Acoustic emission monitoring of activation behavior of LaNi$_5$ hydrogen storage alloy

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Abstract
The acoustic emission technique is proposed for assessing the irreversible phenomena occurring during hydrogen absorption/desorption cycling in LaNi$_5$. In particular, we have studied, through a parametric analysis of in situ detected signals, the correlation between acoustic emission (AE) parameters and the processes occurring during the activation of an intermetallic compound. Decreases in the number and amplitude of AE signals suggest that pulverization due to hydrogen loading involves progressively smaller volumes of material as the number of cycles increases. This conclusion is confirmed by electron microscopy observations and particle size distribution measurements.

Keywords: hydrogen-absorbing materials, intermetallics, acoustic emission

1. Introduction

In addition to limiting energy consumption, low-carbon energy technologies are needed to further reduce CO$_2$ emissions, and alternatives to burning fossil fuels are required. In this regard, hydrogen represents a versatile energy carrier and is seen as an important part of the solution to lowering CO$_2$ emissions. Efficient hydrogen storage is a significant challenge limiting the use of hydrogen as a primary energy carrier [1, 2]. Conventional technologies store hydrogen in the form of compressed gas or liquid; however, several solid-state alternatives are being investigated. The associated materials can be divided into three categories: when physically bound, hydrogen gas is physisorbed to a high-surface-area substrate (e.g. carbon nanotubes, zeolites and metal–organic frameworks); when chemically bound, hydrogen forms a chemical compound with the substrate (e.g. metal hydrides and complex hydrides) and is released via thermal decomposition; in complexes sometimes referred to as chemical hydrides, hydrogen is also chemically bound, but released through a chemical reaction, typically a hydrolysis reaction [1–4]. The solid-state alternatives are safer and theoretically can store more hydrogen per unit volume than liquid or solid storage systems [5]. Many metals and alloys reversibly react with hydrogen to form a hydride, and the regeneration of the metal can be accomplished either by increasing the temperature or by reducing the pressure. Different types of materials have been investigated for this purpose, including LaNi$_5$ and TiFe compounds, Zr- and Ti-based Laves phases, Mg$_2$Ni- and Mg-based materials, and various composites [3, 4]. Among these materials, intermetallic compounds based on LaNi$_5$ attracted attention owing to their fast activation, high storage capacity and long cycle life [6–10]. Such systems are characterized by non equivalent absorption and desorption isotherms in pressure-composition diagrams, which have been ascribed to the $\alpha \rightarrow \beta$ phase transformation. LaNi$_5$ requires activation before it can readily absorb hydrogen and this process usually involves a few to several cycles of hydrogen absorption and...
desorption until reproducible pressure-composition diagrams are obtained. The hysteresis is initially large but is reduced with increasing number of cycles [11]. Two main physical and irreversible microstructural alterations arise from activation: generation of defects (mainly dislocations) and pulverization. These phenomena, which usually occur during the first cycles, need to be thoroughly investigated because they can affect the properties relevant to the potential industrial applications. The effects of initial activation are usually evaluated by ex situ methods, such as scanning and transmission electron microscopy (SEM and TEM) and only a few in situ methods are available, such as neutron and x-ray powder diffraction [12, 13]. In this regard, acoustic emission (AE) is a nondestructive method that can be used for real-time in situ analysis of irreversible phenomena like cracking and dislocation movements. Only a few papers report AE monitoring of absorption–desorption cycles of metal hydride electrodes [14–16]. All these investigations were carried out during electrochemical charging of hydrogen.

The aim of this study was to analyze the AE signals associated with the early absorption and desorption cycles of hydrogen in LaNi5. LaNi5 is known to absorb/desorb hydrogen readily and the microstructural changes during its activation have been well investigated [9, 11, 13]. Here, we attempted to correlate the AE parameters with the processes occurring during the LaNi5 activation via a gaseous route.

