Jurnal Teknologi, 35(F) Dis. 2001: 1–10

$MmNi_5$ AND $MmNi_{4.85}Fe_{0.15}$ AS HYDROGEN STORAGE MEDIUM

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Abstract. The characteristics of $MmNi_5$ and $MmNi_{4.85}Fe_{0.15}$ in storing hydrogen gas were examined in this study. The absorption capacity of the metal was monitored under the influence of temperature and pressure. Due to the limitation on its operating conditions, the range of the temperature chosen was from 298K to 323K while pressure was varied from 2 to 30 bar. Study conducted on $MmNi_5$, showed that the amount of hydrogen absorbed was inversely proportional to the operating temperature. In the study of $MnNi_5$ the maximum absorption was achieved at 298K and exhibited the plateau pressure of 10 bar. The hydrogen content was expressed as weight and the value was calculated to be at 1.20 wt%. As for $MmNi_5$ at 313K abd 323K, the results are pointed at 0.9 wt% and 0.8 wt% whilst the plateau was encountedered at 20 and 24 bar, respectively. Study conducted on $MmNi_{4.85}Fe_{0.15}$ showed inconsistent findings with theory. After thorough examination, it was realized that the misbehavior of the sample was due to the insufficient agrresiveness activations method employed.

Keywords: Metal hydride, hydrogen storage, activation process, plateau pressure, hydrogen absorbed content

Abstrak. Ciri-ciri $MmNi_5$ dan $MmNi_{4.85}Fe_{0.15}$ sebagai medium gas hidrogen telah dilakukan di dalam penyelidikan ini. Keupayaan penyerapan logam tersebut adalah dipengaruhi oleh faktor suhu dan dan tekanan. Julat suhu yang dipilih adalah di antara 298K dan 323K manakala tekanan diubah-ubah dari 2 hingga 30 bar. Dalam penyelidikan ini didapati bahawa jumlah gas hidrogen yang diserap oleh $MmNi_5$ adalah berkadar songsang dengan suhu. Jumlah penyerapan maksimum $NmNi_5$ telah dicapai pada suhu 298K dan pada tekanan plateau 10 m bar. Nilai penyerapan hidrogen pada suhu dan tekanan tersebut adalah 1.20 peratus berat. Bagi penyerapan $MmNi_5$ pada 313K dan 323K, keputusan menunjukkan nilai 0.9 dan 0.8 peratus berat. Masing-masing menunjukkan tekanan plateau didapati pada 20 dan 24 bar. Penyelidikan ke atas $MmNi_{4.85}$ menunjukkan keputusan yang tidak menepati dengan teori. Hasil daripada rujukan dan penyelidikan yang menyeluruh, didapati bahawa proses pengaktifan sampel yang dilakukan adalah tidak mencukupi untuk mengaktifkan $MmNi_{4.85}Fe_{0.15}$.

Kata kunci: Logam hidrid, penyimpanan gas hidrogen, proses pengaktifan, tekanan plateau, jumlah penyerapan hidrogen

1.0 INTRODUCTION

Metal hydride is described as the binary combination of hydrogen gas with metal or metal alloy. A metal hydride is a compound in which there is a metal to hydrogen

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bond. Metal hydrides are special group of metals that has capability to absorb, store and release hydrogen. Most hydrides require moderate presure but are currently expensive, need to operate at high temperature to store a lot of hydrogen and are typically very heavy. Such examples are Magnesium and its alloy. Another drawback is their easiness to get contaminated if dealing with hydrogen of low purity. From a safety point of view, hydrides are intrinsically safe.

The hydrogen absorption behavior can best be appreciated in terms of pressure-composition-isotherms or known as PCT curve. At a given temperature, the hydride material is in equilibrium with a definite pressure of hydrogen. Initially, the metal is essentially free of hydrogen. As the hydrogen pressure is increased, the metal adsorbs hydrogen until the pressure reaches the equilibrium pressure. Up to this point, the solid consists of a solution of hydrogen in the metal [1]. It is also known as α phase. Further addition of hydrogen will not result in an increase in pressure. This point is known as plateau region [2]. In this region, two solid phases coexist; hydrogen saturated metal and hydride phase ($\alpha + \beta$). The supposed static pressure is widely known a equilibrium pressure line. Further enrichment of the solid in hydrogen require a steep increase in pressure [3]. At the end of α phase, the hydrogen saturated metal phase has been consumed and further increase in hydrogen pressure will only cause a small increase in hydrogen content. This represents the solid solution of hydrogen in the hydride phase (β).

