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Local bonding structure in mechanically activated TiH_2 and TiH_2 + graphite mixture

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Abstract

The local bonding structure of mechanically activated TiH_2 and TiH_2/graphite mixture is studied by means of temperature-programmed desorption (TPD), X-ray emission- and absorption-spectroscopy. Ball milling of TiH_2 in the presence of graphite results in a modification of the hydrogen occupation sites. Additional Ti—C bonds from chemical bonding of Ti with carbon, which occupies octahedral interstitials, appears in TiH_2 due to intimate contact between graphite and TiH_2 nanoparticles embedded into an amorphous graphite matrix. Mixed configurations around Ti atoms with proportional combination of local Ti—H and Ti—C bonds significantly decrease the thermal stability of TiH_2.
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Keywords: TiH_2; Graphite; Ball milling; Temperature-programmed desorption; X-ray emission and absorption spectroscopy; TEM; Local bonding structure

1. Introduction

Transition metals are known to accommodate a great amount of hydrogen and have been studied as promising materials for hydrogen storage [1]. The development in metal-hydride technology required a detailed study of hydrogen interaction with metals and alloys. Much work has been performed on titanium hydride, as a model system, because it possesses one of the highest absorptive capacities among the metal-hydrides [2]. High-energy ball milling of Ti in H_2 atmosphere has been shown to be a simple, low-cost and highly effective technique to synthesize titanium hydride nanocrystalline powders at room temperature [3] by crashing the surface titanium oxide and making the fresh titanium surface accessible for interaction with H_2. It is found that mechanical treatment of metal-hydrides greatly improves the hydrogen absorption–desorption kinetics [4], and that the addition of carbon-containing compounds or graphite to metal powders before milling improves the metal-to-hydrogen reactivity [5]. The mechanism of the stimulating effect of graphite addition is not studied in detail, in spite of its importance for efficient synthesis of hydrogen storage materials. In the present work we have studied the local atomic and electronic structure of Ti atoms in mechanically activated TiH_2 and TiH_2/graphite mixtures with the help of temperature-programmed desorption (TPD) and X-ray emission and absorption spectroscopy.

2. Experimental

2.1. Preparation procedure

TiH_2 powder (99% pure, 325 mesh from Aldrich) or mixtures of TiH_2 powder and pyrolytic graphite (99% pure, $S = 3\,m^2/g$) were milled in He flow for 30, 62 and 126 min

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using a flow mechanochemical reactor (average energy intensity of 1.0 kW/kg) at room temperature and atmospheric pressure. A stainless steel container was loaded with 1.8 g of TiH_2 or TiH_2/graphite reaction mixture (1.5 g TiH_2 + 0.3 g graphite) together with 19.8 g of hardened steel balls (3–5 mm diameter). The reactor input was connected to a setup for gas mixture preparation; the outlet was combined on-line with a gas chromatograph to monitor the effluent gas composition. A flow rate of 8–10 ml/min was used. The effluent gas was analyzed every 5–10 min in order to study dynamics of hydrogen evolution from TiH_2 during milling. After each run, the sample was passivated in helium flow for 2–3 h before taking it out on atmosphere for further investigations. The specific surface area S of original and as-milled powders was measured by low-temperature Ar adsorption.

2.2. Temperature-programmed desorption (TPD)

The TPD measurements were carried out at a heating rate of 10 K/min from 290 to 940 K under flow conditions (Ar, flow rate of 100 ml/min). A flow quartz reactor was charged with a 0.1-g sample of testing powder. The testing powder was mixed with quartz powder (∼70 wt.%) in order to minimize the temperature difference between the sample and surroundings of the reactor caused by the heat of hydrogenation/dehydrogenation reaction and to prevent the powder from caking. The reactor with a sample was blown through with Ar before heating. After the hydrogen desorption the sample was quickly (during ∼10–15 min) cooled to room temperature in Ar flow. H_2 emission was monitored continuously with a PC interfaced to a gas chromatograph with a thermal-conductivity detector. The amount of hydrogen emitted was calculated on the base of special calibration through integrating the area under the TPD curve. TPD was accompanied by XRD powder analysis.

2.3. Transmission electron microscopy (TEM)

The TEM and HRTEM measurements were carried out on a Philips EM 420 ST electron microscope with a resolution limit of 0.3 nm and an accelerating potential of 120 kV. The TEM samples were prepared in an ethanol suspension and placed on copper grids covered by a network of amorphous carbon, which permits to distinguish between carbon from the grid and carbon from the sample.

2.4. Soft X-ray fluorescence measurements

X-ray fluorescence measurements were performed at undulator beamline BL27SU at Spring-8 using soft X-ray fluorescence endstation. A well-focused beam, less than 10 μm in vertical direction, allowed to use a slitless spectrometer, which improved a throughput of instrument and detection efficiency. A slitless spectrometer with a spherical VLS (Varied Line Spacing) grating and back-illuminated (BI) charge coupled device (CCD) detector [6] provided an energy resolution of $E/\Delta E = 1000$.

3. Results and discussion

3.1. Kinetics of TiH_2 decomposition under mechanical treatment

Partial decomposition of TiH_2 was induced by mechanical treatment in He flow. The parameters of this process are listed in Table 1. The original TiH_2 powder lost about 5 mol% of H_2 during 60 min of milling (Fig. 1a). After the milling, the specific surface area of the sample increased from 0.32 to 6 m^2/g. Significant broadening of XRD peaks was also observed. The microblock size estimated from XRD patterns is ∼130 Å. Computer fitting of this pattern (quantitative phase analysis) [7] points to a two-phase composition containing ∼60% of $TiH_{1.94}$ cubic ($a = 0.445$ nm, JCPDS 25-982) and ∼40% of TiH_2 tetragonal ($a = 0.319$ nm, $c = 0.435$ nm) phases.

The H_2 evolution from TiH_2/graphite powder was accompanied by formation of CH_4 and C_2H_6 after a short induction period (Fig. 1b). As was shown previously [8], hydrocarbon formation is indicative to close intermixing of hydride and graphite. After 62 and 126 min of milling, TiH_2/graphite

Table 1
Conditions and results of mechanical activation

Sample	Treatment conditions	Phase composition	S (m^2/g)	H_2 evolution (mol/g TiH_2)	Graphite consumption (at.%)
1	TiH_2 as-received	TiH_2 tetragonal ($a = 0.447$ nm; $c = 0.440$ nm; $c/a = 0.98$)	0.32		
2	TiH_2 (1.8 g); He flow; 60 min	$TiH_{1.9}$ cubic ($a = 0.445$ nm); TiH_2 tetragonal ($a = 0.319$ nm; c = 0.435 nm; $c/a = 1.36$)	6	1×10^{-3} (5 mol%)	
3	TiH_2 (1.5 g) + graphite (0.3 g); He flow; 30 min	Graphite, $TiH_{1.9}$ cubic (a = 0.445 nm); TiH_2 tetragonal ($a = 0.317$ nm; $c = 0.438$ nm; $c/a = 1.38$)	48		
4	TiH_2 (1.5 g) + graphite (0.3 g); He flow; 62 min	Graphite, TiH_2 cubic ($a = 0.445$ nm)	38.2	1.2×10^{-3} (∼6 mol%)	∼0.3
5	TiH_2 (1.5 g) + graphite (0.3 g); He flow; 126 min	Graphite, TiH_2 cubic ($a = 0.445$ nm)	52.4	1.05×10^{-3} TiH_2 (∼5.2 mol%)	2.7

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