

Disproportionation of LaNi_5 and TiFe in 4 MPa H_2 at 300 °C

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Abstract

The disproportionation of LaNi_5 and TiFe under 4 MPa H_2 at 300 °C was investigated. It was found that under this condition LaNi_5 reacted with hydrogen disproportionally at a noticeable rate, while TiFe remained stable owing to the lower mobility of its lattice atoms. The disproportionation reactions are discussed in relation to the intrinsic cycling degradations of LaNi_5 and TiFe .

1. Introduction

Many binary intermetallic compounds disproportionate during charging with hydrogen at high temperatures because of the different affinities of the component elements towards hydrogen [1–6]. Although the disproportionation is more favoured thermodynamically, usually it does not take place at low temperatures and only ternary hydrides are formed which are metastable in nature [1, 3, 6]. This is because of the kinetic limitation to the diffusion of the lattice atoms. The disproportionation, however, has been considered by many authors [7–15] as the origin of the intrinsic degradation of LaNi_5 and TiFe as manifested in the decrease in hydrogen transfer capacity and change in the P – C – T curve when cycled in pure hydrogen at ambient temperatures. They proposed that during cycling a more stable binary hydride, such as LaH_2 or TiH_2 , was formed. This mechanism has received some indirect experimental support from Mossbauer spectroscopy [7], temperature-programmed desorption (TPD) [9, 11–13] and magnetic susceptibility measurements [10, 12]. However, using X-ray diffraction (XRD) [9], neutron scattering [16] and extended X-ray absorption fine structure (EXAFS) [17], precipitates such as LaH_2 and nickel in LaNi_5 , or TiH_2 and iron in TiFe , were not observed. Few transmission electron microscopy (TEM) studies have been made on the degraded alloys. So far, it is still an open question whether the disproportionation reaction is the origin of the intrinsic degradation of the alloys upon cycling.

It has been proposed previously by one of the present authors [18] that the intrinsic cycling degradation results from the generation of lattice defects, which depends on the stability of the lattice structure. The difference in

cycling stability between LaNi_5 and TiFe is attributed to their differences in defect generation and metal atom mobilities. It has also been believed that TiFe is more stable than LaNi_5 against the defect generation induced by cycling and the diffusive disproportionation driven by hydrogen. In this work, we report on an investigation of static reactions of LaNi_5 and TiFe with hydrogen at 300 °C and 4 MPa pressure, in order to understand better the disproportionation and intrinsic degradation.

2. Experiments

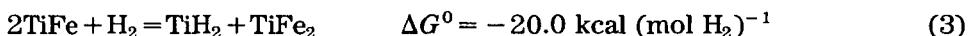
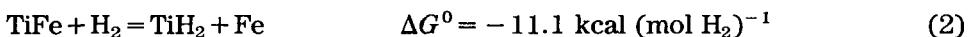
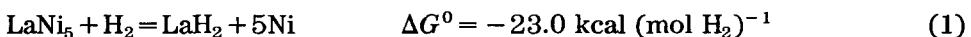
LaNi_5 and TiFe were arc melted under argon protection from the pure elements. XRD showed that the prepared buttons were single-phased LaNi_5 and TiFe respectively. High-purity hydrogen from an LaNi_5 hydride tank (H_2 , more than 99.9999%) was used. Before being subjected to reaction with hydrogen at high temperature, the specimens were activated as usual and pressure cycled 30 times at room temperature between 0.1 and 4 MPa with a period of 20 min. Absorption capacity measurements showed that they had been fully activated.

The activated specimens were heated to 300 °C in 4 MPa H_2 and kept static for 10 days to let the reaction proceed. Falling pressure in the reactor systems was monitored and the progress of the reaction, measured as H:M vs. reaction time, was recorded. Both before and after the reaction, $P\text{-}C\text{-}T$ curves were measured *in situ*.

After reaction for 10 days, TPD measurements were performed to determine the energetics of the hydrogen retained and to clarify the possible reaction mechanisms. A heating rate of 10 °C min⁻¹ from room temperature to 1000 °C was employed and the hydrogen desorption was measured under 0.1 MPa pressure. Curves of hydrogen evolution and evolution rate vs. temperature were obtained.

