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Formation of metal hydrides by mechanical alloying

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Abstract

Metal hydrides ($TiH_{1.9}$, δ-$ZrH_{1.66}$ and MgH_2) have been synthesized by mechanical alloying of metal powders in a hydrogen atmosphere at room temperature. The milling process was monitored using H_2 pressure measurement. The sharp decrease in H_2 pressure during milling indicates a high rate of H_2 absorption into the metal powders. X-ray diffraction analysis of as-milled powders shows convertion to hydrides at short milling times (less than 6 h). Decomposition of the so-formed metal hydrides has been observed during thermal analysis. The results indicate that pulverization and deformation processes occurring during high energy ball impacts play a major role in the hydriding reaction.

Keywords: Mechanical alloying; Hydrides; Hydriding reactions; Mechanosynthesis; Reactive ball milling

1. Introduction

Metal hydrides have a large range of applications such as purification of hydrogen, hydrogen embrittlement in powder metallurgy, control materials in nuclear reactors, and electrodes for batteries and hydrogen storage materials [1]. Metal hydrides are generally produced by exposing metals to hydrogen gas at a convenient pressure and temperature.

Recently, the mechanical alloying technique has been used to produce high temperature metal nitrides at room temperature. A large number of metal nitrides have been produced by ball milling of elemental metals in N_2 or NH_3 atmospheres [2]. In the milling process of Ti in ammonia gas, the formation of the $TiH_{1.9}$ phase was firstly found during the early stage of milling [3]. This suggests that mechanical alloying probably could be a simple and economical method to produce metal hydride powders in high quantity. In this paper, we demonstrate that metal hydrides can be synthesized easily by ball milling of metal powders at a low hydrogen pressure (about 2 atm) and at room temperature. The thermal stability of the thus-formed hydrides has been investigated.

2. Experimental details

The starting materials for ball milling are elemental powders of titanium, zirconium and magnesium with purity greater than 99.9%. The average particle size is about 100 mesh. High purity hydrogen gas is used as the reaction atmosphere. Ball milling was performed in a vertical planetary mill. The mill container was loaded with several grams of metal powder and 20 hardened steel balls (diameter 12 mm) and sealed with a Viton O-ring. The container was evacuated to vacuum (−100 kPa) prior to filling with hydrogen gas. Evolution of H_2 in the container was monitored using a gauge over the pressure range from −100 to 500 kPa.

The crystalline structure of as-milled powders was characterized by X-ray diffraction (XRD) analysis using Co radiation ($\lambda = 0.1789$ nm). The thermal stability was investigated using a Shimadzu differential thermal analyser and a thermogravimetric analyser. Heating was carried out at a rate of 20 °C min^{-1} in a pure Ar flow. The H content of as-milled powders was determined using combustion elemental analysis (CEA) (Carlo Erba 1106). Scanning electron microscopy (SEM) was employed to study the powder morphology.

3. Results

Fig. 1 shows the observed variation in hydrogen pressure during the milling of different metals. The H_2 pressure decreased quickly from 240 to −100 kPa during milling Ti powder for only 5.5 h. The final pressure (−100 kPa) in the container remained unchanged during prolonged milling for up to 67 h. A similar pressure variation was observed in the case of Zr metal; the pressure decreased from 235 to −80 kPa at the end

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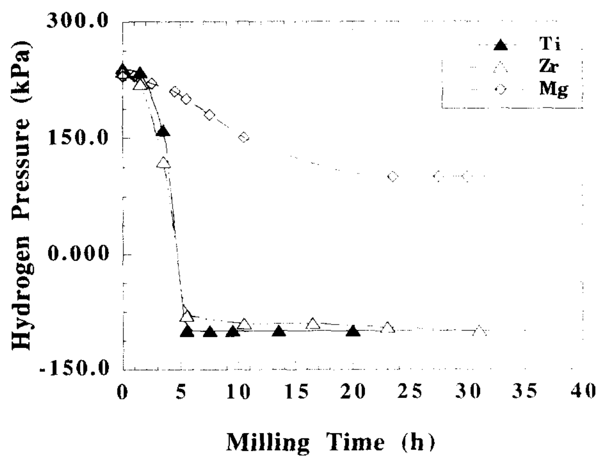

Fig. 1. Variations in hydrogen pressure during the ball milling of Ti, Zr and Mg powders.

