

Cyclic hydrogenation of an LmNi_5 -based alloy with different hydrogen loadings

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Abstract

Cyclic hydrogenation of an LmNi_5 -based alloy up to 3000 cycles at room temperature was conducted. Based on the (P - C - T) curve of the activated alloy, the initial charging pressures were set at four different values so that the saturated hydrogen loadings in equilibrium were controlled at $H/M=1.0, 0.75, 0.50,$ and 0.25 . The cyclic hydrogenation test was made for each loading. The absorption kinetic curves, hydrogen contents, and (P - C - T) curves after 1000, 2000, and 3000 cycles of testing were collected and compared with those of the activated sample. It is observed that the maximum hydrogenation capacities are reduced to 0.95, 0.92, 0.82, and 0.74 for the loadings of 0.25, 0.50, 0.75, and 1.0, respectively. The plateaus for the loadings of 0.25 and 0.50 do not change much, but are lowered and become more sloped for the loadings of 0.75 and 1.0, indicating that non-homogeneous chemical modification has been induced. The X-ray diffraction patterns show broadening of the peaks for all samples, and even the presence of some second phase for the loading of 1.0. The degradation is explained based on reduction of grain size, phase separation, and accumulation of strain energy in the alloy.

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1. Introduction

Hydrogen-absorbing alloys are very promising media in applications such as hydrogen storage, purification, transportation, and heat pump [1–4]. LaNi_5 has excellent hydrogenation properties and is widely used for hydrogen storage. To reduce the cost, LmNi_5 -based alloys are developed by replacing La with misch-metals, and the retaining characteristics are similar to those of LaNi_5 . Durability is an important requirement for repeated absorption and desorption applications. The study of cyclic hydrogenation is helpful to the understanding of degradation and can provide useful information for such applications.

In general, the cycling conditions for hydrogenation can be divided into two types: thermal cycling and pressure-induced cycling. For thermal cycling [5–7], the charging pressure is kept constant initially and the temperature of the alloy is repeatedly increased and decreased in a closed

system. The pressure fluctuates as temperature varies. Alloys at higher temperatures, in general, have higher possibility to undergo reactions such as phase separation and microstructure reordering. For pressure-induced cycling, the temperature is maintained by a water bath. Cyclic hydrogenation/dehydrogenation is made by repeated charging/discharging with hydrogen gas. The pressure of hydrogen may be varied so that the effect of pressure on cyclic hydrogenation can be studied [8–10]. The hydrogenation reaction is generally conducted under the condition that full hydride phase is formed.

In many applications such as in heat pump, fast transfer of heat and hydrogen is the main concern. Partial absorption and desorption of hydrogen is conducted to get the maximum heat transfer rate. Therefore, the degradation behavior of hydrogen storage alloys is different from the case where the hydride is subjected to complete desorption and absorption. Previous studies have not discussed questions related to different levels of degradation which resulted from different contents of hydride phase. In this work, a new concept of measurement was employed to study the effect of different hydrogen loading on the degradation. The parameters of the measurement include

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(P – C – T) curves, kinetics, maximum hydrogen capacity and the phase structure. These parameters enable us to observe the degradation behavior more clearly.

2. Experimental

An LaMnNi_5 -based alloy (HY-T1) was prepared by HyTec Co., Ltd., Taiwan [11]. The composition is approximately $(\text{La}_{0.81}\text{Pr}_{0.09}\text{Ce}_{0.02}\text{Nd}_{0.02})(\text{Ni}_{5.06}\text{Mo}_{0.05})$. For each run, approximately 3 g of alloy powder was loaded into the reactor in a volumetric system which has been previously described [12]. The sample powder was activated at 303 K and 40 atm of hydrogen gas for 30 min (1 atm=101,325 Pa). After several cycles of hydriding and dehydriding (i.e. after activation), the powder was completely dehydrided by vacuum before the (P – C – T) isotherm measurements and cyclic tests were conducted.

In order to study the effect of hydrogen loading on the degradation of hydrogenation, cyclic hydrogenation of the alloy up to 3000 cycles at room temperature was conducted in a closed automatic cycling system. Based on the (P – C – T) curve of the activated alloy, the initial charging pressures were set at four different values so that the saturated hydrogen loadings in equilibrium were controlled by the volumetric method at $H/M=1.0$, 0.75, 0.5, and 0.25. Hydrogen absorption for 300 s and desorption by evacuating with a rotary pump for 900 s were performed in every cycle. The hydrogenation kinetics and capacities were recorded for each cycle. Hydrogen gas of 99.99% purity was used. The temperature was controlled at 303 K by a water bath.

The phase structures of the cycled samples, which had been dehydrided by vacuum, were examined by X-ray diffraction (XRD).