3. Results and discussion

The disproportionation of LaNi_5 and TiFe on reacting with hydrogen were proposed as follows [6, 9]:



Their corresponding equilibrium pressures at 300 °C are less than 10^{-6} MPa, less than 10^{-4} MPa and less than 10^{-5} MPa respectively. Our selected pressure of 4 MPa is high enough to accomplish the disproportionation reactions thermodynamically but too low to result in ternary hydride formation.

Therefore, under the present condition, only the disproportionation reactions are expected to occur.

Figure 1 shows the hydrogen absorption $H:M$ of LaNi_5 and TiFe vs. reaction time at 300°C and 4 MPa pressure. It can be seen that LaNi_5 slowly reacts with hydrogen while TiFe does not react with hydrogen at all. After 10 days the hydrogen absorption by LaNi_5 is $H:M = 0.07$ and the reaction curve can be well fitted to a parabolic equation

$$H:M = kt^{1/2} \quad (4)$$

where $k = 0.452 \times 10^{-2} \text{ h}^{-1/2}$. This parabolic reaction rate suggests that the reaction is controlled by diffusive growth.

The desorption P - C - T curves for LaNi_5 and TiFe measured before and after the reaction with 4 MPa H_2 at 300°C for 10 days are shown in Fig. 2. After the reaction, the plateau for LaNi_5 becomes shortened, slightly slanted, and curved at the two ends. The shortening of the plateau approximately corresponds to 20% disproportionation of LaNi_5 according to eqn. (1) with a hydrogen sorption $H:M = 0.07$. For TiFe there is no change in the P - C - T curve after the reaction, within the accuracy of the present measurement.

In Fig. 3 are shown the TPD spectra of the partially disproportionated LaNi_5 under a hydrogen pressure of 0.1 MPa . Hydrogen desorption begins at about 200°C , accelerates to a maximum around 680°C , and then slows down gradually. Up to 900°C , the hydrogen desorption reaches completion and the hydrogen evolved $H:M$ is 0.07 in agreement with the absorption as shown in Fig. 1.

Our results demonstrate that, at 300°C and 4 MPa , LaNi_5 reacts with hydrogen disproportionally at a noticeable rate. The temperature corresponding to an equilibrium hydrogen pressure of 0.1 MPa for reaction (1) is about 670°C from thermodynamic calculations. In Fig. 3 we find a maximum desorption rate around 680°C , which is close to the equilibrium temperature.

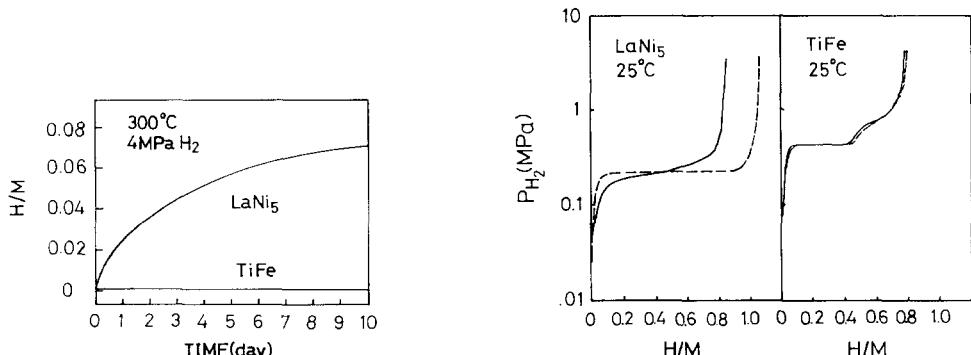


Fig. 1. The hydrogen sorption $H:M$ vs. reaction time at 300°C and 4 MPa pressure for LaNi_5 and TiFe .

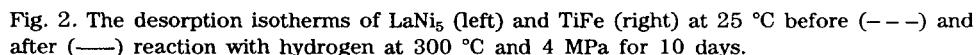


Fig. 2. The desorption isotherms of LaNi_5 (left) and TiFe (right) at 25°C before (---) and after (—) reaction with hydrogen at 300°C and 4 MPa for 10 days.

