Formation of titanium hydride at room temperature by ball milling

LETTER TO THE EDITOR

Formation of titanium hydride at room temperature by ball milling

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Abstract. Titanium hydride with a body centred tetragonal structure was rapidly synthesized at room temperature by ball milling titanium powders under a hydrogen atmosphere. The structure evolution was monitored by x-ray diffraction and Rietveld analysis. Unit cell volume dilation suggests the hydrogenation process begins with the formation of a titanium–hydrogen solid solution followed by the formation of titanium hydride. Dehydrogenation of the hydride produced by milling and titanium hydride prepared by standard techniques was investigated by thermogravimetric analysis (TGA). The hydride formed by the milling process has lower initial and final dehydrogenation temperatures and a slightly narrower dehydrogenation temperature range compared to hydride prepared by traditional methods. The extremely fine particle size, large surface area and lattice defects introduced by milling are believed to be responsible for modification of the hydrogen storage behaviour.

Recent work has shown that combining gas absorption with ball milling may result in new types of phase transition which cannot be realized by either method alone. For instance, some mixtures of binary early transition metals with zero, or near-zero, heat of mixing have been amorphized by ball milling under hydrogen [1, 2], nitrogen [2, 3] and even oxygen [4] atmospheres. It was suggested that the amorphization is due to cooperative alloying and gas–metal chemical reactions. In addition, a large number of metal nitrides have been synthesized by ball milling pure elements under nitrogen or ammonia gas at room temperature [5–8]. The success of nitride synthesis by ball milling leads naturally to the possibility of synthesizing other metal–metalloid or metal–gas compounds such as oxides and hydrides by this method.

Metal hydrides have a number of possible applications as hydrogen storage media and in battery technology. Titanium hydride has a high storage capability and can be charged to different hydrogen contents, hence it has been widely studied. However TiH_2 is difficult to prepare and very resistant to decomposition. The traditional method to prepare TiH_2 is to expose Ti metal to H_2 at elevated temperature and/or pressure. A typical procedure involves outgassing the metal above $1000\,°C$, and then reacting with H_2 at about 1 atm pressure at $400\,°C$ for several hours and cooling slowly in order to attain the maximum hydrogen content [9]. The success of nitride synthesis by ball milling in gaseous atmospheres points the way to new methods of hydride production. In general, it is observed that the absorption of hydrogen into metals using traditional processes occurs more rapidly than nitrogen absorption. In addition, ball milling often modifies the behaviour of the milled system due to the storage of large amounts of deformation energy in lattice defects. Here, we report

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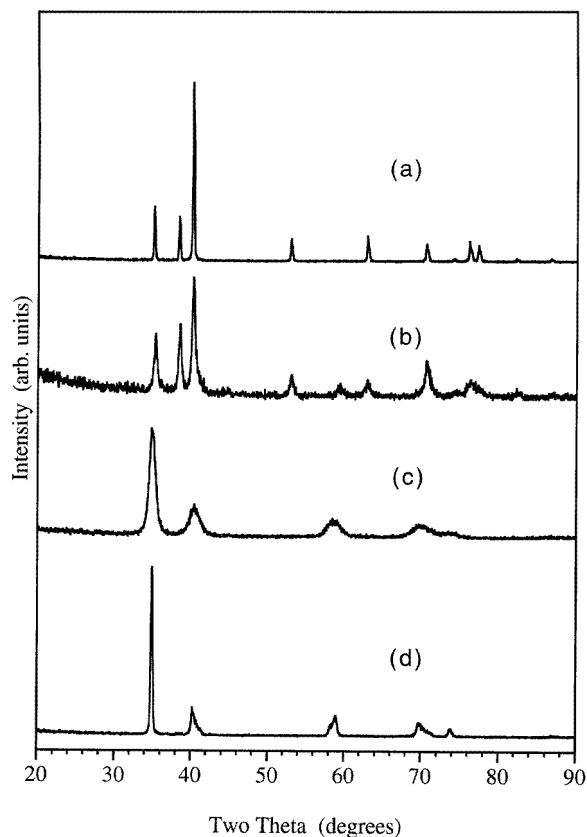
Figure 1. XRD patterns for titanium powders milled for 0 (a), 0.5 (b) and 3 h (c) under a hydrogen atmosphere, as well as the titanium hydride TiH$_{1.73}$ prepared by high-temperature gas absorption (d).

the synthesis of titanium hydride at room temperature by ball milling and an analysis of its hydrogen storage and dehydrogenation properties compared to those of titanium hydride prepared in the usual manner.

