

# DECOMPOSITION BEHAVIOUR OF AS-RECEIVED AND OXIDIZED TiH<sub>2</sub> POWDER

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Titanium hydride powder which is used for making aluminium foams was characterised by thermal analysis, mass spectrometry, diffractometry and transmission electron microscopy combined with electron micro-diffraction. Mass spectrometry showed that hydrogen release from as-received TiH<sub>2</sub> powder in argon shows two decomposition peaks while after pre-treatment in air the first decomposition stage is eliminated and the second shifted to higher temperatures depending on the nature of heat treatment. This is a useful property since it improves aluminium foam generation. The effect was attributed to oxide layers around the cores of TiH<sub>2</sub> particles which build up during heat treatment and act as diffusion barriers to hydrogen. Diffraction experiments and TEM yielded information about the structure of these oxide layers. They could be shown to be about 100 nm thick consisting of a mixture of two different titanium oxides, namely tetragonal TiO<sub>2</sub> and hexagonal Ti<sub>3</sub>O.

## 1. INTRODUCTION

Aluminium foams are porous metallic structures, which combine properties of cellular materials with those of metals. The high stiffness-to-mass ratio leads to a variety of applications especially in automotive industry.

Metals can be foamed in various ways [1]. One very promising method is the *powder compact melting process*: a powder mixture of an alloy and a blowing agent is compacted and then heated [2]. Above the decomposition threshold of the blowing agent hydrogen is released which blows bubbles in the melting alloy. Clearly, the melting temperature of the alloy and the temperature range of decomposition of the blowing agent have to be coordinated. The often observed formation of irregular, crack-like pores is one of the deleterious side effects occurring if the decomposition takes place far below the melting point of the alloy (Fig.1).



Fig. 1. Aluminium foam sandwich panels. Regular (left) and irregular (right) pore structure.  
(Courtesy: W. Seeliger)

Hydrides were shown to be suitable for foaming aluminium [3]. TiH<sub>2</sub> leads to the highest foam expansion among all hydrides investigated as proved by thermal desorption spectroscopy, differential thermal analysis, and thermogravimetric analysis measurements. Hydrogen release from TiH<sub>2</sub> starts around 400°C, which is markedly lower than the melting point of most commercial aluminium alloys [4]. To minimize this temperature mismatch the

melting point of the metal can either be lowered by further alloying – with possible unwanted side effects – or the decomposition threshold of the blowing agent can be raised by thermal pre-treatment.

If TiH<sub>2</sub> powder is pre-heated in air an oxide layer is formed on the surface of the particles. This layer delays gas release from the particles, so that during foaming hydrogen is released only after the melting temperature of the alloy is reached [5]. On the other hand, pre-treatments lead to hydrogen losses which lowers their foaming potential. The task is therefore to find treatments which form a sufficiently thick oxide layer while a minimum of hydrogen is lost.

In this paper we examine the release of hydrogen from TiH<sub>2</sub> powder in the as-received state and the influence of various pre-treatments in air. For this purpose the decomposition of TiH<sub>2</sub> powder was examined by thermogravimetric analysis (TGA) together with mass spectrometry (MS). The morphology of the powder was obtained by scanning electron microscopy (SEM) and the present phases were detected with *ex-situ* X-ray diffraction experiments (XRD). First *in situ* X-ray diffraction experiments at the Berlin electron storage ring company for synchrotron radiation (BESSY) combined with transmission electron microscopy (TEM) were used to gain information about the structure of the oxide layer covering the hydride particles.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Sample preparation

TiH<sub>2</sub> powder supplied by Chemetall GmbH, Frankfurt (purity 99%) was used in this study. The physical and chemical properties together with the average size of the powder are given in Table 1.

material	density [g/cm <sup>3</sup> ]	chemical analysis [%]	Colour	decomposition temperature [°C]	particle size distribution [μm]		
					D(v.90)	D(v.50)	D(v.10)
TiH <sub>2</sub>	3.76	98.8	Grey	400	30.79	14.14	3.18

Table 1: Physical and chemical properties for the titanium hydride powder used.

Fig. 2 shows the morphology of the as-received TiH<sub>2</sub> powder obtained by SEM. The morphology of the powder is angular, the particle size is variable and the powder surface irregular.