Metal hydrides that are suitable for hydrogen storage commonly have high hydrogen retentive capacity. Low dissociation temperatures are also desired because hydrogen can be released at a lower temperature. Many attempts have been made to develop binary and ternary hydrides for improving the capacity and the reaction kinetic uptake of hydrogen. The presence of additional elements of $FeTi_{1.2}$ on the structure and hydrogen absorption and desorption behaviour of Mg-35wt%$FeTi_{1.2}$ will enhance the kinetics but the results showed the decreasing absorption capacity [4].

The intermetallic compounds of rare earth and transition metals have attracted special interest in the last few years. This is because some of them have been found to absorb and desorb large quantities of hydrogen at ambient temperature and at much lower pressure compared with other group of metals. It should also be noted that the heat of formation is quite low as would be expected with such an unstable compunds. $LaNi_5$ has been found to be the most remarkable intermetallic. It has excellent hydrogen absorption characteristics such as high storage capacity, low plateau pressure and high chemical stability. One of the disadvantages of using $LaHi_5$ is its cost. Attempts therefore, have been made to develope cheaper material by replacing expensive Lanthanum using low cost ingredients such as mischmetal (Mm) which is a mixture of rare earth elements.

Studies on metal hydrides have led to the development of hydrogen storage in a big scale and other important applications. Different properties of metal hydrides and the nature of its exothermic reaction lead to the invention of heat pump. Other important application can be seen in hydrogen driven motor vehicles system.

2.0 METHODOLOGY

The metal hydride system test rig was designed and fabricated purposely to obtain the optimum conditions of the parameters such as pressure and temperature, leading to the maximum hydrogen capacity. The system is equipped with numerous control valves, gauges and electronic indicator for precise data taking. The reactor is made of 316 stainless steel material with a total volume of 250 cm^3. It is equipped with a perforated dip pipe, which is to enhance the mass transfer efficiency of the gas-alloy inside the reactor. The gas is released in the reactor via 0.5-mm holes uniformly distributed along the perforated pipe. A quick coupling installed at the top of the reactor for easy and fast sealing of the reactor. At the beginning of the experiment, the metal-hydrogen system test rig was subjected to leak test. This is essential in order to determine whether the piping and all the components in the system are leak-free. This is to avoid errors in performing the material and energy balance of the system and will also minimize the risk of fire and explosion when dealing with highly flammable gase such as hydrogen.

The metal-hydrogen system was pressurized under high pressure of 35 bar. The maximum allowable pressure for the system is about 40 bar. The system was maintained under this condition for 24 hours. The leakage test at the joining and fittings, mainly piping line and reactor openings, was conducted by using Combustible Gas Detector. The metal-hydrogen system is also considered leak-free if there is no reduction of pressure in the applied pressure of 35 bar.

The determination of hydrogen content in the samples was obtained by manipulation of temperature and pressure. In this study, the chosen temperature was 298 K, 313 K and 323 K respectively. An activation of the alloy samples ($MmNi_5$ and $MmNi_{4.85}Fe_{0.15}$) was carried out initially. The sample was placed in a reactor under high pressure of 30 bar. It was carried out at ambient temperature of 298 K. This process is essential in order to purge out the impurities such as O_2 and N_2. The activation was also carried out to activate the sample in terms of expanding the lattice parameters of the metal alloys. The sample was pressurized under high pressure of 30 bar for several hours. Hydrogen gas then vented out. This process was repeated several times and finally the sample alloy was left overnight and outgassing the hydrogen was done the next day.

The weight of the sample was about 200 g. and after the activation was established, the pressure was applied to the system at the desired value say at 2 atm and at ambient temperature of 298 K. The pressure drop obtained during the adsorption was recorded. The applied pressure was increased to 2 atm intervals. Similar steps were conducted for different temperatures of 313 K and 323 K. During the measurement of the absorbed hydrogen, the reactor was kept in a water bath to keep the temperature constant. The temperature was observed by a temperature indicator that was linked to the thermocouple attached to the top of the reactor.