Elemental titanium powder with a purity of 99.98% and particle size of −325 mesh was used as the starting material. A standard titanium hydride (−325 mesh TiH$_{1.73}$ powder from Research Organic/Inorganic Chemical Corp., Sun Valley, CA, USA) was used as a reference for the hydrogen storage and dehydrogenation behaviour. The titanium powders were milled in a Shaker mixer/mill (Spex 8000) with hardened steel vial and balls and initially about 200 kPa of hydrogen pressure. Before filling the vial with hydrogen, it was evacuated to 10^{-4} mbar. After every $\frac{1}{2}$–1 h of milling, a Sievert-type gas–solid reactor coupled to the milling vial was used to measure the amount of hydrogen absorption and to load fresh hydrogen gas into the vial. This procedure was continued until the pressure did not change with further milling. The total hydrogen absorbed was calculated based on the pressure decrease (see below).

Structural information was monitored using a Philips PW 1700 x-ray diffractometer (XRD) with Cu Kα radiation. The structure parameters were refined by Rietveld analysis using the x-ray diffraction data [10]. The dehydrogenation characteristics for both milled

and standard TiH$_x$ samples were analysed using a Shimadzu thermogravimetric analyser (TGA) with a heating rate of 20 K min^{-1} under flowing argon.

During milling, it was found that the pressure of hydrogen decreased very quickly, especially after milling for 0.5–2 h. Sometimes, all of the fresh hydrogen charge was absorbed within minutes of filling the vial. There was a detectable temperature rise in the vial due to the release of the absorption enthalpy. The quantity of absorbed hydrogen was estimated, based on the following equation:

$$\Delta n = 2V_i(P_0 - P_i)/RT_i - V_s(P_i - P_{i-1})/RT_s \tag{1}$$

where V_i and V_s are the volume of the reference container and the vial, T_i and T_s the temperature of the gas in the reference volume and sample chamber, P_{i-1} and P_i the initial and end pressure of the whole system for the ith milling stage and P_0 the initial pressure in the reference volume.

The hydrogen content was determined as approximately TiH$_{0.8}$ and TiH$_{1.8}$ for samples milled for 0.5 and 3 h respectively. The hydrogenation rate is extremely fast especially since milling and absorption occur at close to room temperature.

The formation of the hydride during milling (and topping up of the vial with H$_2$ gas) can be further confirmed from the XRD patterns in figure 1 and the Rietveld analyses based on them (table 1). The initial powder is hexagonal closed packed as expected (figure 1(a)); for the sample milled for 0.5 h (figure 1(b)) both the peaks corresponding to Ti metal and titanium hydride are considerably broadened due to both a reduction of the particle size and hydrogen absorption. It is apparent that in the early stages the major phase is very fine Ti (actually titanium–hydrogen solid solution), and a small amount of titanium hydride. For the sample milled for 3 h (figure 1(c)), all the peaks corresponding to Ti have disappeared, and the XRD pattern shows a pseudo-face-centred-cubic pattern. The pattern for TiH$_{1.73}$ produced by standard techniques (body centred tetragonal in $I4/mmm$) is shown in figure 1(d) for comparison. They compare very well except for considerable peak broadening in the pattern from the hydride produced by milling. This pattern (1(c)) is also in excellent agreement with that of the TiH$_{1.73}$ powder milled under argon [11]. More detailed analysis with the Rietveld refinement program indicates that the crystallite size of the sample in figure 1(c) is only about 27 nm†. Hence, we can conclude that a nanocrystalline titanium hydride was synthesized at room temperature after a very short milling process.

More information about the process can be obtained from the Rietveld analysis results in table 1. Compared to the original Ti powder, the Ti sample milled for 0.5 h exhibits a crystallite size reduction from 114 nm to about 29 nm and the unit cell volume increases from 17.62 to 17.72 Å^3. The expansion of the unit cell volume is evidence of hydrogen solution in the Ti matrix. Hence, it would appear the first stage of the hydrogenation proceeds via the formation of a titanium–hydrogen solid solution. In addition, this sample also contains some titanium hydride. The refinements show that the TiH$_x$ has a larger c/a ratio and a smaller unit cell volume than TiH$_2$. Although the Rietveld fit for this sample is not perfect ($R_B \sim 10\%$), presumably due to local variation of hydrogen content, we can still conclude that the initial hydride has a relatively low-hydrogen composition due to a shortage of available hydrogen. After milling for 3 h, the c/a ratio decreases and unit cell volume increases. The volume expansion provides indirect information about the hydrogen composition. By comparison to the TiH$_{1.73}$ powder prepared by traditional methods, it

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† When measured in this way, 'crystallite size' refers to the mean size of coherently diffracting crystal domains and does not indicate how the crystallites are assembled into particles or grains or how the particles are assembled into agglomerates.