3. Results and discussion

3.1. Capacity degradation

The cyclic hydrogenation test was made for each loading. Fig. 1 shows the hydrogen contents for different hydrogen loadings under different numbers of absorption–desorption cycling. Although there are some fluctuations in the capacity due to the equipment control system, it is clear that the hydrogenation capacities for $H/M=0.25$ and 0.5 loadings do not change much, while that for $H/M=0.75$ decreases gradually with the cycling. For the loading of $H/M=1.0$, the degradation becomes very fast above 1000 cycles. Only 74% of the initial hydrogen capacity is preserved after 3000 cycles.

3.2. The kinetics of hydrogen absorption

The kinetic curves of absorption after 1000, 2000, and 3000 test cycles were recorded and compared with that of

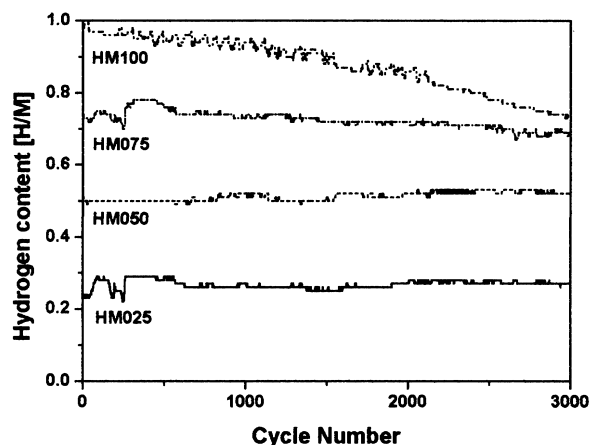


Fig. 1. Variation of hydrogen contents for different hydrogen loadings with the number of cycling. HM025 stands for the loading of $H/M=0.25$. Similar designations are given for other loadings.

activated sample, as shown in Fig. 2. For hydrogen loadings $H/M=0.25$ and 0.5, both cycled and activated samples exhibit similar features. As the hydrogen loading increases to $H/M=0.75$, the hydrogen absorption capacity starts to decrease with the number of cycles. For the hydrogen loading $H/M=1.0$, severe degradation takes place as the cycling proceeds to 2000 and 3000 cycles. Based on this result, there may be some microstructural change due to heavy hydrogen loading so that the hydrogenation capacities become lowered. The degradation depends not only on the number of cyclings, but also on hydrogen loading.

3.3. (P – C – T) curves

Fig. 3 presents the room-temperature (P – C – T) curves for the alloy with various hydrogen loadings before and after cyclic hydrogenation of 3000 cycles. For $H/M=0.25$ and 0.50, although the maximum hydrogenation capacities after cycling decrease slightly to 0.95 and 0.92, respectively, the curves are essentially similar to that of the activated

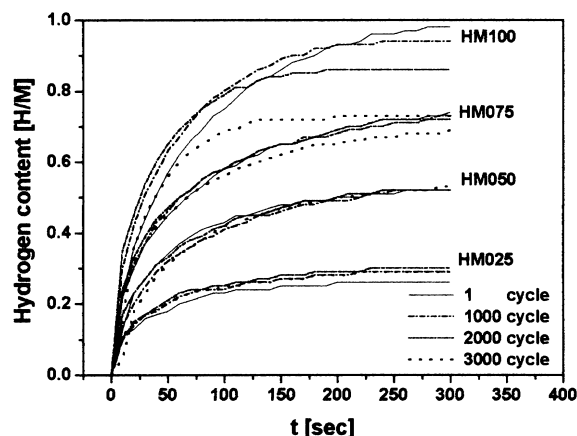


Fig. 2. Hydrogen absorption kinetic curves for different hydrogen loadings at 303 K.

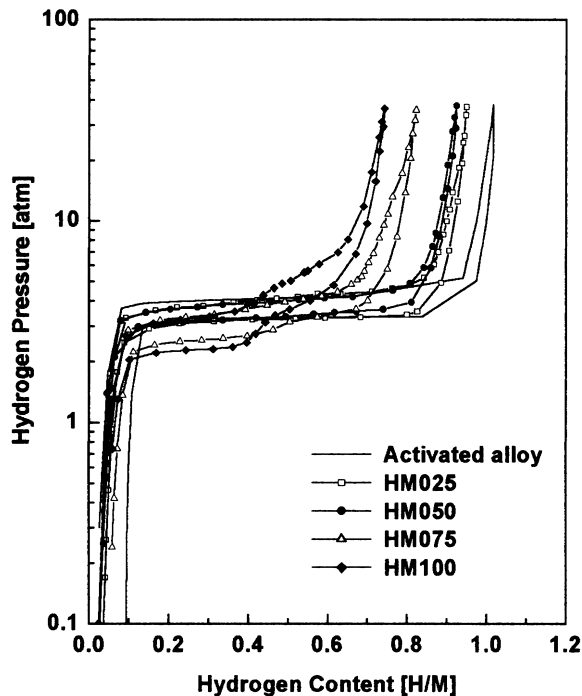


Fig. 3. (P - C - T) curves for various hydrogen loadings before and after 3000 test cycles.

sample. This indicates that the composition of the alloy is not changed. This agrees with the fact that the kinetics of hydrogen absorption at low hydrogen loadings is unchanged during 3000 hydrogenation cyclings.

