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Mechanochemical synthesis of ultrafine $TiAl_3$ powder and its catalytic effect on dehydrogenation of Li_3AlH_6

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Abstract

Ultrafine $TiAl_3$ powder has been mechanochemically synthesized using a reaction between $TiCl_3$, $AlCl_3$ and Mg. $MgCl_2$ byproduct was removed from the product mixture by dissolving it selectively in distilled water. This ultrafine $TiAl_3$ whose primary particle size is about 100 nm shows a quite good catalytic effect on reducing the dehydrogenation temperature of Li_3AlH_6. Although its catalytic ability does not exceed well-known titanium chlorides, the inevitable loss in hydrogen storage capacity by introducing catalyst is less with $TiAl_3$ than with $TiCl_3$.

Keywords: Hydorgen storage materials; Alanates; Mechanochemical synthesis; Catalyst

1. Introduction

Akali and alkali-earth metal alanates (aluminum hydrides) have attracted much interest as lightweight hydrogen storage materials for on-board applications since Bogdanovic and Schwickardi [1] discovered that reversible hydrogen storage and accelerated kinetics in sodium alanate ($NaAlH_4$) could be achieved by doping with Ti-containing catalysts. The catalytic role of Ti in alanates is, however, still poorly understood, although various attempts to understand what form of Ti resides in alanates have been made so far [2–9]. The results of recent investigations [2,4,6,8] seem to support a conjecture that Ti in situ forms $TiAl_3$ when introduced into alanates, although there is another conjecture that Ti substitutes for metal sites in alanates [3,7,9].

If Ti does form $TiAl_3$ in alanates and act as an effective catalyst, it is worthwhile to confirm its efficacy by adding $TiAl_3$ instead of $TiCl_3$ into alanates because $TiCl_3$ reduces hydrogen storage capacity of alanates by reacting with part of alanates to form impotent salts such as NaCl and LiCl even before dehydrogenation. In fact, Balema et al. [2] and Resan et al. [10] have recently attempted to confirm the catalytic ability of $TiAl_3$ by dispersing $TiAl_3$ powder prepared by ball milling arc melted sample and commercial powder (<150 μm), respectively, into $LiAlH_4$. They showed that the addition of $TiAl_3$ indeed decreased the dehydrogenation starting temperature of $LiAlH_4$ by about 10 °C, although it may not be significant. It is desirable to produce as fine $TiAl_3$ powder as possible because it should play an active catalytic role with minimum amount [11,12]. Mechanical milling is one of the simple and cost-effective methods for producing $TiAl_3$ powders [13,14]. However, it might be difficult to obtain fine $TiAl_3$ particles using conventional milling techniques because $TiAl_3$ is relatively ductile and thus they easily agglomerate during milling [14].

In this paper, we report the synthesis of ultrafine $TiAl_3$ particles using a mechanochemical reaction. Their catalytic effect on the dehydrogenation of Li_3AlH_6 has also been confirmed and compared with that of $TiCl_3$. The main reason to adopt Li_3AlH_6 instead of $LiAlH_4$ in the present study is that the hydrogen pressure needed for reverse hydrogenation reaction is estimated to be an order of 10^4 bar [15].

2. Experimental procedures

Ninety-nine percent pure $TiCl_3$ and 99.9% pure $AlCl_3$ were purchased from Sigma–Aldrich and 99.8% pure Mg was from Alfa-Aesar. A mixture of $TiCl_3$, $AlCl_3$ and Mg with a molar ratio of 1:3:6 was prepared and then a 1 g mixture was charged together with seventeen 7.9 mm diameter Cr-steel balls into a tool-steel vial under an Ar atmosphere in a glove box. The ball-to-powder weight ratio (BPR) was approximately 35:1. The mixture was milled in a SPEX 8000 mill for 4 h. The milled powder was rinsed in distilled water and filtered in order

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to remove chloride formed during milling. The powder was characterized by X-ray diffraction (XRD) using Bruker D8 Advance with Cu Kα radiation and scanning electron microscopy (SEM) using FEI XL-30 FEG.

