

Hydriding Reactions Induced by Ball Milling

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Abstract

Hydriding reactions between metal powders (Ti, Zr and Mg) have been realised by ball milling at room temperature. Metal-hydrides ($\text{TiH}_{1.9}$, $\text{ZrH}_{1.66}$ and MgH_2) were obtained at short milling times. The milling process was monitored using H_2 pressure measurement. The sharp decrease of H_2 pressure during milling indicates high rates of H_2 absorption and hydriding reactions. Decomposition of the so-formed metal-hydrides has been observed during thermal analysis. Results indicate that pulverisation and deformation processes occurring during high-energy ball impacts play a major role in the hydriding reaction.

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, 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.

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 atms) and at room temperature. The thermal stability of the so-formed hydrides has been investigated.

2. Experimental details

The starting materials for ball-milling are elemental powders of titanium, zirconium and magnesium (99.9%, 150 μ m). High purity hydrogen gas is used as the reaction atmosphere. Ball milling was performed in a vertical rotation ball mill. The mill container was loaded with several grams of a metal powder and 20 hardened steel balls ($\phi=12$ mm), and sealed with a Viton O-ring. The container was evacuated to vacuum (-100kPa) prior to filling with hydrogen gas. Evolution of H₂ in the container was monitored using a gauge over the pressure range from -100 kPa 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 analyzer (DTA) and a thermogravimetric analyzer (TGA). Heating was carried out at a rate of 20°C/min in a pure Ar flow. H content of as-milled powders was determined using combustion elemental analysis (Carlo Erba 1106) (CEA). Scanning electron microscopy (SEM) was employed to study powder morphology.

3. Results

Fig. 1 shows the observed variation in hydrogen pressure during the milling of different metals. The H₂ pressure decreased quickly from 240 kPa to -100 kPa during only 5.5 hours of milling for Ti powder. The final pressure (-100 kPa) in the container remained unchanged during prolonged milling up to 67 hours. A similar pressure variation was observed in the case of Zr metal, the pressure decreased from 235 kPa to -80 kPa at the end of 5.5 hours. After 31 hours of milling, the pressure stabilised at -100 kPa.

In the case of Mg, the pressure decreased to 105 kPa after 23.5 hours of milling. Prolonged milling did not change the H₂ pressure. The large decrease of hydrogen pressure during milling indicates a substantial absorption of H₂ into the powder particle surface. Most of the hydrogen gas was

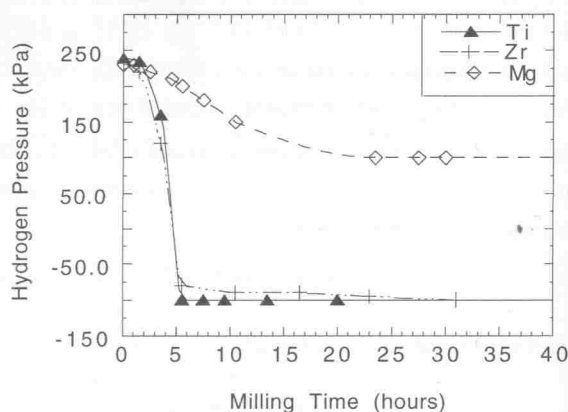


Fig. 1 Variation in hydrogen pressure during the ball milling of Ti, Zr and Mg

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. The different final pressures presumably depend 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. 2a is the XRD pattern recorded from Ti powder milled in H_2 for 5.5 hours. It consists of a full set of diffraction peaks of the cubic $TiH_{1.9}$ phase. In addition, the so-formed $TiH_{1.9}$ phase was stable during prolonged milling for up to 150 hours, with only a reduction of particle size being observed. The XRD pattern, presented in fig. 2b, shows that the 48h as-milled Zr powder has a structure consistent with the tetragonal δ - $ZrH_{1.66}$ phase. Finally, MgH_2 phase has been identified in the XRD pattern taken from the Mg powder milled in H_2 for 47.5 hours (fig. 2c). The unreacted metals have not been found in these XRD patterns. Therefore, all metals milled in H_2 converted to respective hydrides after milling for appropriate times.

