



Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: [www.elsevier.com/locate/jallcom](http://www.elsevier.com/locate/jallcom)

## The effects of nanometric nickel (n-Ni) catalyst on the dehydrogenation and rehydrogenation behavior of ball milled lithium alanate ( $\text{LiAlH}_4$ )

R.A. Varin\*, L. Zbroniec

Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

### ARTICLE INFO

**Article history:**

Received 21 June 2010

Accepted 14 July 2010

Available online 21 July 2010

**Keywords:**

Solid state hydrogen storage

Hydrogen storage materials

Desorption temperature and kinetics

Lithium alanate ( $\text{LiAlH}_4$ )

Nanometric nickel additive

Ball milling

X-ray diffraction (XRD)

Differential Scanning Calorimetry (DSC)

### ABSTRACT

A comprehensive study of the effects of nanometric Ni (n-Ni) additive having a specific surface area (SSA) of 9.5 and 14.5  $\text{m}^2/\text{g}$  on the dehydrogenation and rehydrogenation behavior of mechanically (ball) milled  $\text{LiAlH}_4$  has been carried out using Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and volumetric hydrogen desorption in a Sieverts-type apparatus under 0.1 MPa  $\text{H}_2$  pressure. The  $\text{LiAlH}_4 + 1$ , 5 and 10 wt.% n-Ni mixtures were processed by a simple mixing as well as low energy and high energy mechanical (ball) milling in a unique magneto-mill. No decomposition during milling up to 1 h has been observed for  $\text{LiAlH}_4 + 5$  and 10 wt.% n-Ni. A mixing of  $\text{LiAlH}_4 + \text{n-Ni}$  still results in the melting of  $\text{LiAlH}_4$ . In contrast, doping with 5 and 10 wt.% n-Ni combined with high energy ball milling completely eliminates melting of  $\text{LiAlH}_4$ . Volumetric dehydrogenation studies show that throughout the entire temperature range from 100 °C to 250 °C a  $\text{LiAlH}_4 + \text{n-Ni}$  nanocomposite system ball milled under high energy mode always desorbs hydrogen in a solid state without any melting in two stages I and II. Stage I is related to the transformation of  $\text{LiAlH}_4$  into  $(\text{Li}_3\text{AlH}_6 + \text{Al} + \text{H}_2)$  and Stage II is related to the transformation of  $\text{Li}_3\text{AlH}_6$  into  $(\text{LiH} + \text{Al} + \text{H}_2)$ . The apparent activation energy of Stage I and II equals  $\sim 70$  and  $\sim 100$  kJ/mol, respectively. This can be compared with the apparent activation energy of ball milled undoped  $\text{LiAlH}_4$  equal to about 90 kJ/mol for both Stage I and II as reported in Ref. [9]. It is also shown that n-Ni is a very potent catalyst destabilizing a ball milled mixture of  $\text{LiAlH}_4 + 5$  wt.% to the extent that it is capable to desorb slowly quite substantial quantities of hydrogen at RT, 40 and 80 °C. The rate of  $\text{H}_2$  release during storage at this temperature range can be easily regulated by increasing or decreasing temperature. These virtues make the  $\text{LiAlH}_4 + 5$  wt.% n-Ni mixture a potential hydrogen storage material for applications where a continuous supply of hydrogen is required for a prolonged service time as, for example, in some chemical processes where the presence of a reducing atmosphere is required. Rehydrogenation attempts of ball milled dehydrogenated  $\text{LiAlH}_4 + 5$  wt.% n-Ni have been made. The dehydrogenation temperatures were selected in such a manner as to rehydrogenate either starting from the  $(\text{Li}_3\text{AlH}_6 + \text{Al})$  (dehydrogenation at 120 °C) or from the  $(\text{LiH} + \text{Al})$  (dehydrogenation at 170 and 250 °C) phase composition. Rehydrogenation temperatures and pressures of  $\text{H}_2$  were in the range of 55–250 °C and 0.2–10 MPa, respectively. Unfortunately, no successful rehydrogenation has been observed under these conditions.

© 2010 Elsevier B.V. All rights reserved.