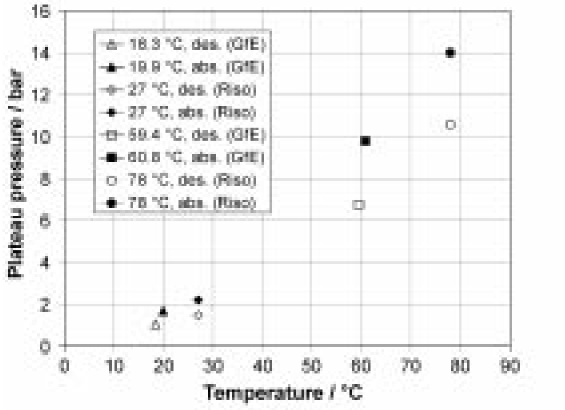

Fig. 2 Plateau pressures as a function of temperature for $MmNi_{4.94}Sn_{0.15}$/Hydralloy E77; data observed in this work (Risø) compared with supplier data (GfE)

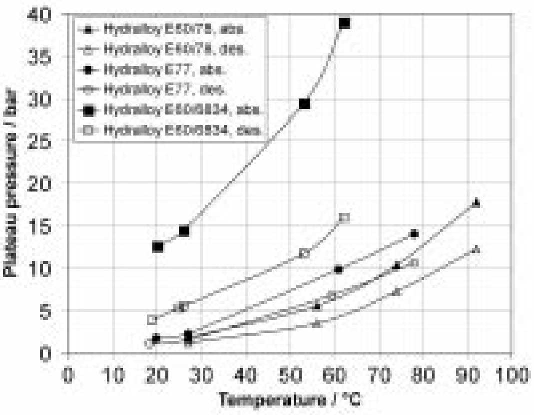

Fig. 3 Plateau pressures as a function of temperature for 3 different $MmNi_{5-x}Sn_x$ alloys

$MmNi_{4.94}Sn_{0.15}$/Hydralloy E77 as a function of the hydrogen pressure at 27 and 78°C during absorption and desorption. The observed plateau pressures (equilibrium pressure at half storing capacity) as a function of temperature for the alloy $MmNi_{4.94}Sn_{0.15}$/ Hydralloy E77 compared with data from the alloy supplier are given in Fig. 2; showing a very good agreement. Generally, the plateau pressures varied with the alloy and a notable hysteresis occurred during absorption/desorption cycling. Figure 3 shows a comparison of the plateau pressure – temperature relations for the investigated $MmNi_{5-x}Sn_x$ alloys.

Morphological changes

SEM micrographs of the samples before and after the exposure to repeated hydrogen absorption and desorption showed that the relatively coarse powders (~100 μm) were broken into very fine particles (~5 μm) exhibiting extended submicrocracking; this was attributed to the mechanical stresses build up in the particles as a result of the dimensional changes associated with the hydriding/dehydriding processes which can be 20–25 vol%. This is illustrated in the case of $MmNi_{5-x}Sn_x$/Hydralloy E60/6834 in Fig. 4 (before) and Fig. 5 and Fig. 6 (after).

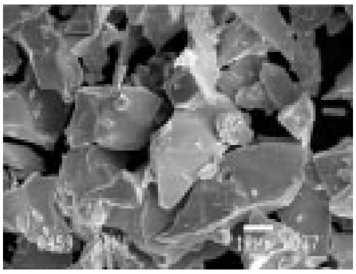

Fig. 4 SEM of $MmNi_{5-x}Sn_x$/Hydralloy E60/6834 before hydriding (bar length: 10 μm)

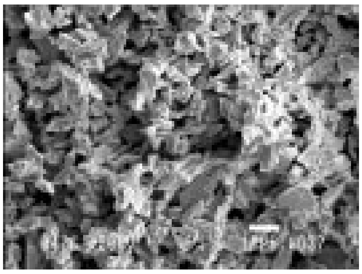

Fig. 5 SEM of $MmNi_{5-x}Sn_x$/Hydralloy E60/6834 after cycling in H_2 (bar length: 10 µm)

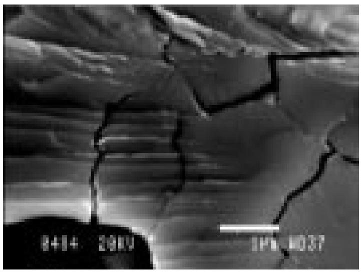

Fig. 6 SEM of $MmNi_{5-x}Sn_x$/Hydralloy E60/6834 after cycling in H_2 exhibiting extended submicrocracking (bar length: 1 µm)

Conclusions

The investigated commercially available hydride-forming alloys of the $MmNi_{5-x}Sn_x$ type could be activated easily for hydrogen storage at temperatures below 75°C and a hydrogen pressure of 5 MPa. They exhibited equilibrium pressures for absorption and desorption of hydrogen in temperature – pressure ranges suitable for application in a storage tank to be operated at temperatures provided by an engine cooling system (80–90°C). The hydrogen storage capacity attainable by cycling between 0.1 and 5 MPa was at maximum ~1.3 mass% and decreased during prolonged cycling. This indicated that the alloys readily reacted with impurities in the hydrogen gas. As the ratio of hydrogen gas to alloy in the applied experimental set-up were ~1000 times larger than would be the case in a storage tank, investigations applying the microbalance are well suited to do accelerated impurity sensitivity tests.

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