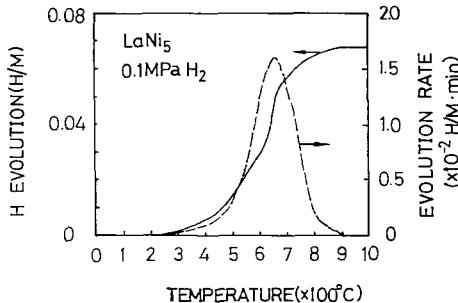
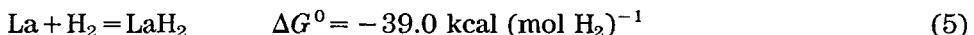


Fig. 3. TPD of LaNi_5 under 0.1 MPa H_2 pressure after reaction with hydrogen at 300 °C and 4 MPa for 10 days.

This agreement together with the absorption (H:M) and P - C - T measurements strongly suggest (since we have not performed structural analysis) that, under the condition mentioned above, LaNi_5 reacts with hydrogen via the disproportionation mechanism as expressed in eqn. (1).

As the disproportionation proceeds via diffusion of La and Ni atoms and involves precipitation of nickel and LaH_2 , composition fluctuation and residual strain related to the misfit between the phases may be built up in both the matrix and the precipitates, which will influence the energetics of hydrogen occupancy. These effects may account for the slanting and curvature of the P - C - T curve, and the hydrogen desorption below the equilibrium temperature 670 °C during TPD measurement. As the reversed reaction of the disproportionated LaNi_5 is also controlled by the diffusions of lanthanum or nickel, kinetic hysteresis is responsible for the desorption above the equilibrium temperature of 670 °C. The desorption may be extended to a temperature higher than 900 °C according to reaction (5) [9]:



TiFe reveals higher stability against disproportionation, due to the lower mobilities of the titanium and iron lattice atoms. This supports the previous suggestion that the activation energy for metal atom diffusion and the enthalpy for defect formation in TiFe are higher than those in LaNi_5 [18]. Our results for TiFe are in good agreement with some previous investigations. Reilly [6] found that, even after keeping TiFe in hydrogen at a temperature as high as 450 °C for several months, there was no observable disproportionation. Chu *et al.* [19] reported that the mechanically alloyed amorphous TiFe did not crystallize in annealing at 400 °C. There was not even any atomic-range structural modification. All these confirm that the diffusion of lattice atoms in TiFe is almost negligible at temperatures below 450 °C.

Based on the previous proposition [18], our observation here has two implications. First, the higher mobility of lanthanum or nickel in LaNi_5 can account for the lower stability of LaNi_5 on extended cycling as compared with TiFe . Hydrogen provides the driving force for the lanthanum atoms in LaNi_5 or the titanium atoms in TiFe to segregate to defects and pin them.

These defects may consist of vacancies, dislocations, stacking faults, free surfaces etc., which are generated by cyclic hydriding and dehydriding. These pinned defects may degrade the hydrogen sorption properties either by suppressing the phase transition as proposed for TiFe by Ahn *et al.* [11] or by changing the hydrogen energetics in or nearby as supposed for LaNi₅ by Goodell [20]. The faster the diffusion, the more and larger the pinned defects, consequently the faster the degradation.

Secondly, the low mobility of lattice atoms in TiFe at 300 °C strongly suggests the exclusion of disproportionation as a general mechanism for the cycling degradation. It has been found [7–15, 20] that the regeneration of cycled TiFe and LaNi₅ can usually be accomplished by annealing at 300 °C in vacuum. If there is disproportionation during cycling, for example in charged TiFe, then the question may be asked: how can the reversed proportionation proceed at 300 °C at which the process is kinetically impossible? We believe that 300 °C and vacuum are only necessary conditions for the desorption of hydrogen trapped by the defects and for the depinning and elimination of defects through thermal activation processes. For extensively cycled LaNi₅ and TiFe, one generally observes [7–15, 20] broadening of the XRD peaks, changes in the *P–C–T* curve and widely distributed TPD spectra, which support the defect generation as the origin of the intrinsic degradation of both LaNi₅ and TiFe on cycling [18].

4. Conclusion

The behaviour of LaNi₅ and TiFe in 4 MPa H₂ at 300 °C was examined. It was found that under this condition LaNi₅ reacted with hydrogen disproportionally at a noticeable rate, while TiFe was inert to hydrogen because of the lower mobility of its lattice atoms. The difference in mobility of metal atoms between LaNi₅ and TiFe can account for their different cycling stabilities. On the other hand, the low mobility of metal atoms in TiFe strongly suggests the exclusion of disproportionation as a general mechanism for the intrinsic cycling degradation in most cases.

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