Table 1. Rietveld refinement parameters for the titanium and titanium hydrides.

| Sample | Lattice parameters | | | Unit cell volume | Particle size | Strain | Fit parameters | |
	a (Å)	b (Å)	(Å^3)	(nm)	(%)	GOF	R_B (%)
Ti	2.9519(2)	4.6887(4)	17.691(6)	114(4)	0.095	1.31	2.51
Milled Ti (0.5 h)[a]	2.952(3)	4.695(3)	17.72(5)	29(3)	0.305	1.42	7.60
[b]	3.106(3)	4.439(7)	42.8(2)	34(10)	0.47	1.42	10.93
Milled Ti (3 h)[b]	3.178(2)	4.394(3)	44.38(9)	27(2)	1.01	1.27	1.94
Standard TiH$_{1.73}$	3.1613(6)	4.3971(9)	43.94(3)	164(17)	0.309	2.5	6.81

[s] Hexagonal close packed titanium.
[b] Tetragonal titanium hydride.

would appear that both hydrides have similar hydrogen composition because of the similar lattice parameters and unit cell volume. This agrees very well with the previous analysis using equation (1).

The TGA results for desorption of samples produced by milling for 3 h and of the standard hydride are shown in figure 2. There are some subtle differences in the dehydrogenation behaviour. First, the desorption start temperature for the ball milled sample is approximately 687 K, compared to approximately $\sim$772 K for the other one. Second, the dehydrogenation end temperature for the milled sample is about 974 K, compared to 1079 K for the standard hydride. The dehydrogenation temperature range is also slightly narrower for the milled hydride than the standard sample (287 K and 307 K respectively). The ratio of the desorbed hydrogen for the milled sample to the standard sample is about 81%, contrary to expectation from the XRD and closed volume manometric procedure. Some weight gain can also be seen at high temperature for both samples, especially the milled one. This may be attributed to oxidation or nitrogenation due to impurities in the shielding gas. Because of the large active surface of the sample produced by milling, this effect will be more rapid and will distort any calculation of the amount of desorbed hydrogen.

Titanium metal is well known for its tightly adherent oxide film. This makes it suitable for use in very aggressive environments without suffering corrosive attack. In the standard procedure for titanium hydride production discussed earlier, the initial 1000 °C anneal in high vacuum is designed to modify the oxide film. After this annealing treatment, something approaching the true hydrogen absorption characteristics of Ti is thought to be observed by exposure to H_2 gas at 400 °C or above. Reference to a standard Ellingham diagram for the reaction $Ti + O_2 = TiO_2$ shows that at 1000 °C the equilibrium partial pressure P_{O_2} $< 10^{-27}$ atm, indicating that standard high-vacuum conditions at 1000 °C are not sufficient to reduce the oxide layer. It is therefore likely that the standard activation treatment does not expose free Ti surface, and consequently that measurements of the hydriding behaviour made under such conditions do not reveal the true properties of the metal. The treatment is however sufficient to cause some non-stoichiometry in the form of oxygen vacancies [12]. There is a possibility that this may facilitate hydrogen diffusion into the metal through the oxide layer at 400 °C. In contrast, the procedure described here has resulted in rapid hydrogen absorption to TiH$_{1.8}$ at room temperature, by milling in hydrogen.