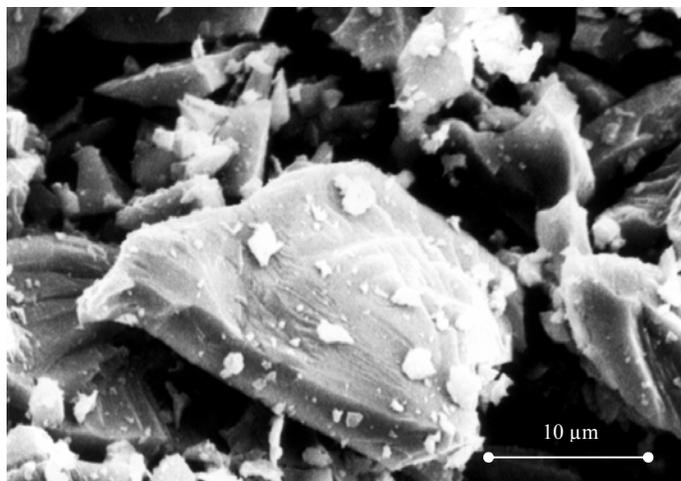


Fig. 2. SEM micrograph of as-received TiH<sub>2</sub> powder.

Pre-treatments of the powders were carried out isothermally under air at various temperatures (480°C, 500°C, 520°C) for 90, 180 and 360 minutes. For TEM and diffraction investigations the powders were cold pressed to small tablets with 6 mm diameter and then heat treated in air.

## 2.2. Thermoanalysis

To study the release of hydrogen as a function of heating rate and temperature in our precursor, 150 mg of either as-received or heat treated powder were filled into an Al<sub>2</sub>O<sub>3</sub> sample crucible. The sample crucible was mounted in a Netzsch Simultaneous Thermal Analyzer STA 409C, equipped with a silicon carbide furnace, which was connected to a quadrupole mass spectrometer via a skimmer coupling system (Fig. 3).

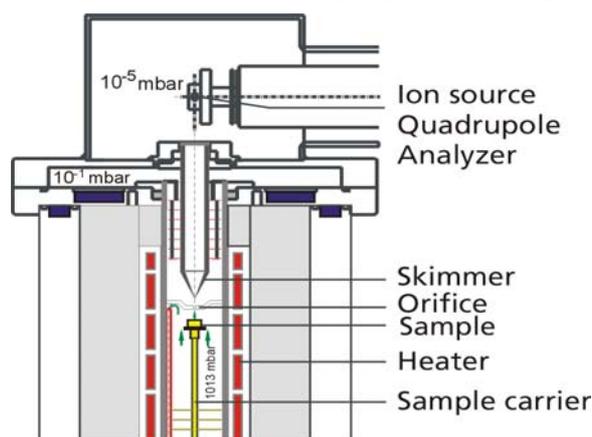


Fig. 3. Simultaneous thermal analyzer-Mass spectrometry with skimmer coupling system.

To obtain highest sensitivity the mass spectro-meter was equipped with a SEV amplifier. After positioning of the filled crucible, the thermobalance was evacuated three times and back filled with argon prior to heating the sample under continuous argon flow (flow rate 250 cm<sup>3</sup>/min) with a constant heating rate 10 K/min from room temperature up to 1200°C.

## 2.3. X-ray diffraction

A Bruker AXS diffractometer D8 equipped with a graphite monochromator and scintillation counter was used to determinate the phases of TiH<sub>2</sub> powder before and after the heat treatments in the air. The scattering patterns in the scattering angle (2θ) region from 15° to 90°, at step of a 0,02°s<sup>-1</sup> and acquisition time of 5 s per step acquired using CuK<sub>α</sub> radiation were sufficient to determine various oxides on the surface. The XRD patterns of as-received and heat treated samples were compared with the standards from the JCPD standard diffraction database.

To monitor the powder decomposition even more accurately, we performed in-situ XRD experiments at the KMC2 beamline at BESSY. The high intensity of the synchrotron source and the use of the area sensitive detector (Bruker AXS Histar) allowed the acquisition of complete XRD patterns every 10 seconds during the heat treatment with constant heating rate. The angle range of diffraction was chosen in such a way that we detect at least one scattering peak for each component.

## 2.4. Transmission electron microscopy

The effects of heat treatment under air were characterized by TEM in Philips CM30 (300 kV), equipped with an EDS spectrometer. The tablets were cut in to sizes suitable for

TEM specimen preparation by mechanical polishing and subsequent ion tinning in an ion beam milling machine.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effects of the pre-heat treatments under air

Coupling of thermogravimetry with mass spectrometry permits a detailed insight into the course of decomposition associated with the desorption of gaseous products from  $\text{TiH}_2$ . The pre-oxidised powders show a different decomposition behaviour when analysed with mass spectrometer at a constant heating rate in argon (Fig. 4).

