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Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal characterization of titanium hydride in thermal oxidation process

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ARTICLE INFO

Article history: Available online 13 February 2012

Keywords: Titanium hydride XPS SEM DTA-TG Oxidation

ABSTRACT

We investigated the thermal behavior of titanium hydride with different particle size at the different atmospheres using the thermal analysis techniques. The results demonstrated that the smaller particle has larger reactivity and showed less stable at higher heating rates. Even in the thermal plasma with inert atmosphere, titanium hydride was partially oxidized and an effective oxidation occurs in thermal plasma reactor with oxygen as reactive gas. Milling process changed the stoichiometry of titanium hydride from TiH_2 to TiH_y and the amount of hydrogen in titanium hydride affects its oxidation behavior.

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1. Introduction

Titanium hydride is a chemical compound of titanium and hydrogen. The powder is grey to black in color with particle size $(d_{50}: 3-50 \,\mu\text{m})$. The true density of the powder is $3.8 \,\text{g/cm}^3$ [1]. This powder can be used as a high-purity hydrogen storage material or as a foaming agent for the aluminum foam manufacturing process. This material has various applications as a bonding material (glass-metal and ceramic-metal) in wide areas from alloys to inter-metallic compounds. Stable titanium hydride powder of high purity can yield hydrogen at elevated temperatures in a reversible reaction. Therefore, it is able to resist most chemical reagents, but is attacked at elevated temperature by oxidizing agents and acids [2].

Earlier there was disagreement among researchers about the different dynamic schemes of titanium hydride (TiH₂) thermal oxidation [3–5]. According to Hartmann, finely dispersed titanium hydride mixed with air ignites at 713 K [6]. But Anderson and Fleshman investigated the ignition temperature for fine TiH_{1.92} powder and found it to be 873 K [7]. According to Antonova [8], the oxidation of TiH_{1.54} starts at 773–823 K and the process is limited by the diffusion of oxygen through the TiO₂ film. The presence of hydrogen from the hydride phase is not taken into account. The chemical composition of the samples should exhibit a strong influence in the oxidation dynamics. Even though titanium hydride is extremely sensitive to the experimental atmosphere, especially such atmospheric factors as oxygen, and heat, few studies have

deeply investigated the effect of the amount of hydrogen in titanium hydride [4].

In this study, the oxidation behavior of titanium hydride with different particle sizes was investigated under air and inert atmospheres using TG-DTA and thermal plasma reactor. A brief analysis of titanium hydride was carried out in terms of physical, chemical and thermal properties in thermal oxidation process. The effect of milling on TiH₂ particles has been studied. Both Xray diffraction and TG-DTA was used to analyze the structural changes as well as to study the kinetics of transformation. The effect of thermal plasma on the oxidation process has been analyzed in an argon atmosphere. The main purpose of this study to investigate the reactivity of titanium hydride powders in air and in an inert medium at high temperature. A detailed thermal analysis of the dehydrogenation and the steps of oxide phase formation towards titanium oxide has been carried out. The conversion efficiency has been studied for titanium hydride to titanium dioxide.

2. Materials and methods

The titanium hydride (TiH_2) as starting material was purchased from Sigma Aldrich (98% pure). Milling experiments were performed with TiH₂ powders (<50 µm) using a high energy ball mill (Fritsch Pulverisette – S4) with zirconia vials and balls of 3 mm diameter. Zirconia vial has an internal diameter of 33 mm and a height of 20 mm with a capacity of 50 ml. Toluene was used as a milling medium to carry out wet milling. This solvent acts as a process control agent restricting the oxidation process through milling. Milling was carried out with a rotational velocity of 300 rpm. A sequence of 30 min milling with 30 min rest intervals to avoid too high of a temperature rise. The powders were milled for up to 2 h

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^{0040-6031/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2012.02.010



Fig. 1. XRD spectrum of pure (98%) TiH₂ powder and milled powder (2 h).

with a ball-to-powder weight ratio of 5:1, keeping the number of balls constant at 25.