Li_3AlH_6 was mechanochemically synthesized by milling 95% pure $LiAlH_4$ and 95% pure LiH purchased from Sigma–Aldrich as follows. A mixture of $LiAlH_4$ and LiH with a molar ratio of 1:2 was prepared and then a 5 g mixture was charged together with ten 14.0 mm and thirty 9.5 mm diameter zirconia balls into a silicon nitride vial under an Ar atmosphere in a glove box. The BPR was approximately 37:1. The mixture was milled in a Fritsch P4 planetary mill at 350 rpm for 4 h 30 min.

In order to confirm the catalytic effect of $TiAl_3$ synthesized in the present work on dehydrogenation of Li_3AlH_6, 5 mol% $TiAl_3$ was dispersed into Li_3AlH_6 by milling them with a SPEX 8000 mill for 30 min at the same milling condition as the $TiAl_3$ synthesis. $TiCl_3$ was also dispersed for comparison. The dehydrogenation behavior of Li_3AlH_6 with and without catalysts was analyzed by differential scanning calorimetry (DSC) using NETSCH DSC204 and thermogravimetry (TG) using NETSCH TG209 coupled with NETSCH QMS403C. The heating rate was 2 °C/min and the flow rate of 99.9999% Ar gas was 50 ml/min for both DSC and TG measurements.

3. Results and discussion

XRD patterns of the mixture of $TiCl_3$, $AlCl_3$ and Mg milled for 4 h and rinsed in water after the milling are presented in Fig. 1. $TiAl_3$ and $MgCl_2$ are identified as reaction products after milling (Fig. 1a). It is found that $TiAl_3$ has the $L1_2$ structure, although $D0_{22}$ is the most energetically stable [16]. $L1_2$-$TiAl_3$ rather than $D0_{22}$ has been observed usually observed during milling, because the $L1_2$ structure is kinetically advantageous [13]. Starting materials such as $TiCl_3$, $AlCl_3$ and Mg are not observed, which indicates that the following reaction is completed during milling.

$$TiCl_3 + 3AlCl_3 + 6Mg \rightarrow TiAl_3 + 6MgCl_2 \qquad (1)$$

As shown in Fig. 1b, relatively pure $L1_2$–$TiAl_3$ is easily obtained, as $MgCl_2$ formed during milling is dissolved in water and insoluble $TiAl_3$ is filtered.

Fig. 2 shows SEM micrograph of the $TiAl_3$ powder obtained in the present work. The primary particle size is around 100 nm and it exhibits an irregular shape, although most particles are agglomerated. It is ultrafine, compared to coarse particle size (>10 μm) of $TiAl_3$ obtained from milling of a mixture of Ti and Al powders [14]. It can be concluded that this chloride-mediated mechanochemcal reaction is very effective in reducing product particle size, as Tsuzuki and McCormick [17] already showed for various mechanochemical reaction systems.

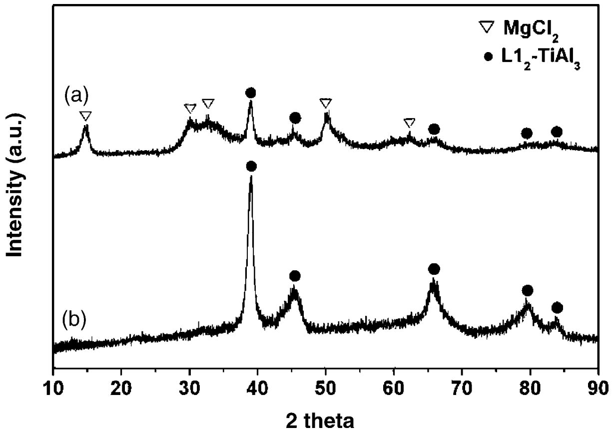

Fig. 1. XRD patterns of (a) $TiAl_3$/$MgCl_2$ synthesized by mechanical milling and (b) $TiAl_3$ obtained by rinsing in water after the milling.