Representative sample was studied under a scanning electron microscope (SEM). The morphology of the surface of the samples was examined under magnification of 2020X. The system flow design is shown in Figure 1.

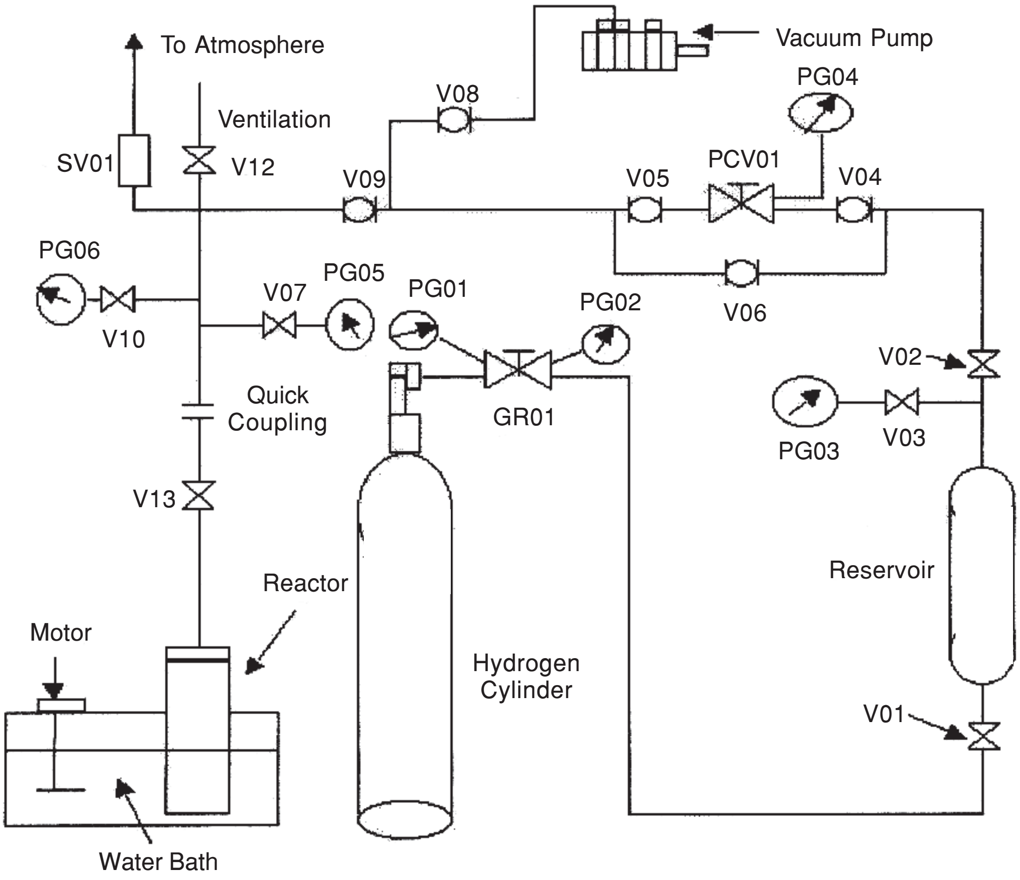

Figure 1 System Flow Design

3.0 RESULTS AND DISCUSSION

Micrographs of $MmNi_5$ obtained by the Scanning Electron Microscope (SEM) conducted at a magnification of 2020X revealed a different discovery on the surface of the metal before and after the activation process. Sample of $MmNi_5$ before and after activation process is presented in Figure 2 and Figure 3 respectively.

The visible occurrence of cracking after the activation process as shown in Figure 3, indicated that the activation was carried out successfully. The effect of activation on