For $H/M=0.75$ and 1.0 , it is found that the plateaus are lowered and become more sloped. Hydrogenation capacities are drastically reduced to 0.82 and 0.74 , respectively. This implies that a non-homogeneous chemical modification in the lattice sites has been induced. In addition, the microstructure is distorted due to heavy cyclic loading of hydrogen, to be discussed in the next section.

3.4. Crystal structure

The X-ray diffraction patterns of uncycled and cycled samples are shown in Fig. 4. Silicon is used as an internal standard. All samples belong to the $CaCu_5$ -type structure. However, the peaks are broadened for cycled alloys, and the presence of some second phase for the hydrogen loading of $H/M=1.0$ is observed. Peak broadening in AB_5 -type alloys is known to be caused by reduction of grain size and accumulation of strain energy in the alloy [5,13]. The peak broadenings in terms of the full width at half maximum (FWHM) for three selected peaks (101), (110), and (002) are determined for all samples. The values are listed in Table 1. In general, the broadening increases with hydrogen loading. Furthermore, the broadening is smaller for the (002) peak but more pronounced for the (101) and (110) peaks, indicating non-uniform strain along different axes. The lattice parameters are calculated for all samples, as also listed in Table 1.

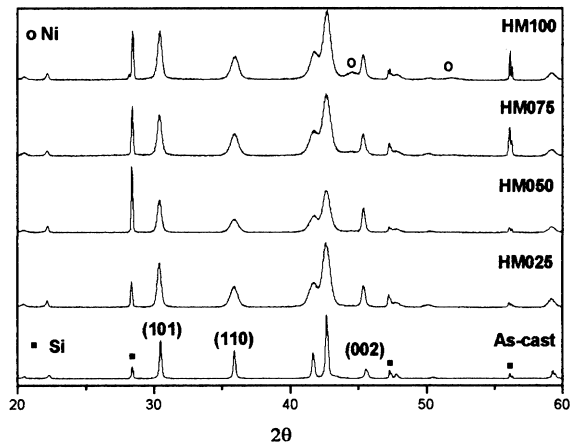
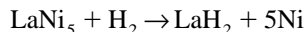


Fig. 4. XRD patterns of the samples before and after 3000 hydrogenation cycles for various hydrogen loadings.

Expansion of the unit cell volume is observed after hydrogen loading, especially for higher hydrogen loadings. This implies larger sites for hydrogen accommodation, leading to lower desorption pressures. This is observed for HM075 and HM100, Fig. 3, although the volume expansion is smaller for MH100.

Based on the (P - C - T) curves and the X-ray diffraction analysis, crystal lattice defects could be generated during the cyclic hydrogenation. Furthermore, as the hydrogen loading increases, the heat generated on hydrogenation becomes higher. Not only lattice defect but also phase separation may be induced. The alloys at high temperatures may undergo the following phase separation reaction [6,14]:



The second phase in the X-ray diffraction patterns is considered to be Ni cluster produced from this reaction, as marked in Fig. 4. These byproducts may be related to the capacity degradation, as neither La nor Ni form reversible hydrides at the investigated pressures.

4. Conclusion

The effect of hydrogen loading on the degradation of hydrogenation was conducted. According to the results of

Table 1
Lattice parameters and peak broadenings of the samples before and after 3000 cycles of hydrogenation

Sample	a (Å)	c (Å)	Cell volume (Å ³)	FWHM (°)		
				(101)	(110)	(002)
As-cast	5.003	3.981	86.30	0.18	0.18	0.26
HM025	4.992	3.997	86.27	0.34	0.64	0.30
HM050	5.001	3.991	86.43	0.30	0.68	0.26
HM075	5.012	3.983	86.63	0.36	0.62	0.28
HM100	4.993	4.000	86.35	0.40	0.66	0.34

absorption kinetic curves ($P-C-T$) curves, and XRD analysis, the degradation depends not only on the number of cycling, but also on hydrogen loading. The degradation can be explained based on reduction of grain size, phase separation, and accumulation of strain energy in the alloy.

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