Theoretical analyses of the titanium hydride oxidation in an argon plasma and with an argon plasma using oxygen gas were carried out using the thermodynamic software FACTSAGE; experiments were conducted in a thermal plasma reactor. The pressure in the reactor was 750 Torr, with input power varying from 6 to 9 kW. Thermal analyses of the milled and the as received titanium hydride were performed within a temperature range 21-927 °C using a Rigaku, Thermoplus TG 8120 thermal analyzer. The rate of heating was varied as 5, 10, 15, 20 and 25 °C/min in air medium. The phase analysis was carried out for the as received and milled powders using an X-ray diffractometer (DMAX 2500, Rigaku Co.). Microstructural characterizations of the powders were carried out using SEM (Model S-4200, Hitachi). The bonding characteristic between the Ti and H was analyzed using the XPS (X-ray Photoelectron Spectroscopy, K-Alpha and Thermo Scientific). The stoichiometric amount of hydrogen in the titanium hydride powder was determined by inductively coupled plasma atomic emission spectroscopy (Thermo electron EA 1112).

3. Results and discussion

Fig. 1 displays the XRD patterns of the as received and the milled TiH_2 particles. The XRD pattern reveals the presence of pure, sharp TiH_2 peaks. Uniform background shifting can easily be observed. The peak shape proves quite well the crystalline nature of the

powder. XRD analysis was performed on the as received and milled TiH_y powders. Titanium hydride peaks were found in the form of TiH₂ as major peaks before milling; loss of hydrogen gas can be observed after milling. TiH₂ has its most intense peak at $2\theta \sim 52.2^{\circ}$ (Space group – I4/mmm) (JCPDS file no. 09-0371). TiH₂ transforms into TiH_{1.924} (Space group – Fm $\bar{3}$ m/225), (JCPDS file no. 25-0982) after 2 h milling.

Micron sized powders can be observed with irregular shapes in a distorted orientation in the SEM image of the pure titanium hydride powders is shown in Fig. 2(a). The sizes of the powders range over more than two orders of magnitude from 0.5 to 50 μ m. Average particle size is nearly equal to 35 μ m. The powder size decreases with respect to the milling time. It is observed that after 2 h of milling the powder size decreases and cracking can be observed on the surface area. Still, some original powders were left behind that retained their size after milling.

The inset pictures in Fig. 2(b) show that cracking on the surface occurs due to the milling. Titanium hydride powder was fractured through the milling process and milled powders show typical morphology having $d_{50} \sim 20 \,\mu\text{m}$ after the milling process. The SEM image of the surface of a titanium hydride particles oxidized at 927 °C is shown in Fig. 2(c). This shows that the change in morphology from the titanium hydride powder corresponds to the formation of a continuous protective film on the surface. The presence of such a film is confirmed by the change of sample color in the experiment. At temperature 927 °C the oxide phase represented about 6% of the total weight change (not shown in figure, from the EDS data). Oxide phases were not observed in the SEM image, which is due to the oxygen dissolution in the titanium hydride. Although the upper level of the powder does change its color, the as received powder at the base of the alumina crucible in the TG-DTA experiment retains the original color. So this confirms the partial oxidation of titanium hydride in these experiments.

TG-DTA analysis was carried out in air medium from 5 °C/min to 25 °C/min in steps of 5 °C and the results are presented in Fig. 3(a). Dramatic physical changes occur in both the as received and the milled powders after analysis. The powder changes from blackishbrown to light yellow. The initial and final temperature of the as received and milled powder decomposition also relate to the heating rate. Thermogravimetry loss weight curves for the as received powder show that the weight loss increases with the increasing heating rate shown in Fig. 3(b). During the process of thermal decomposition for both the as received as well as the milled powders, loss of weight begins at 500 °C; this loss of weight ends when the temperature is around 927 °C. According to Chen and Williams [9] TGA reveals that weight loss of 1.72 wt.% occurred from 387 to 736 °C. This is quiet well in agreement with our result is shown in Fig. 3(d). We found that the endothermic reaction correspond to the temperature domain of the weight loss. This endothermic reaction corresponds to the decomposition, which releases H₂ gas from



Fig. 2. FE-SEM image of titanium hydride powders with: (a) as-received (d_{50} : 35 µm), (b) milled powder (2 h) (d_{50} : 20 µm), and (c) SEM image of the surface of a titanium hydride particle oxidized at 927 °C.