2. Materials and methods

We used a commercial LaNi5 powder from Saes Getters. Hydrogenation cycles were carried out with hydrogen of 99.999% purity in the system shown in figure 1(a). Hydrogen flows through 6-mm-diameter steel pipes from a pressurized cylinder (200 bar) located outside the building. A special pressure reducer located near the tank allows keeping the line pressure up to 18–20 bar (pressure limit of the system), while a further pressure regulator PCV-2 ensures that a lower pressure is maintained. After passing the pressure-reducing valve V2, hydrogen flows through the valve V3 and meets the first ‘T’ junction. From this point on, it can proceed in the flowmeter (MFC) direction during charging, when valves V6, V7 and V4 are closed. Alternatively, it can flow back through valve V6 during the download, when valves V3, V4 and V5 are closed, and allowing the passage through the flowmeter and valve V7. The filters F1 and F2 prevent the powdered hydrides from damaging the flowmeter. The system can measure the flow, pressure and temperature in the storage hydrides. Pressure and temperature can be controlled. A National Instruments data acquisition system collects the signals and sends them to a computer where a LabVIEW program displays and records the data. The tests were carried out on a 12 g sample at room temperature with a normalized hydrogen flow of 10 Nml min−1 and a maximum pressure of 15 atm.

The first six cycles were monitored in situ by AE using the setup of figure 1(b). An AMSY-5 AE system by Vallen Systeme GmbH was used to monitor and record the AE signals during the tests. The threshold setting was 35 dB and the total gain and sampling rate were set at 34 dB and 2 MHz, respectively. Two PZT sensors with a resonance frequency of 150 kHz (Deci, type SE150-M) were used for AE detection. The studied frequency range was 100–450 kHz. One sensor was in contact with the reactor and the other was connected to a thermocouple that acted as a waveguide. The morphology and size distribution of the particles were investigated using a Hitachi S-2500 scanning electron microscope and a Malvern Mastersizer laser particle sizer, respectively.

3. Results and discussion

Figure 2(a) shows the evolution of the cumulative acoustic emission activity recorded during the absorption phase for six cycles. There is a significant acoustic activity that persists during all the cycles. A strong decrease in the number of hits was measured when passing from the first to the second cycle, and the acoustic activity was steady after the third cycle. This observation agrees with previous reports [11, 17]. The desorption pressure is only slightly affected

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**Figure 1.** (a) System used for hydrogen cycling of LaNi5; (b) experimental setup for AE monitoring.
by the number of cycles, while the absorption pressure progressively decreases, with the most significant decrease occurring between the first and second cycle. This is likely to indicate that, from the third cycle on, reproducible conditions have been achieved (activation of the compound). For most intermetallic compounds [10], only the absorption curve is significantly modified during the first cycle, suggesting that defect generation and pulverization mostly occur during the first absorption cycle. In particular, the presence of a large hysteresis is the consequence of an energy loss caused mainly by irreversible dislocation formation and, secondly, by decrepitation.

The evolution of acoustic emission reflects irreversible phenomena and agrees with this description of physical events. This was also confirmed from the analysis of the desorption phase (figure 2(b)). The acoustic activity is significantly lower in the desorption than in the absorption phase, in agreement with the theory that identifies absorption as the most critical phase during the hydrogen cycling of alloys. Note the similarity in the curves of figures 2(a) and (b) after the second cycle, suggesting that most irreversibilities occur during the first cycle.

Figure 2(c) shows the cumulative amplitude of AE signals (logarithmic scale) as a function of time for the first absorption cycle. This graph reflects the growth rate of acoustic activity and related microscopic phenomena. After a small initial acoustic activity, a significant increase in the signal amplitude occurred at the beginning of the absorption plateau, followed by a sudden decrease near the end of the plateau. The large acoustic activity during the pressure plateau can be ascribed to the formation of the $\beta$ phase and the related production of lattice defects and decrepitation.