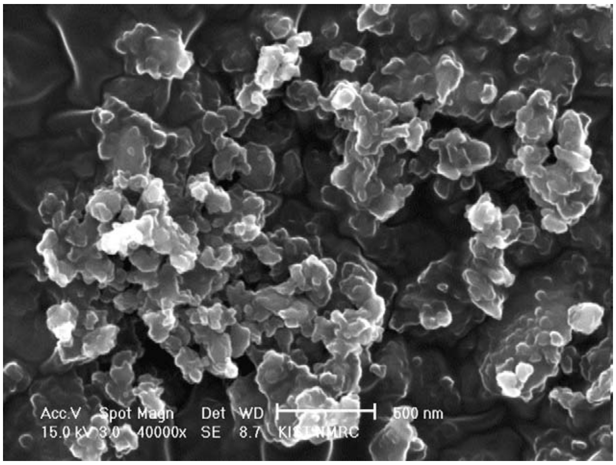

Fig. 2. SEM micrograph of the synthesized $TiAl_3$ powder.

XRD patterns of Li_3AlH_6 catalyzed with $TiAl_3$ and $TiCl_3$ are presented in Fig. 3. It seems that $TiAl_3$ is stable in Li_3AlH_6 without any reaction or transformation (Fig. 3a), although most of $TiAl_3$ peaks except for (2 2 0) overlap with those of Li_3AlH_6. It is believed that $TiCl_3$ dispersed into Li_3AlH_6 reacts with part of Li_3AlH_6 and forms LiCl and $TiAl_3$ as reaction products. While the formation of LiCl is clear as shown in the XRD pattern (Fig. 3b), the formation of $TiAl_3$ is not evident with a small amount of $TiCl_3$. This is presumably because the crystallite size of $TiAl_3$ in situ formed in Li_3AlH_6 is too small to identify with XRD. However, Graetz et al. [6] reported that the formation of nanocrystalline $TiAl_3$ in $NaAlH_4$ catalyzed with 2 and 4 mol% $TiCl_3$ was observed by high-energy X-ray absorption and we also observed the obvious formation of $TiAl_3$ in Li_3AlH_6 catalyzed with 17 mol% $TiCl_3$ using XRD [18].

Fig. 4 shows DSC curves of Li_3AlH_6 with and without catalysts. All specimens exhibit big endothermic peaks according to the following dehydrogenation reaction:

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \qquad (2)$$

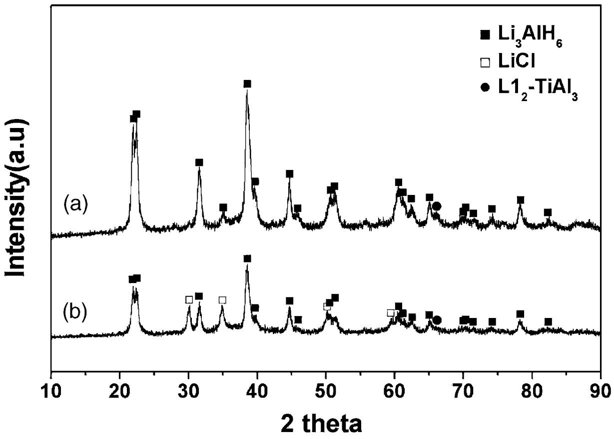

Fig. 3. XRD patterns of Li_3AlH_6 catalyzed with (a) $TiAl_3$ and (b) $TiCl_3$.

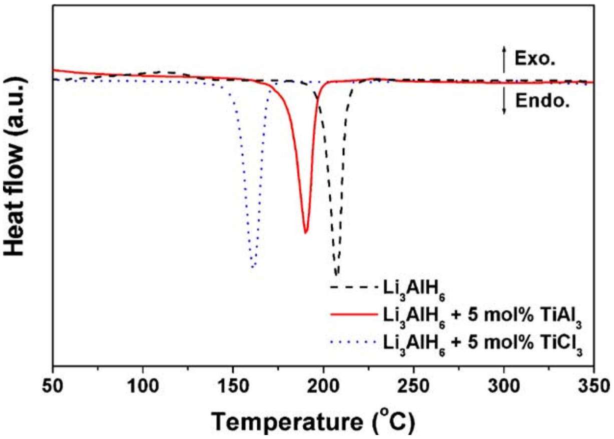

Fig. 4. DSC curves of Li_3AlH_6 with and without catalysts.