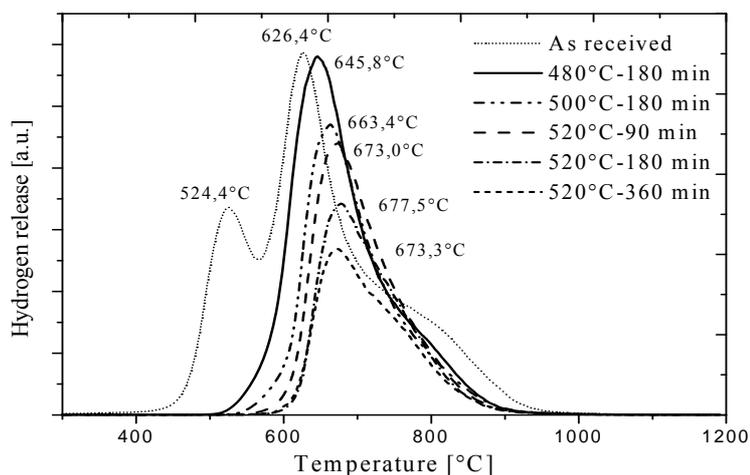


Fig. 4. Mass spectrometry on as-received and heat treated  $\text{TiH}_2$  powders at a heating rate of 10 K/min in argon atmosphere.

The as-received titanium hydride powder shows two decomposition peaks. Gas release starts already at 400°C. Heat treatment at 480°C for 180 minutes eliminates completely the first decomposition stage and increases the temperature at which maximum gas expansion occurs. Decomposition of  $\text{TiH}_2$  is impeded due to the slow diffusion of the hydrogen through the oxide layer. Longer treatments up to 360 min or treatments at higher temperatures up to 520°C shift the peak position to even higher temperatures. The total amount of the hydrogen set free decreases with longer times and higher temperatures. Therefore, by selecting the heat treatment parameters appropriately, one can tailor the decomposition characteristics of the blowing agent.

#### 3.2. Oxygen layer on titanium-hydride powder

XRD patterns for  $\text{TiH}_2$  powder heat treated in air at 520°C for 90, 180 and 360 min are shown in Fig. 5 and are compared with those for the as-received powder. The unmarked peaks in Fig. 5 correspond to  $\text{TiH}_2$  or sub-stoichiometric  $\text{TiH}_x$  compounds. The phase composition of the as-received powder was identified, from powder diffraction files, as  $\text{TiH}_{1.924}$  with a fcc crystal structure ( $a=4.448 \text{ \AA}$ ). After annealing in air, the peaks are shifted to higher angles, indicating hydrogen loss.  $\text{Ti}_3\text{O}$  and  $\text{TiO}_2$  (rutile) are detected with hexagonal and tetragonal crystal structure, respectively.

Changes in the colour of the  $\text{TiH}_2$  powder were observed during heat treatment in air. The initially grey-black powder turned green at 500°C, blue at 480°C, and light brown to dark brown at 520°C. Coloration of the powder indicates that the oxidation process occurs at the powder surface and hence a surface oxide is being produced, which influences the optical

properties. Composition, quantity and thickness of oxidation products are sensitive to a heating rate, heating method and holding time.

In-situ diffraction measurements at BESSY showed that the oxide composition did not change significantly during the decomposition of the powder. After the initial change of the  $\text{TiO}_2$  intensity, the amount of the oxides stayed constant, while the concentration of the hydrogen increased considerably. The structure of titanium hydride changed on higher temperatures to  $\beta$ -phase because of the loss of hydrogen. After cooling the sample consisted of mixture of  $\alpha$ -Ti and  $\delta$ - $\text{TiH}_{1.5}$ . Advantage of the in-situ measurements is the possibility to monitor exactly the phase transition, using only one sample for the whole range of temperatures.

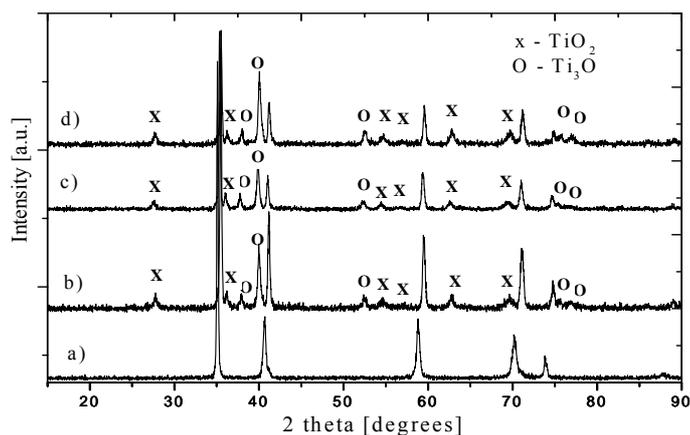


Fig. 5. XRD patterns for  $\text{TiH}_2$  powder a) as-received and pre-heat treated in air at  $520^\circ\text{C}$  for b) 90 min c) 180 min d) 360 min