It is generally accepted that dislocations are generated during hydrogen cycling because of the difference in the lattice parameters between the $\alpha$ and $\beta$ phases. The $\alpha \rightarrow \beta$ phase transformation involves a lattice expansion exceeding 20% [9, 10]. These phenomena, according to the evolution of AE signals, appear to become significant soon after the first third of the absorption plateau. During the desorption phase, a peak is observed at the beginning of the desorption plateau, followed by an almost steady state until the end of the test. For the second hydrogenation cycle (figure 2(a)), the absorption plateau is characterized by a lower increase in acoustic activity compared with that for the first absorption cycle. The desorption phase shows a steady acoustic activity throughout the whole test. From the third cycle on, owing to the increasing repeatability of the cycles, both absorption and desorption phases show a similar and repeatable activity as a function of time, without significant intensification, as shown in figure 2(d). These results agree with the previously observed saturation in the particle size after a few absorption/desorption cycles [9].

![Figure 2](image_url)
Table 1. Relative distribution (%) of durations and amplitudes of AE events for the three stages of absorption (I, II, III abs) and for the desorption phase (des) of the first hydrogenation cycle.

| Duration (µs) | 0–199 | 200–399 | 400–599 | 600–1199 | 1200–1599 | >1600 |
|--------------|-------|---------|---------|----------|-----------|-------|
| I abs        | 64.19 | 18.24   | 8.78    | 7.43     | 0.68      | 0.68  |
| II abs       | 18.26 | 24.71   | 17.29   | 27.96    | 6.55      | 5.23  |
| III abs      | 30.18 | 42.09   | 19.49   | 8.02     | 0.22      | –     |
| Des          | 78.96 | 17.49   | 1.94    | 1.29     | 0.16      | 0.16  |

| Amplitude (dB) | 35–49 | 50–59 | 60–69 | 70–79 | 80–89 | 90–99 |
|----------------|-------|-------|-------|-------|-------|-------|
| I abs          | 79.05 | 18.24 | 2.71  | –     | –     | –     |
| II abs         | 63.62 | 31.58 | 4.54  | 0.26  | –     | –     |
| III abs        | 77.95 | 19.60 | 2.23  | 0.22  | –     | –     |
| Des            | 89.81 | 8.90  | 1.29  | –     | –     | –     |

Figure 3. Rise time versus energy for the (a) first and (b) third absorption stages and (c) desorption phase of the first hydrogenation cycle; (d) rise time versus energy for signals with amplitude >70 dB recorded during the second stage of the first hydrogenation cycle.

In order to gain better insight into the mechanisms responsible for the AE signals, the absorption phase has been subdivided into three stages, named I, II, III abs. The first stage goes from the onset of the test up to the knee of the number of hits versus time curve, which corresponds to the onset of continuous AE (0–5000 s). The second stage proceeds till the end of the absorption plateau (5000–14 700 s), and the third stage includes the last part of the test (after 14 700 s). Table 1 summarizes the relative distributions of the AE event amplitudes and durations for the three stages of absorption and for the desorption phase of the first cycle.

In the first stage, approximately 80% of the signals is characterized by low-medium amplitude (35–50 dB) and duration (≤400 µs). These signals are not to be ascribed to decrepitation, because this phenomenon is not likely to occur in absence of activation. This behavior is also confirmed by the correlation between energy and rise time (figure 3(a)), where the signals mainly belong to one population characterized by a long rise time of up to 1400 µs and a low energy of up to 500 eu. The energy of the acoustic emission signal is evaluated as the integral of the squared amplitude over the signal duration and is expressed in
energy units (1 eu = 10^{-14} V^2 s). During hydrogen absorption, a gradient of defects is created from the sample surface toward the bulk, because the defects are firstly generated at the surface. The defect-rich zone then expands into the bulk as the hydrogen concentration increases. The dislocations so generated and their movements are typical phenomena that lower the amplitude of the AE signals [18]. In contrast, the growth of cracks and brittle failure (cleavage), which are nondiffusive phenomena, raise the amplitude [18]. The second stage shows more signals of higher amplitude (50–80 dB) and medium-long duration (400–1600 µs). These signals, as shown in figure 3(d), are characterized by energies higher than those of the first stage. The signals stronger than 70 dB have a short rise time (<400 µs) and high energy.