Fig. 3. (a) DTA analyses of the titanium hydride powder with $35 \,\mu$ m particle size (TiH₂, as received) with various heating rate from $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $15 \,^{\circ}$ C/min, $20 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min were carried out in air medium. (b) TG of the titanium hydride powder with $35 \,\mu$ m particle size (TiH₂, as received) with various heating rate from $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min were carried out in air medium. (c) DTA thermal analyses of the milled titanium hydride powder $20 \,\mu$ m particle size varying $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min (d) TG as inset) was carried out in air medium. (d) TG of the milled titanium hydride powders $20 \,\mu$ m particle size varying $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min were carried out in air medium. (d) TG of the milled titanium hydride powders $20 \,\mu$ m particle size varying $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min were carried out in air medium. (d) TG of the milled titanium hydride powders $20 \,\mu$ m particle size varying $5 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min, $10 \,^{\circ}$ C/min and $25 \,^{\circ}$ C/min were carried out in air medium.

the powder. As the process shifts towards the high temperature, the milled powder shows a more intense peak that correlates to the oxidation is shown in Fig. 3(c). This confirms that the reduced particle size enhances the reactivity of oxidation.

Fig. 4 provides a graph showing the comparison of the heating rate with the onset temperature for the as received and the milled powders. The reaction rate increases with respect to the reduction in the particle size during milling. As a result, the onset temperature is reduced dramatically in comparison to that of the as received powders. Similarly, the DTA shows the reverse reactivity in the cases of both the as received and the milled powders. The onset temperature for the milled powder is higher in comparison to that of the as received powder. As exothermic and endothermic reactions play crucial roles in this analysis, the reaction process is longer in the milled powder compared to that of the as received powder. Oxidation is more effective in the case of the milled powder because the residence time of the reactivity is longer and more effective in the milled powder.

TG-DTA analyses showed notable differences in the lower temperature, which are probably due to the surface area reduction after milling, as can be seen in Fig. 3. There are peaks obtained



Fig. 4. Heating rate versus onset temperature of as received triangle (fill) for TG, triangle (blank) for DTA, and milled: square (fill) for TG, square (blank) for DTA.



Fig. 5. XPS analysis of TiH_2 samples: (a) the whole spectrum (b) Ti 2p scan (c) O 1s scan.

at 200–300 °C/min that remain constant. The intensity decreases with the higher heating rate. DTA-curves of the samples show that the most intensive oxidation process takes place in the temperature range corresponding to the higher hydrogen release from TiH₂. Table 1 provides a comparison study of the TG-DTA thermal analysis from the as received and milled powders. This shows the partial oxidation of titanium dioxide. The titanium hydride was subjected to an elemental analysis test to determine the exact amount of hydrogen content in the sample. The stoichiometric amount shows that the hydrogen content is around 1.95 wt.% in the sample, as calculated by using ICP-OES.

As for the X-ray photoelectron spectrum (XPS) of the TiH_2 powders, Fig. 5(a) shows the full spectrum of the TiH_2 powders; Fig. 5(b) displays the spectrum for the Ti 2p level. The full pattern represents

Table 1 The comparison of thermal reaction for raw and milling powders at 20 °C/min heating rate.

Thermal reaction	Raw powder	Milled powder	Reaction process
1st exothermic	250	250	Formation of oxyhydride
2nd exothermic	550	550	Formation of hydroxides
1st endothermic	620	620	The release of H ₂ gas
3rd exothermic	873	873	Formation of dioxide

the peaks for Ti, O and C. Ti exhibits a peak Ti $2p_{3/2}$ at 464.5 eV. The second major peak of Ti $2p_{1/2}$ is at 454.5 eV. The peak positions are found to match with earlier reported data [10,11]. The O 1s spectra presence at 532.7 eV can be attributed to TiOH or Ti–H₂O. This indicates the existence of different titanium–oxygen compounds within the interface regions.

Fig. 6(a) and (b) provides a thermodynamical plot of TiH₂ as a function of temperature. This plot shows the equilibrium amounts of moles of species formed with respect to temperature. The chemical equilibrium compositions in the various systems were calculated using a software program (FACTSAGE), which is based on Gibb's free energy minimization. The sample is inactive and remains the same in an argon atmosphere. Plasma gases are also taken into account in these thermodynamic calculations, but are not shown in the plots due to their higher content. The graph shows that at temperatures above 4800 K, which are found inside the plasma jet, only the mono atomic H and Ti are stable. The possible reactions that may take place in this zone during the reaction process are given in Table 2.

Thermodynamic plots show the formation of solid Ti in the argon atmosphere plasma. The efficiency of the oxidation process depends on the temperature and treatment of the environment, which quite well agrees with Gromov et al. [3]. This oxidation process also depends on the flow rate of the reactive gases oxygen



Fig. 6. (a) Free energy minimization plot for the Ti–H plots in argon atmosphere. (b) Free energy minimization plot for the Ti–H plots in argon + nitrogen atmosphere.

Table 2

The possible reactions occur during the reaction process in argon atmosphere.