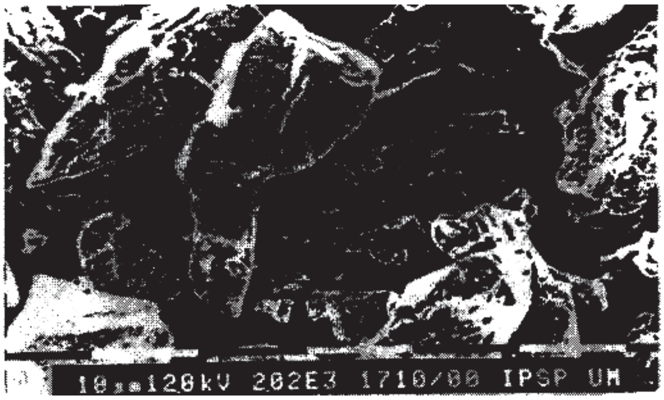

Figure 2 $NmNi_5$ Before Activation Process

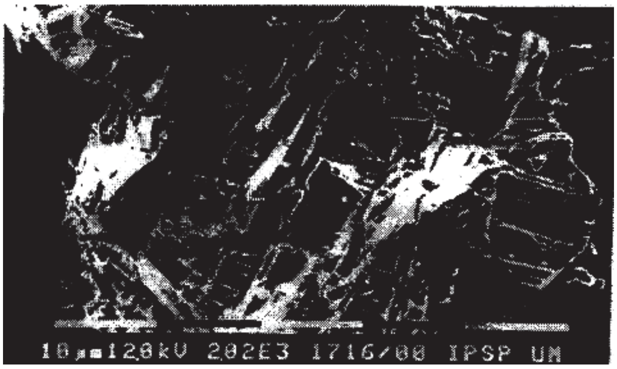

Figure 3 $MmNi_5$ After Activation Process

Ti_2Ni and $LaNi_5$ were seen as brittle fractured surface, cracked zone and eroded surface [5]. Sample under high pressure could caurse particle embrittlement as well as cracking on the metal surface. These phenomenon were also observed in the activation of $MmNi_5$. In hydride forming metals, the formation of hydrides, which have volumes 15 to 25% greater than the corresponding metal, cause stresses and tend to crack the metal.

The surface study of $MmNi_{4.85}Fe_{0.15}$ revealed that no change of surface structure was observed for this sample before and after activation process. These are shown in Figure 4 and Figure 5 respectively. This evidence clearly indicated that the activation process was unsatisfactory and more rigorous method used suggested for activation of $MmNi_{4.85}Fe_{0.15}$.

The effect of applied hydrogen pressure and temperature on the absorption of $MmNi_5$ is shown in Figure 6. It was shown clearly that at the α-phase region, the pressure ascends rapidly. The α-phase region indicated the physical adsorption and chemisorption. This also indicated the dissociation of hydrogen molecules into hydrogen atom. The region is known as a solid solution of hydrogen on the metals. The increase

Figure 4 $MmNi_{4.85}Fe_{0.15}$ before activation process

Figure 5 $MmNi_{4.85}Fe_{0.15}$ after activation process

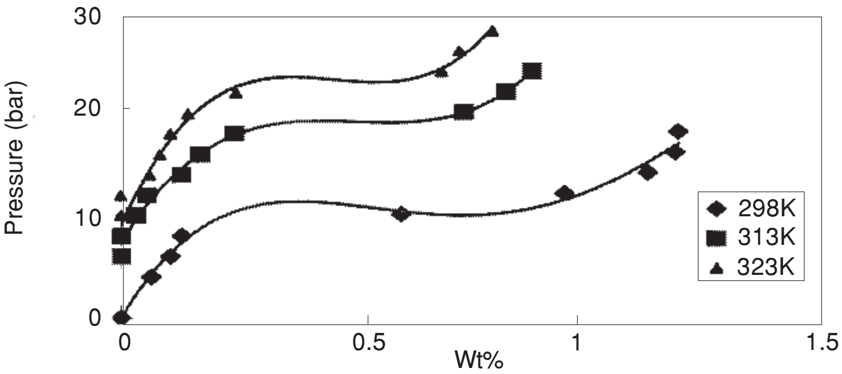

Figure 6 The effect of applied hydrogen pressure and temperature on the absorption of $MmNi_5$

of operating temperature clearly showed the decrease of hydrogen being adsorbed. This was expressed as weight percent as stated on Figure 6.

Further increase in pressure will result in formation of β-phase. In this region, α-phase and β-phase coexist and reaction started to occur. The pressure at which wide plateau region existed normally known as plateau pressure or equilibrium pressure. Clearly at this point, the amount of hydrogen absorbed increased significantly. This point is normally the point of interest since researchers could easily charge the hydrogen at the particular pressure. For $MmNi_5$, the plateau pressures at 298 K, 313 K and 323 K were 10 bar, 20 bar and 24 bar respectively.