These features can be ascribed to pulverization phenomena that reduce the particle size. This reduction can be clearly seen in figure 4 showing the particle size distributions of the powder before (a) and after (b) the first hydrogenation cycle.

Figure 5 shows the morphology of the as-received powder (a), (b) and the powder after one (c), (d) and six (e), (f) hydrogenation cycles. SEM observations indicate that the finer particles resulted from the transgranular fracture of the larger particles, as shown in the inset of figure 4 and in figures 5(c) and (d). Signals related to the particle pulverization are present in the second stage, together with signals similar to those of the first stage due to the generation and movement of lattice defects. The third stage still exhibits some signals typical of the second stage, thus suggesting that decrepitation is ending (figure 3(b)). The signals of desorption phase are similar to those of the first absorption stage, thus pointing out that contraction due to the $\beta \rightarrow \alpha$ transformation is less important than expansion due to the $\alpha \rightarrow \beta$ transformation (figure 3(c)).

Similar conclusions can be drawn for the second cycle, even though the pulverization-related signals are less numerous and have a lower duration and amplitude compared with those of the first stage (figures 6(a) and (d)). This observation can be explained considering that during the first cycle, hydrogen loading produced extensive fracturing of larger particles with an intricate network of fine and randomly oriented cracks (figure 4(b)). The size of the subparticles delineated by cracks is comparable to that of the particles observed at the end of the following cycles [11]. This explains
how the pulverization phenomenon becomes less critical as the number of cycles increases, since it involves smaller and smaller volumes that decrease the number and amplitude of AE signals. In particular, internal stresses can be released by pulverizing large particles, but larger particles still have high densities of defects and cracks. As the particle size decreases, the change in the particle volume due to absorption/desorption may become more elastic [7, 19]. As a consequence, elastic internal stresses can dominate the volume expansion of small particles, thus reducing the acoustic activity and signal amplitude. For the following cycles, the signals occurring during the pressure plateau are seldom characterized by an amplitude higher than 60–65 dB. The signals related to the particle pulverization decrease with the number of cycles, together with the signals related to the generation of lattice defect. This can be due to the material reaching the dislocation saturation density, an event that takes place after the first cycle.

To further demonstrate the good correlation between the AE signals and physical phenomena occurring during hydrogen cycling, we compare in figure 7 the hysteresis factor and the normalized number of hits as a function of number of cycles. The hysteresis factor is a parameter that is often used as a measure of the extent of hysteresis. This factor has been estimated as $1/2RT \ln(P_{\text{abs}}/P_{\text{des}})$, where $P_{\text{abs}}$ and $P_{\text{des}}$ are the absorption and desorption plateau pressures, respectively [20]. The normalized number of hits has been evaluated as $\text{hits}_n/\text{hits}_1$, with $n = 1$–VI. Both curves indicate that the comparatively large pressure hysteresis of the first cycle decreased significantly in subsequent cycles and approached steady-state values after a few cycles.

4. Conclusions

In conclusion, our results demonstrate that the AE technique can be successfully used for the in situ monitoring of irreversible physical phenomena occurring during hydrogen cycling, namely, dislocation formation and
decrepitation. These were ascribed to different types of signals, characterized by low-medium amplitude (35–50 dB) and short duration (≤400 µs) and higher amplitude (>70 dB) and shorter rise time (<400 µs), respectively. Energy is also an important parameter to differentiate between AE signals, and a low rise time (<600 µs) and high energy were identified as distinctive features of decrepitation signals. Our results suggest that the AE parameters recorded during absorption and desorption of hydrogen in intermetallic compounds can be used to identify and follow the time sequence of different involved processes, and they compare well with electron microscopy and particle size measurement. This method could therefore become a useful tool in the evaluation/optimization of new metal hydrides for hydrogen storage.

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