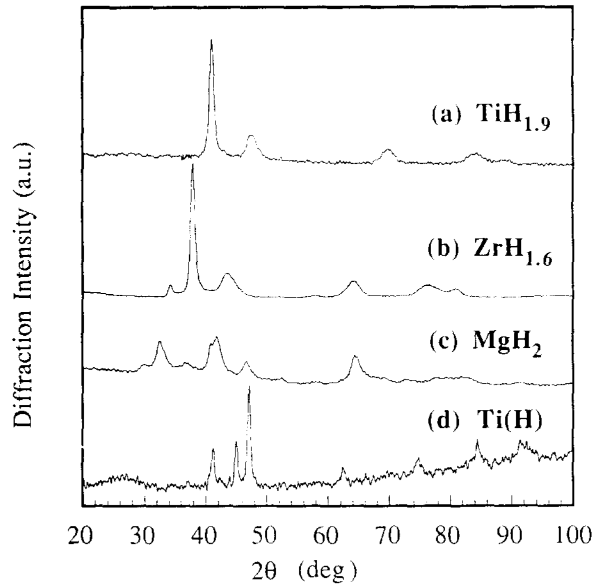

Fig. 2. XRD patterns of as-milled powders: curve (a), Ti powder milled for 5.5 h; curve (b), Zr powder milled for 48 h; curve (c), Mg powder milled for 47.5 h; curve (d), Ti pre-milled in vacuum for 17 h and subsequently exposed to H_2 for 6 h.

of 5.5 h. After milling for 31 h, the pressure stabilized at -100 kPa. In the case of Mg, the pressure decreased to -100 kPa after milling for 23.5 h. Prolonged milling did not change the H_2 pressure. The large decrease in hydrogen pressure during milling indicates a substantial absorption of H_2 into the powder particle surface. Most of the hydrogen gas was absorbed in Ti and Zr powders under milling, where the pressure attained -100 kPa. The different rates of pressure decrease indicate that Ti and Zr powders have a higher absorption rate of H_2 than Mg does. The different final pressures presumably depend on both different surface areas and solubilities of H in various metals.

The XRD patterns of different as-milled powders are shown in Fig. 2. Fig. 2(a) is the XRD pattern recorded from Ti powder milled in H_2 for 5.5 h. It consists of a full set of diffraction peaks of the cubic $TiH_{1.9}$ phase with no detectable peaks from a pure Ti phase. Thus α-Ti is converted to $TiH_{1.9}$ after milling in H_2 for only 5.5 h. In addition, the thus-formed $TiH_{1.9}$ phase was stable during prolonged milling, with only a reduction of particle size being observed. The XRD pattern, presented in Fig. 2(b), shows that the 48 h as-milled Zr powder has a structure consistent with the tetragonal δ-$ZrH_{1.66}$ phase. Finally, a MgH_2 phase has been identified in the XRD pattern taken from the Mg powder milled in H_2 for 47.5 h (Fig. 2(c)). Unreacted Zr and Mg metals have not been found in these XRD patterns. Therefore all metals milled in H_2 converted to their respective hydrides after milling for appropriate times.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) results of the Ti as-milled powder are shown in Fig. 3. The DTA curve shows an endothermic peak at 588 °C. TGA reveals that a weight loss of 1.72 wt.% occurred from 387 to 736 °C. Comparing DTA and TGA curves, we find that the endothermic reaction range covers the temperature domain of weight loss. This suggests that the endothermic reaction corresponds to the decomposition of $TiH_{1.9}$ with the release of H_2 gas from the powder. XRD analysis of DTA and TGA samples confirm that the $TiH_{1.9}$ phase returned to α-Ti after heating. Similar DTA and TGA curves were obtained for the Mg as-milled powder (Fig. 4). An endothermic reaction takes place at 382 °C. The weight loss is 0.50 wt.% in the temperature range 304–483 °C. Pure Mg and MgO_2 were obtained after heating. MgO_2 presumably results from oxidation during heating. In the case of the Zr as-milled powder, the DTA curve consists of two ex-

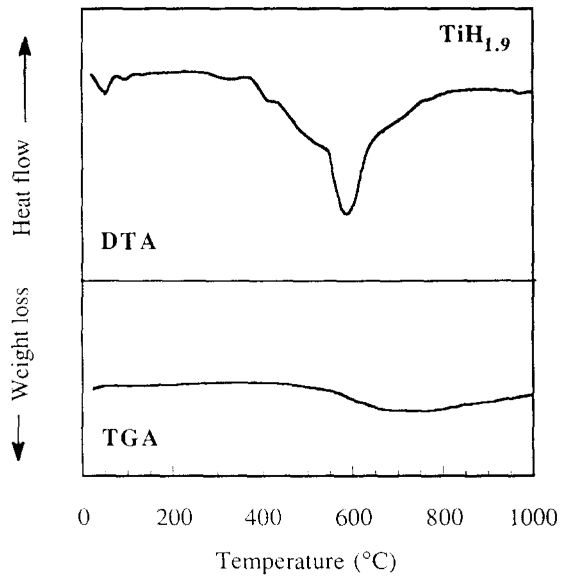

Fig. 3. DTA and TGA curves of Ti as-milled powder.