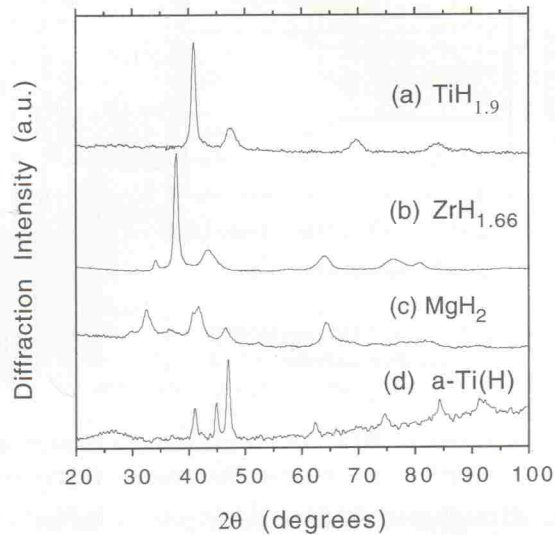


Fig. 2 XRD patterns of as-milled powders:
 (a), Ti powder milled in H_2 for 5.5h;
 (b), Zr powder milled in H_2 for 48h;
 (c), Mg powder milled in H_2 for 47.5h;
 (d), Ti pre-milled in vacuum for 17h and subsequently exposed to H_2 for 560h.

DTA and TGA results of the Ti as-milled powder are shown in fig. 3. The DTA curve shows an endothermic peak at $590^\circ C$. TGA analysis reveals that a weight loss of 1.72 wt.% occurred from $390^\circ C$ to $740^\circ C$. 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

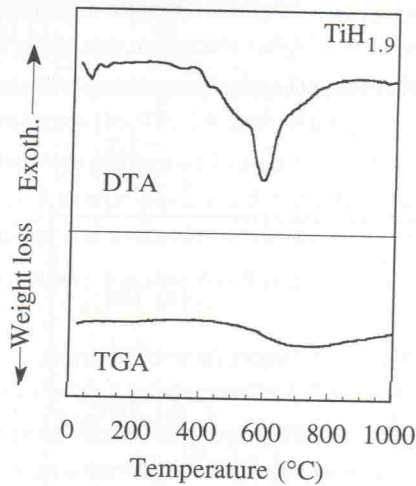


Fig. 3 DTA and TGA curves of Ti as-milled powder

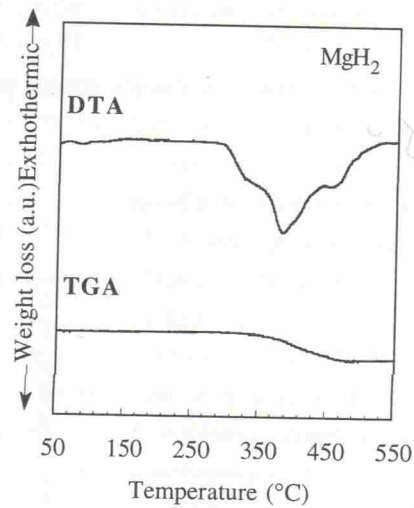


Fig. 4 DTA and TGA curves of Mg as-milled powder

reaction takes place at 380°C. The weight loss is 5.60 wt.% in the temperature range of 300°C–480°C. Pure Mg and MgO₂ were obtained after heating. MgO₂ presumably results from oxidation during heating. In the case of the Zr as-milled powder, the endothermic reactions are at the temperature range from 700°C to 800°C. The total decrease in weight is 0.66 wt.%. Thus, ball milled metal-hydride powders are thermal metastable and decompose at specific temperatures.

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

The H content (wt.%) of the as-milled powders determined using CEA are tabulated in Table 1, as well as the weight loss of each hydride during TGA heating and the available H content. The available H 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 (wt.%) of the as-milled powders is higher than the TGA weight losses during annealing. The difference is most likely as a result of oxidation, as previously mentioned.

A complementary experiment has been carried out to investigate the role of high-energy ball impacts in the hydriding reaction process. A pure titanium powder was firstly milled in vacuum (-100 kPa) for 17 hours. 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 300 hours (Fig. 5). 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.2d).