Without catalysts, Li_3AlH_6 start to decompose releasing H_2 gas (dehydrogenation) at about 190 °C and the peak temperature is about 210 °C. On the other hand, the dehydrogenation of Li_3AlH_6 containing $TiAl_3$ start at about 160 °C and exhibit the peak at about 180 °C. This decrease in dehydrogenation temperature is quite large compared to those of Balema et al. [2] and Resan et al. [10]. This might be attributed to the ultrafine particle size of $TiAl_3$ prepared in the present work. However, the catalytic effect of ultrafine $TiAl_3$ is not comparable to that of $TiCl_3$ showing the dehydrogenation starting temperature of about 130 °C. It is not fully understood yet why there exists a difference in catalytic ability between $TiAl_3$ and $TiCl_3$. This is presumably because the in situ formation and dispersion of $TiAl_3$ by the reaction between $TiCl_3$ and Li_3AlH_6 is more advantageous than the direct dispersion of $TiAl_3$ in aspects of the uniform dispersion and fine particle size of the catalyst and oxide layers on the surface of the $TiAl_3$ particles formed during the preparation decrease the catalytic ability.

TG curves show the amount of released hydrogen as well as the dehydrogenation temperature region (Fig. 5). Li_3AlH_6 without catalysts releases about 4.8 wt.% during dehydrogenation, which is lower than the theoretical hydrogen storage capacity 5.6 wt.% due to the low purity of raw materials and the partial decomposition of Li_3AlH_6 during mechanochemical preparation. It is noted that Li_3AlH_6 catalyzed with $TiAl_3$ releases larger amount of hydrogen (4.5 wt.%) than $TiCl_3$ (4.0 wt.%) as expected. This is because $TiCl_3$ decomposes part of Li_3AlH_6 during milling for dispersion before dehydrogenation and thus decreases the hydrogen storage capacity of Li_3AlH_6. Therefore, it will be favorable to add $TiAl_3$ instead of $TiCl_3$ into alanates in order to minimize the loss in hydrogen storage capacity.

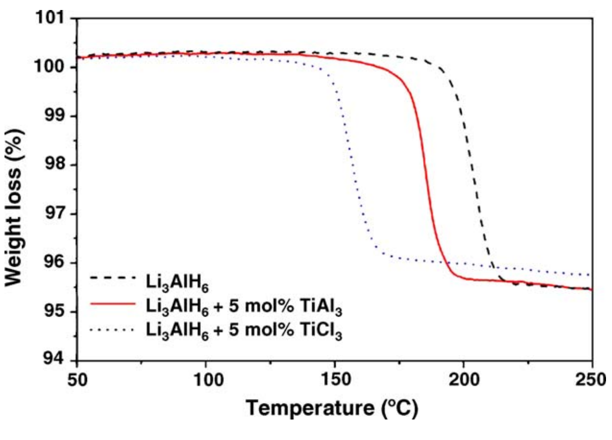

Fig. 5. TG curves of Li_3AlH_6 with and without catalysts.

4. Conclusions

Ultrafine $TiAl_3$ powder has been synthesized using a mechanochemical reaction between $TiCl_3$, $AlCl_3$ and Mg. The primary particle size of $TiAl_3$ is around 100 nm and its particle shape is irregular. The addition of ultrafine $TiAl_3$ decreases the dehydrogenation temperature of Li_3AlH_6 by about 30 °C compared to Li_3AlH_6 without any catalyst. Although $TiCl_3$ is more effective in reducing the hydrogenation temperature, it is demonstrated that the use of ultrafine $TiAl_3$ catalyst is more favorable than $TiCl_3$ in terms of hydrogen storage capacity.

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