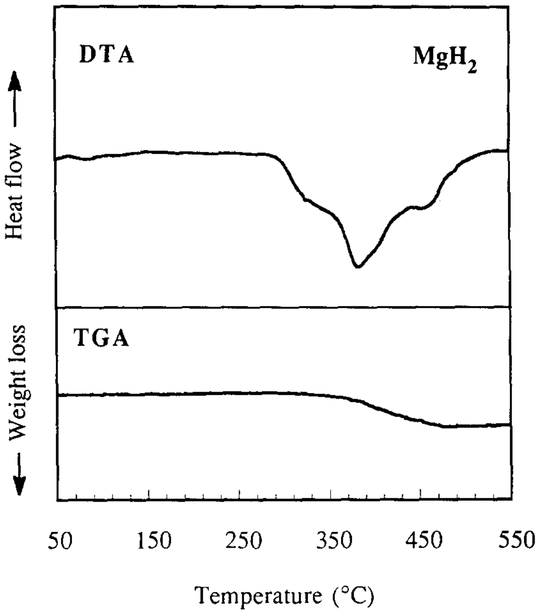

Fig. 4. DTA and TGA curves of Mg as-milled powder.

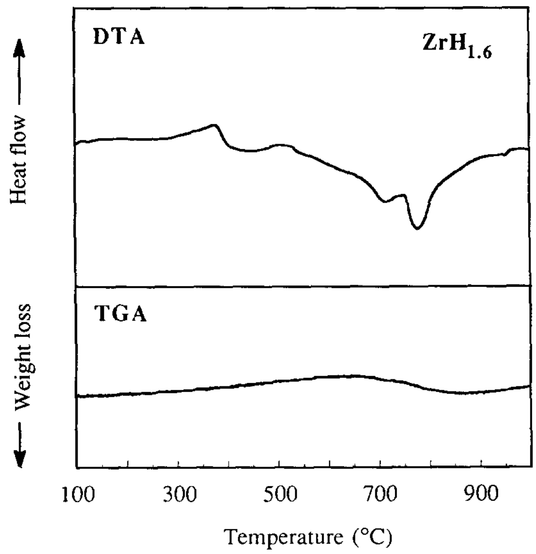

Fig. 5. DTA and TGA curves of Zr as-milled powder.

othermic reactions (375 and 508 °C) and two endothermic reactions at 717 and 779 °C (Fig. 5). The equilibrium diagram of Zr–H [4] suggests that the two exothermic reactions at low temperatures are probably phase transformations between different hydrides and the endothermic reactions are due to decomposition of the hydrides. The total decrease in weight is 0.66 wt.% from 634 to 870 °C. Thus ball-milled metal hydride powders are thermal metastable and decompose at specific temperatures. A slight oxidation occurred during heating, as indicated by the TGA curves.

The H content (weight per cent) of the as-milled powders determined using CEA are listed in Table 1, as well as the weight loss of each hydride during TGA heating and the available H content. The available H

Table 1
H contents and thermogravimetric analysis weight losses of as-milled powders and available H contents

Sample	Measured H content (at.%)	Measured H content (wt.%)	Available H (wt.%)	Weight loss (wt.%)
Ti	62.6	3.38	3.3	1.72
Zr	56.0	1.55	1.6	0.66
Mg	66.2	7.46	14.9	5.60

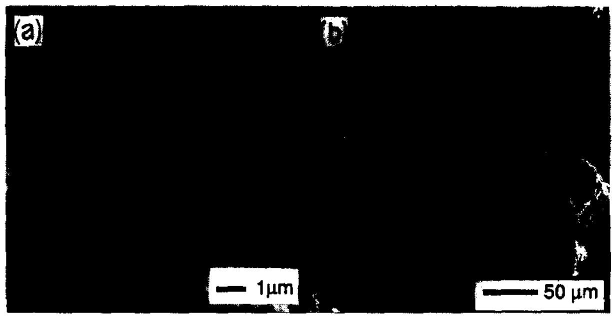

Fig. 6. SEM pictures of Ti as-milled powders: (a) 5.5 h in H_2; (b) 17 h in vacuum.

content is calculated from the starting hydrogen pressure and the amount of starting powder. The results show that a high content of H exists in the as-milled powders (e.g. 2:1, H in Ti and Mg). However, the H content (weight per cent) of the as-milled powders is higher than the TGA weight losses during annealing. The difference is most likely a result of oxidation, as previously mentioned.

