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Scanning electron microscopy, X-ray diffraction and thermal analysis study of the TiH_2 foaming agent

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ABSTRACT

The decomposition of commercially available TiH_2 was investigated while performing different thermal treatments. TiH_2 powder, which is widely used as a foaming agent, was heat treated at 450 °C for various times, from 15 min to 120 min. Scanning electron microscopy (SEM) images of the surfaces at different magnifications were obtained and interpreted. A Bragg–Brentano X-ray diffractometer was used to measure the X-ray diffraction (XRD) spectra on all five samples. A close examination of the diffraction spectra showed that for an as-received sample and samples undergoing the longest thermal treatment (1 and 2 h) these spectra can be explained as deriving from cubic $TiH_{1.924}$, while for the other two samples they can be explained as deriving from tetragonal $TiH_{1.924}$. A constant-unit-cell-volume phase transition between the cubic and tetragonal phases in TiH_{2-y}-type compounds had been described in the literature. The unit-cell parameters obtained from measured spectra confirm that within the measurement uncertainty the unit-cell volume is indeed constant in all five samples. Thermo-gravimetry (TG) and differential thermal analysis (DTA) measurements were performed on all the samples, showing that the intensity of the dehydrogenation depends on the previous treatment of the TiH_2. After the thermal analysis XRD of the samples was performed again and the material was found to exhibit a Ti-like unit cell, but slightly enlarged due to the unreleased hydrogen.

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1. Introduction

Titanium hydride can be used as a catalyst in the reversible dehydrogenation of other hydrides and carbon nanotubes [1–3]. It is also used as a catalyst in the preparation of titanium compounds [1,4,5], as a source of pure hydrogen [1], in the manufacturing of ceramic and glass seals from a mixture of active metal titanium or titanium hydride in powder form and titanium coatings [1]. It is also well known as a blowing agent in the production of aluminium foams and some other foam-like structures produced by the powder metallurgy route [6,7]. For these purposes extensive studies of titanium hydride as well as of dehydrogenation and their effect on the formation of alloy foams have been performed (e.g. [8,9]). Thermal analysis was applied to determine hydrogenation kinetics, structural analysis of several non-dehydrogenated and partially dehydrogenated TiH_2 samples was performed in addition. Structural analysis was found to be useful complement to thermal analysis since phase changes follow TiH_2 dehydrogenation. It also proved useful to demonstrate surface Ti oxide without surface spectroscopies.

Differential scanning calorimetry (DSC) shows that hydrogen is normally liberated at approximately 495 °C [10] and that a heat treatment in air delays the hydrogen evolution and shifts it to higher temperatures. The gas evolution is rapid at relatively high temperatures (the melting point of the powder material). The formation and liberation of H_2 take 3–5 min [10]. When TiH_2 powder is pre-treated in air at a

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certain temperature, the decomposition of the hydride is delayed. Liu et al. [11] made a study of the dehydrogenation of TiH_2 powders that was based on a high-temperature X-ray diffraction (XRD) experiment. The $TiH_{2(s)} \rightarrow TiH_{x(s)} + H_{2(g)}$ reaction, $1.5 < x < 2$, took place when the temperature was below 550 °C. Bhosle et al. [12] observed the dehydrogenation of TiH_2 that occurred in two steps, $TiH_2 \rightarrow TiH_x \rightarrow \alpha\text{-}Ti$, where $0.7 < x < 1.1$. Kennedy [10] observed the dehydrogenation of TiH_2 during a heat treatment at various temperatures and he found a difference in the coloration of the powders. At the lowest temperature, 400 °C, the initially black powder turned to olive green, at 450 °C, to purple, and at 500 °C and 550 °C, to blue. The colour of the powder is the simplest way to estimate the level of oxidation.

This study was started to investigate dehydrogenation of pre-treated TiH_2 used as a foam agent in Al-foam preparation. Optimizing of dehydrogenation process for this includes desired features like higher temperature gas component release. The oxidation of the powder particles was supposed to help delay hydrogen release, into the temperature region of the foaming reaction in aluminium, between 680 °C and 750 °C. Additional oxide layers on the surface of the TiH_2 powder particles actually do delay the gas release, although the problem is to find the optimal thermal treatment for the most efficient usage of the pre-treated foaming agent.