### 3.3. TEM on oxide layers

TEM yielded additional information about the structure of the oxide layer covering the hydride particles. Figure 6a shows a typical bright field (BF), TEM micrograph of the as-received  $\text{TiH}_2$  particle. The surface of the  $\text{TiH}_2$  particle does not show any signs of oxide layers in this image. The BF image of the heat treated titanium hydride particle in air at  $480^\circ\text{C}$  for 180 min is demonstrated in Fig.6b. The oxide layer of the particle marked by A is clearly visible in this image from both sides of the plate-like particle. The oxide layers are nanocrystalline, which can be observed from the typical rings pattern of selected area electron diffraction patterns (SAED). The corresponding (SAED) patterns with the  $[110]$ -zone axis of the  $\text{TiH}_2$  particle is shown on Fig.6b. The thickness of the oxide layer measured by TEM is about 100 nm.

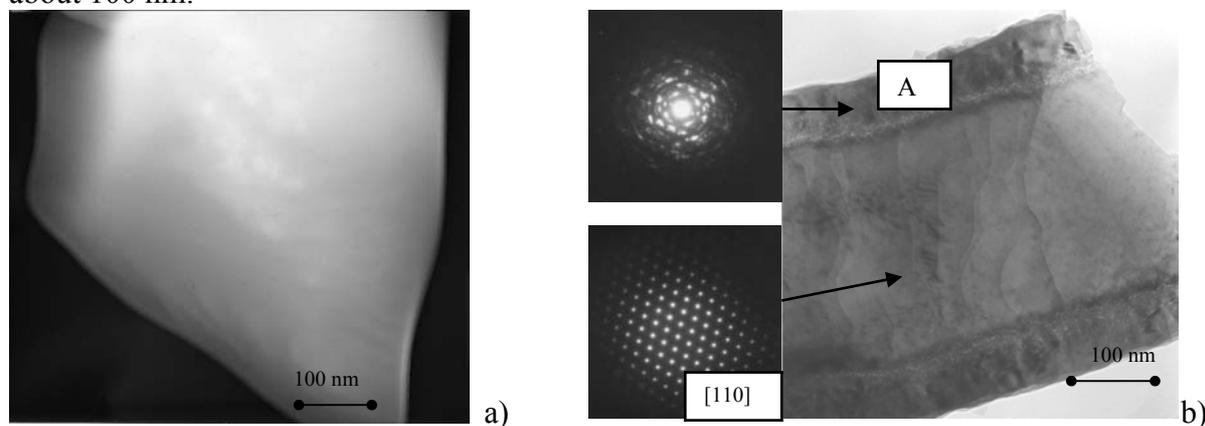


Fig. 6. Bright field TEM image and corresponding electron diffraction pattern of the a) as-received  $\text{TiH}_2$  powder b)  $\text{TiH}_2$  powder heat treated in air at  $480^\circ\text{C}$  for 180 min.

The lattice parameters of the oxide layers obtained from SAED and XRD are listed in Table 2. The results given by two methods agree well with each other.

TEM oxide	XRD	
	$d_{exp}$	TiO <sub>2</sub> d
4.6	4.5	4.7
3.2	3.2	3.2
2.8		2.8
2.3	2.29	2.3
2.2	2.18	2.2
2.1	2.05	2.1
1.9		1.9
1.6	1.6	1.6

Table 2. Lattice parameters of TiO<sub>2</sub> and Ti<sub>3</sub>O (480°C-180 min) measured by TEM/SAED and XRD.

#### 4. SUMMARY

MS and XRD experiments showed that the decomposition of as-received TiH<sub>2</sub> powder in argon occurs in two stages. Heating as-received TiH<sub>2</sub> at 10 K/min in argon leads to hydrogen release at 400°C. Heat treatment at 480°C for 180 minutes eliminates completely the first decomposition stage and increases the temperature at which gas evolution occurs. Oxide layers around the cores of titanium-hydride particles formed during annealing in air acts as a very effective diffusion barrier. XRD and TEM experiments showed the formation of TiO<sub>2</sub> and Ti<sub>3</sub>O during heat treatment. We have shown that results from different methods can be combined to form a more complete picture of decomposition of TiH<sub>2</sub> and that various methods provide complementary information.

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