The milling process used introduces a high degree of complexity to the problem. Powder particles are subjected to repeated high-energy collisions and the crystallite size is rapidly reduced from 114 to 29 nm. It is believed that there is a large instantaneous temperature rise in the most heavily deformed parts of the powder particles which will decay rapidly.
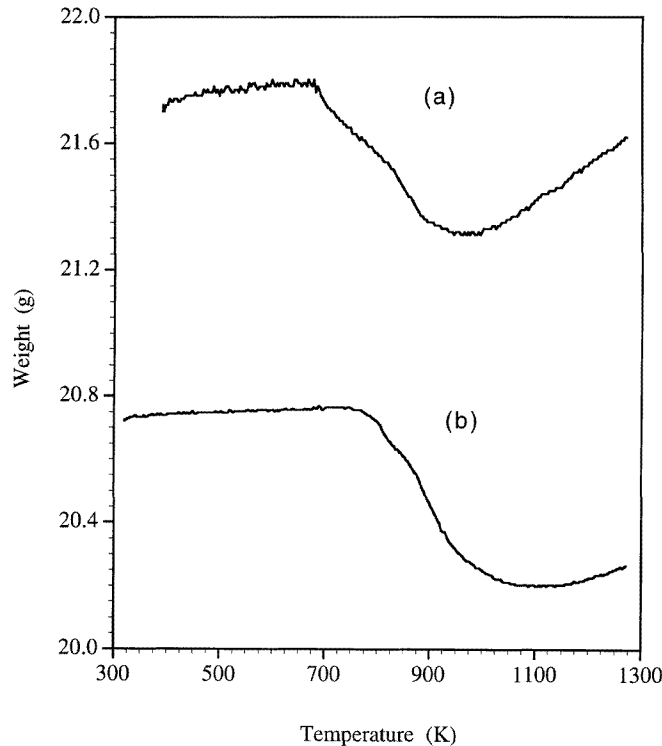
Figure 2. TGA curves for titanium hydrides prepared by ball milling for 3 h under a hydrogen atmosphere (a) and prepared by the standard method (b).

Individual crystallites exist within powder particles in the range 0.5–1 μm and these are often packed together in large agglomerates (up to 500 μm). Milling introduces a high concentration of lattice defects (as shown by strain broadening in XRD) and exposes clean metal surface by mechanical removal of oxide films. Clearly our understanding of such a process is imperfect; however certain general observations may be made.

If the driving force for hydrogenation scales with the enthalpy of formation then TiH_2 ($\Delta H_f = -14.96$ kJ mol^{-1}) [13] is expected to have a smaller thermodynamic driving force than say TiN (-336.6 kJ mol^{-1} [14]) and yet hydrogenation occurs at a much higher rate than nitrogenation during ball milling under N_2 [5–9]. This is not surprising since the bulk diffusion coefficient for H in Ti ($D_H = 1.8 \times 10^{-12} \exp\{-51.8 \times 10^3/RT\}$ [15]) is twelve orders of magnitude larger than that for N in Ti ($D_N = 0.012 \exp\{-189.5 \times 10^3/RT\}$ [15]) at the average milling temperature of 323 K. It may be argued that the very localized temperature excursions experienced by the powder momentarily produce conditions akin to the standard treatment at 400 °C. This however ignores the fact that the milled powder continues to absorb H vigorously at room temperature during topping up of the milling vial. The structure of the milled powder has clearly been altered such that H is readily absorbed at room temperature. Milling appears to have changed both the thermodynamics and kinetics of hydride formation.

It is likely that this is due to the complex milled microstructure. The milled powder consists of near-perfect crystal domains of order 30 nm (XRD particle size measurements) separated by regions of disorder, most likely dislocation walls and tangles. Many such

domains together form a crystal or particle of dimensions 0.1–1 μm. SEM imaging in similar systems has shown that particles are agglomerated into much larger entities of order 1–100 μm [11].

Given this structure, we envisage a mechanism where

(i) the large amount of clean Ti surface generated in the mill gives a very effective substrate for dissociative chemisorption of H_2 molecules to give H atoms,

(ii) the high density of lattice defects makes the diffusion of H very rapid within the disordered regions separating the nanocrystalline domains and

(iii) the tiny crystallite size allows bulk diffusion in the Ti crystallites to occur rapidly because of the very small diffusion distances involved ($\sim$15 nm).

The greater ease of decomposition of TiH$_x$ formed by milling (figure 2) is in accord with these general principles.

The hydrogenation of Ti, which normally requires temperatures in the region of 400 °C, has been achieved at room temperature by ball milling Ti under a hydrogen atmosphere. The hydrogenation proceeds via the formation of a Ti–H solid solution during the initial stages of milling followed by rapid formation of the hydride phase. The hydrogenation was accomplished in a stepwise fashion by topping up the milling vial periodically at room temperature, and the metal continued to absorb during this procedure. Because of this, it is possible to view the milling as merely a complex activation process.

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