It was observed that the maximum hydrogen absorption capacity depended on the operating temperature. Increasing the temperature clearly will result in decreasing of hydrogen content in the metal. At 298 K, the maximum hydrogen content was 1.20 wt% and at 313 K, it was found to be around 0.90 wt%, whilst at 323 K, the capacity reduced to 0.80 wt%.

The effect of applied hydrogen pressure and temperature on the absorption of hydrogen on $MmNi_{4.85}Fe_{0.15}$ is shown in Figure 7.

As the hyrogen pressure increased to as high as 30 bar at 298 K, the results showed only slight increment in hydrogen content. Similar findings were found at 313 K and 323 K.

The region of α-phase existed at the initial stage, whereas the formation of β-phase region could not be clearly identified even though the applied pressure was increased steadily. From Figure 7, plateau pressure was not observed at any point of pressures. Therefore, it was concluded that the maximum absorption of hydrogen into the lattice structure did not take place. There could be many reasons for the unsuccessful ab-

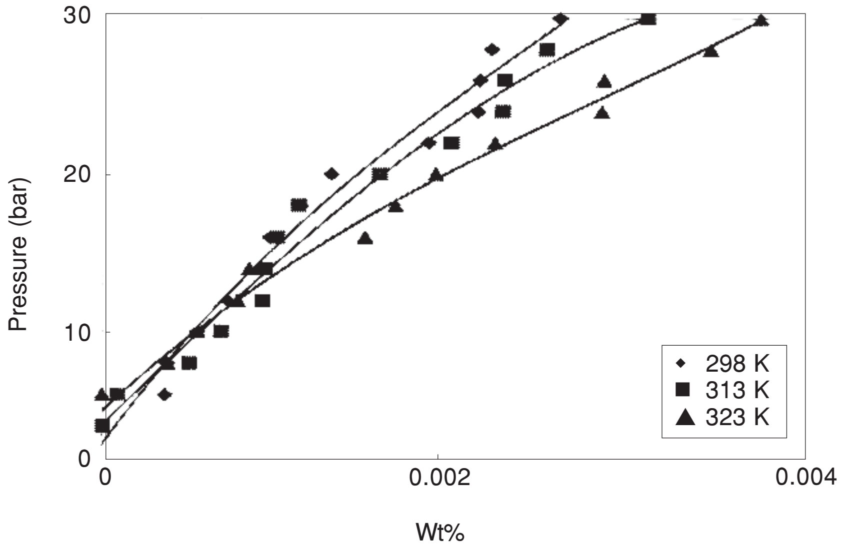

Figure 7 Effect of applied hydrogen pressure and temperature on $MmNi_{4.85}Fe_{0.15}$

sorption of the hydrogen gas. Nevertheless, the most probable cause of the failure was the metal alloy not being fully activated.

From the findings, it was obvious that the activation method employed was suitable for $MmNi_5$, but was not recommended for $MmNi_{4.85}Fe_{0.15}$. $MmNi_{4.85}Fe_{0.15}$ seems to be more sensitive to oxygen contamination than $MmNi_5$. The addition of the third component let to more sensitive hydrides and particularly effective in lowering the plateau pressure [6].

4.0 CONCLUSIONS

One of the most promising applications of metal hydrides is the hydrogen storage. The changes of PT relations with hydride composition for selected metal hydrides affect greatly on the system performance and the cost effectiveness. In the course of evaluating the best properties of metal hydrides, equilibrium P-C-T relations and hydriding properties must be known for the absorption process.

Equilibrium PCT relations of $MmNi_5$ and $MmNi_{4.85}Fe_{0.15}$ was experimentally studied and the behavior of the metal-hydrogen system can be systematically adjusted and altered to give the maximum performance reliability. Such parameters like temperature and pressure are the vital factors influencing the uptake of hydrogen into the metal. The surface study using the SEM showed the effect of activaton on the samples. There are many ways that could be used to activate the sample and the method employed in the experiment was particularly suitable for $MmNi_5$.

ACKNOWLEDGEMENT

The authors would like to express their sincere thanks to the Head of Membrane Research Unit, Prof. Dr. Hamdani Saidi for sponsoring this work under project IRPA 72051.

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NOTATIONS

Mm	Mischmetal
α	Solid solutions of hydrogen in the metal
β	Solid solution of hydrogen in the hydride phase
$\alpha + \beta$	Hydrogen saturated metal and hydride phase coexist