2. Material and Methods

Samples were prepared by the heat treatment of reagent-grade TiH_2 (Sigma-Aldrich, −325 mesh) at 450 °C for different times: 15 min, 30 min, 60 min and 120 min. The temperature of 450 °C was chosen based on a preliminary thermal analysis, which showed that the used TiH_2 powder exhibits intensive decomposition at temperatures just above 450 °C. An overview of the heat treatments for individual samples is given in Table 1.

The prepared specimens were analyzed by X-ray diffraction (XRD) using a Bruker AXS D4 Endeavor diffractometer with Bragg–Brentano geometry and Cu K_α radiation at $\lambda = 0.15406$ nm. The other details are as follows: 20° to 90° 2θ range, 0.02° step size, and 10 s per channel acquisition time. The morphology of the powders was analyzed by field-emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss).

Thermo-gravimetric (TG) analyses and differential scanning calorimetry (DSC), using a Netzsch Jupiter 449 simultaneous thermal analysis instrument coupled with a mass spectrometer (MS) (Netzsch QMS 403C Aëolos quadrupole), were employed. The analyses were performed in an Ar atmosphere at a purge rate of 50 mL min^{-1}, from 40 °C to 800 °C, with a heating rate of 10 °C/min using an Al_2O_3 crucible with a lid. The evolution of H_2 and H_2O was monitored by m/z fragments of 2 and m/z fragments of 17 and 18, respectively.

Table 1 – Parameters of heat treatments for individual samples.

Sample no.	Treatment temperature/°C	Treatment time/min
1	As-received	0
2	450	15
3	450	30
4	450	60
5	450	120

The particle size and the size distribution of the powders were measured using the dynamic light-scattering method (DLS) with a laser-diffraction particle size distribution analyzer LA-920 HORIBA-Jobin Yvon.

3. Results and Discussion

3.1. SEM Analysis of TiH_2

The mean particle size of the as-received TiH_2, measured by dynamic light scattering (DLS), was determined to be 12.6 μm with a unimodal size distribution and remained constant throughout the thermal treatments. A FE-SEM micrograph of the TiH_2 powder (Fig. 1a) shows irregularly shaped particles at low magnification, whereas Fig. 1b and c displays micrographs of the cleaved surfaces at a higher magnification, showing the different structural planes of the particles. After 15 min of thermal treatment the surface oxidation reduced the visual smoothness of the surface (Fig. 1d and e). Longer treatment times resulted in an even more rugged surface, where a greatly increased number of isolated, bright, nano-sized grains of oxide can be observed (Fig. 1f). Ti oxide presence on surface of the TiH_2 particles has already been observed in several studies [e.g. 13,14].

3.2. XRD

The XRD spectra measured of all five TiH_x samples are shown in Fig. 2. The indexing in Fig. 2 corresponds to an FCC TiH_x cubic cell of $a \approx 0.44$ nm [15,16]; however, the splitting of the peaks in samples 2 and 3 suggests a tetragonally deformed TiH_x unit cell, possibly with cell parameters close to those from [15,16] ($a \approx 0.447$ nm, $c \approx 0.440$ nm). The most intense peak corresponding to Ti oxide of the rutile structure is located at approximately $2\theta = 27.5°$, and this peak can be barely discerned in the XRD of samples 4 and 5, corresponding to longest thermal treatments.

To confirm that the diffraction peaks' splitting indeed corresponded to the tetragonal deformation of the unit cell, all the peaks were observed over a narrow range and their positions were determined (Fig. 3).

From Fig. 3b, c, d and f it is clear that for samples 2 and 3 large splits of the order of 1° appear for the indices 200, 220, 311 and 400. The splits at these indices are consistent with a tetragonal deformation since $d_{200} \neq d_{002}$, $d_{220} \neq d_{202}$, $d_{311} \neq d_{113}$ and $d_{400} \neq d_{004}$ in the tetragonal system.

For samples 1, 4 and 5 several d_{hkl} can be calculated from different reflections and the corresponding unit-cell parameters thus determined as $a_1 = (0.4446 \pm 0.0008)$ nm, $a_4 = (0.4428 \pm 0.0006)$ nm and $a_5 = (0.4424 \pm 0.0008)$ nm. This corresponds to the unit-cell volumes of $V_1 = (87.9 \pm 0.5)\,10^{-3}$ nm^3, $V_4 = (86.8 \pm 0.4)\,10^{-3}$ nm^3 and $V_5 = (86.6 \pm 0.5)\,10^{-3}$ nm^3. For tetragonal samples 2 and 3 different interplanar distances d_{hkl} corresponding to different reflections are calculated, from which the unit cell and the derived parameters for samples 2 and 3 can be

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