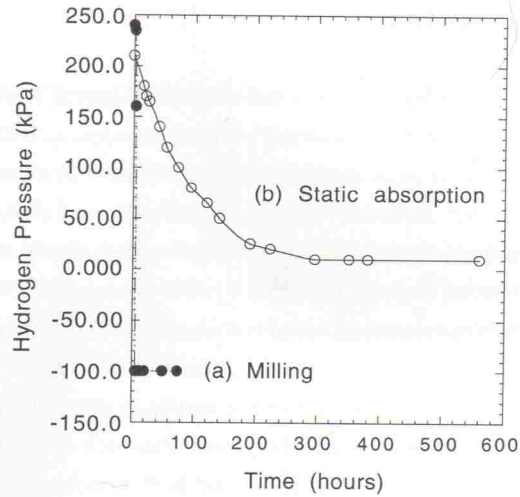


Fig. 5 (a), H₂ pressure change during milling of Ti in H₂; (b), H₂ pressure change during static absorption of H₂ into the pre-milled Ti powder.

The SEM pictures of the Ti powder milled in H₂ 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 a SEM picture of the Ti powder milled in vacuum for 17 hours. The particles have an irregular shape and the particle sizes are between 50-200 μm . The large difference in particle size of above two powders clearly shows the embrittlement effect of hydrogen during milling process and ease of particle size reduction.

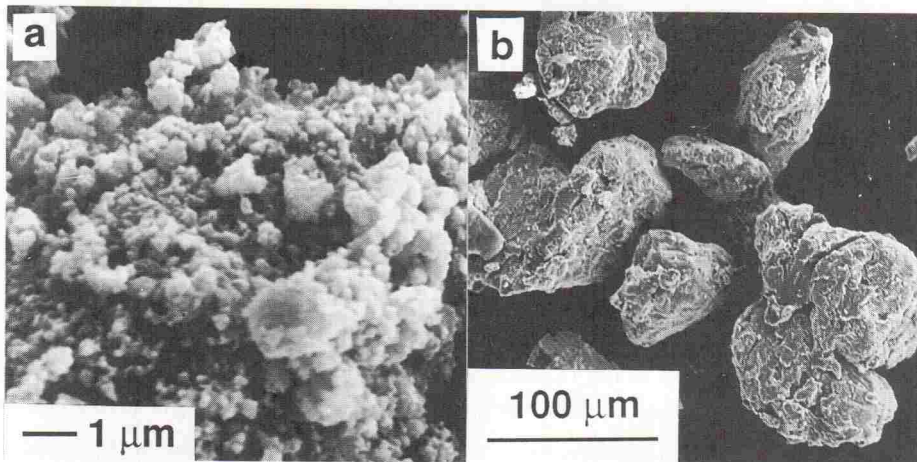


Fig.6 SEM pictures of Ti as-milled powders : (a) 5.5h in H₂; (b) 17h in vacuum.

4. Discussion

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 so-formed hydrides have high H content and about the same thermal stabilities as hydrides produced with conventional methods^[2]. 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 H₂ then is decomposed into free H atoms which react 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 nitriding reaction^[3] indicate that the H-metal reaction kinetics are fast. In this regard, compared to N in metals, H atoms have high mobility in most metal lattices even at low temperature^[4]. Furthermore, plastic deformation and lattice stress are known to accelerate the H diffusion process^[5]. Our experiment 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 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.

The analysis of H content suggests that the hydriding reaction induced by mechanical alloying can be carried out completely provided sufficient hydrogen gas is available. Excess H₂ was supplied in the case of Mg powder, thus some unreacted H₂, giving rise to a positive final pressure, remained when Mg was fully converted to MgH₂. By contrast, the available hydrogen content in the cases of Ti and Zr powders was either just sufficient or less than that required to form stoichiometric hydrides. Thus all the hydrogen was absorbed into the powders during milling, resulting in a partial vacuum in the mill container. The results of 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 of the available hydrogen content. Thus, ZrH₂ 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. Conclusion

TiH_{1.9}, δ-ZrH_{1.66} and MgH₂ have been produced by ball milling of pure metal powders in hydrogen gas at room temperature. The hydriding process has two steps as follows : hydrogen is firstly absorbed on new particle surfaces created by pulverization during initial milling. The absorbed H₂ then is decomposed into free H atoms which react with metal to form metal-hydrides under further high-energy ball impacts. Results indicated that pulverization and deformation processes occurring during high-energy ball impacts play a major role in the hydriding reaction. The so-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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