The SEM picture of the Ti powder milled in H_2 for 5.5 h is shown in Fig. 6(a). The powder particles have a spherical shape with a particle size below 1 μm. Fig. 6(b) is an SEM picture of the Ti powder milled in vacuum for 17 h. The particles have an irregular shape and the particle sizes are between 50 and 200 μm. The large difference in particle size of above two powders clearly shows the embrittlement effect of hydrogen during the milling process and ease of particle size reduction.

A complementary experiment has been carried out to investigate the role of high energy ball impacts in the hydriding process. A pure titanium powder was firstly milled in vacuum (−100 kPa) for 17 h. The milling process was then stopped and the as-milled powder was exposed to hydrogen gas at a pressure of 210 kPa. The hydrogen pressure was found to decrease gradually with increasing time and saturated at 10 kPa after about 6 h. The powder was examined using CEA and a H content as high as 24 at.% was found. However, the powder still has an α-Ti structure and the titanium hydride phase is not found with XRD analysis (Fig. 2(d)).

4. Discussion

The above experimental results show that metal hydrides can be synthesized during short milling times by mechanical alloying of metal powders in hydrogen at room temperature. The thus-formed hydrides have a high H content and about the same thermal stabilities as hydrides produced with conventional methods [5]. The hydrogen pressure variations during milling suggest that the hydriding process has two steps as follows. Hydrogen is firstly absorbed on new particle surfaces created by pulverization during initial milling. The absorbed H then reacts with metal to form metal hydrides under further high energy ball impacts.

Full transformation of the metals to metal hydrides has been observed when the hydrogen pressure decreases to a stable level. The high absorption rate and the short milling time for the hydride phase formation compared with the nitriding reaction [3] indicate that the H–metal reaction kinetics are fast. In this regard, in comparison with N in metals, H atoms have a high mobility in most metal lattices even at low temperatures [6]. Furthermore, plastic deformation and lattice stress are known to accelerate the H diffusion process [7]. Our experimental results of the pre-milled Ti powder show that the absorption rate of hydrogen without milling is slower than the absorption rate under milling. In addition, little hydride is formed without continuous milling. Thus high energy ball impacts have a crucial role in enhancing (promoting) the reaction. We further speculate that the embrittlement of the metal by hydride formation enhances fracturing and particle size reduction, resulting in a large surface area for hydrogen absorption. As a consequence, the required diffusion lengths for reaction are shortened. Furthermore, the continuous fracturing processes prevent surface passivative oxide or hydride layers which inhibit the hydriding reaction. Thus fracturing of particles and stress effects during ball impacts may be the dominant driving force in hydride formation during mechanical alloying.

Possible local temperature rise, induced by ball impacts, may also contribute to the hydriding reaction. However, the exact impact mechanism is still obscure. More detailed studies are needed to investigate the reaction mechanism during mechanical alloying.

The analysis of H content suggests that the hydriding reaction induced by mechanical alloying can be carried out completely provided that sufficient hydrogen gas is available. Excess H_2 was supplied in the case of Mg powder; thus some unreacted H_2, giving rise to a positive final pressure, remained when Mg was fully converted to MgH_2. By contrast, the available hydrogen content in the cases of Ti and Zr powders was either just sufficient or less than that required for stoichiometric hydrides. Thus all the hydrogen was absorbed into the powders during milling, resulting in a partial vacuum in the mill container. The results in Table 1 show that the available hydrogen content is about the same as the measured hydrogen content in the Ti and Zr as-milled powders and the hydrogen content in Mg as-milled powder is about half the available hydrogen content. Thus ZrH_2 is not formed because of insufficient hydrogen gas. Therefore, we conclude that hydrides with different H contents can be produced by controlling the hydrogen pressure.

6. Conclusions

$TiH_{1.9}$, δ-$ZrH_{1.66}$ and MgH_2 have been produced by ball milling of pure metal powders in hydrogen gas at room temperature. The results indicated that pulverization and deformation processes occurring during high energy ball impacts play a major role in the hydriding reaction. The thus-formed hydrides decomposed at different temperatures during heating. Therefore mechanical alloying is a simple and inexpensive method of producing high H content metal hydrides.

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