Reaction process	Temperature range
$Ti(s) + H_2(g) \rightarrow TiH_2(s)$	<800 K
$2\text{Ti}(l) \rightarrow \text{Ti}(s)$	1300-2300 K
$2H(g) \rightarrow H_2(g)$	2300-3300 K
$Ti(g) \rightarrow Ti(l)$	2300-3300 K

in the thermal plasma process. DTA-curves support the idea that the most intensive oxidation process takes place in the temperature range of 21-927 °C, which correspond to the maximum of the hydrogen release from the TiH₂ [12–16]; shows that the thermal plasma oxidation of the sample results in the formation of water vapors in the high temperature zone. The hydrogen content in the sample reacts with oxygen and comes out as water vapor. The possible sequential reactions, shown in Fig. 6(b), are summarized in Table 3.

Table 3

The possible sequential reactions occur at argon atmosphere with reactive gas oxygen.

Reaction process	remperature
$\begin{array}{c} Ti_{3}O_{5}\left(s\right)+H_{2}\left(g\right)\rightarrow TiO_{2}\left(g\right)+H_{2}O\left(g\right)\\ Ti_{2}O_{3}\left(l\right)+2OH\left(g\right)\rightarrow Ti_{3}O_{5}\left(s\right)+H_{2}\left(g\right)\\ 2TiO\left(g\right)+O\left(g\right)\rightarrow Ti_{2}O_{3}\left(l\right)O\left(g\right)+H\left(g\right)\rightarrow OH\left(g\right)\\ Ti\left(g\right)+O\left(g\right)\rightarrow TiO\left(g\right)\\ Ti\left(g\right)+Ti\left(g\right)=0\left(l\right)+TiO\left(g\right)\\ \end{array}$	Below 1300 K 2300–2800 K 2800–3800 K 3800–4300 K 4200–4800 K



Fig. 7. XRD plot of oxidized product obtained from titanium hydride in thermal plasma and TG-DTA method (r: rutile, a: anatase).

 TiO_2 and water vapor $H_2O(g)$ are found to remain stable at room temperature. TiO_2 can be collected from the inner wall of the reaction tube. The product obtained after the thermal plasma treatment, was found to be a mixture of anatase and rutile phases (with the predominance of anatase for TiH_2). Fig. 7 displays the XRD graphs of the oxidized product obtained from titanium hydride after oxidation. The oxidized product obtained from the TG-DTA clearly shows that the rutile phases are more dominant in titanium dioxides. This results in thin films on the sample surface and prevents further oxidation, whereas the oxidized product obtained after thermal plasma treatment with oxygen as reactive gas shows a mixture of anatase and rutile phases and complete conversion of titanium dioxide from titanium hydride.

Complete conversion of titanium hydride to titanium oxide does not take place. Mixtures of golden-green (Ti_yHO_x) and goldenyellow (TiO) with some brown color powder (TiH_{2-x}) form [3]. When thermal plasma oxidation takes place in oxygen as reactive gas the resulting product is titanium oxides. Therefore, the proposed oxidation reaction in argon plasma with oxygen as reactive gas is as follows

$$TiH_{\gamma} \rightarrow TiH_{\gamma-\chi} \rightarrow TiO \rightarrow Ti_2O_3 \rightarrow Ti_3O_5 \rightarrow TiO_2.$$
(1)

It was found that the increase in the input power in the thermal plasma resulted in an increase of the electron concentration. Furthermore, an admixture of H_2O vapors resulted in the quench box inside the thermal plasma reactor. Indeed, hydrogen in TiH_y is known to exist in atomic form which is able to react with oxygen and then to move into the lattice vacancies [17–19].

4. Conclusion

The physical and chemical properties of titanium hydride show that this material is very sensitive to oxidizing agents. Thermal analysis suggests that the oxidation mechanism of titanium hydride depends on the oxidation method chosen to make the process effective. The dynamics of the oxidation of titanium hydride, TiH_y is likely to follow the reaction path TiH_y \rightarrow TiH_{y-x} \rightarrow TiO \rightarrow Ti₂O₃ \rightarrow TiO₅ \rightarrow TiO₂. The oxidation of TiH₂ in argon plasma with oxygen as the reactive gas was found to lead to mixtures of titanium oxides of different oxidation degrees. The oxidation process is effective for the higher thermal plasma input power. In these cases the presence of hydrogen in the

hydride phases indicates the considerable influence on the oxidation dynamics.

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