

Desorption of hydrogen from blowing agents used for foaming metals

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Abstract

Hydrogen desorption from TiH_2 , ZrH_2 , and MgH_2 was studied by thermal desorption spectroscopy (TDS), differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Loose hydride powders as well as powder compacts of zinc and various hydrides were studied. It was found that during the powder compaction process free surfaces on the hydride powder particles were created. As a consequence, the desorption temperature of the hydride in the precursor was lowered in comparison to loose powder exposed to air. Foam expansion of zinc was highest for TiH_2 which also exhibits the highest desorption rate at the melting point of zinc, followed by ZrH_2 and MgH_2 which decompose at lower temperatures and are therefore less effective for foaming. The desorption kinetics of Al and AlSi7 compacts containing TiH_2 were also studied for matters of comparison. The much lower foam expansions compared to Zn foams could be explained by higher hydrogen losses at temperatures below the melting point of Al and AlSi7.

Keywords: metal foam, thermal desorption spectroscopy (TDS), differential thermal analysis (DTA), thermogravimetric analysis (TGA), powder processing

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1 Introduction

Metals can be foamed in various ways [1]. One very promising method is based on mixtures of metal powders and blowing agents which are first densified to a foamable precursor and are then foamed by melting [2]. The blowing agent entrapped in the metallic matrix after densification builds up an internal gas pressure upon heating of the compact and leads to foam formation. Alternative routes for producing foamable precursors include liquid state processing of metal and blowing agent powders [3] and thixocasting of mixtures of metal and blowing agent powders [4]. In any case the solidification temperature of the metal and the gas decomposition temperature range of the blowing agent have to be co-ordinated to ensure satisfactory foaming results [5]. If the blowing agent releases gas far below the melting point the metal will be expanded already in the solid state which yields crack-like pores and a heterogeneous pore structure. If the blowing agent decomposes far above the melting point the viscosity of the melt will be too low to allow for the formation of a stable foam.

Aluminium and zinc alloys are especially suitable for foaming due to their relatively low melting points and favourable liquid properties. Titanium or zirconium hydride (TiH_2 , ZrH_2) has been shown to be the best blowing agent for these alloys because strong hydrogen release takes place between 400 and 600°C which coincides well with the m.p. of Zn (419.5°C) and Al (660°C). Blowing agents have been characterised by thermal analysis to characterise their decomposition temperature and to derive their suitability for foaming (DSC/DTA: [6], TGA: [2],[3],[7]). The thermal signal obtained in DSC or DTA measurements can be misleading because the essential quantity is gas release, not reaction enthalpy. This can be seen by considering ZrH_2 . Thermal analysis suggests that this agent has a maximum of the decomposition peak at 700°C while hardly showing reaction heat at 419.5°C. Nevertheless, ZrH_2 is well suited for foaming zinc. One other deficiency of the characterisation work carried out on blowing agents up to the present is that only loose powders have been investigated. Analysing foamable precursor with the blowing agent embedded in the metal would be interesting because changes in the decomposition behaviour caused by the powder compaction procedure and by the surrounding metallic matrix can be anticipated. Gravimetry has been used to detect mass changes during the decomposition of loose blowing agent powders but it is not sensitive enough to detect the relatively small gas quantities released from foamable precursors at the beginning of decomposition. This is a consequence of the low weight fraction of hydrogen in the hydrides (for example 4 wt.% in TiH_2) in combination with their low weight fraction in precursors (0.3-0.5 wt.%) (the decomposition of carbonates which

are also used as blowing agents for making foams can be measured more easily due to the higher molecular mass of CO₂). We therefore carry out a study in which we detect the released hydrogen directly by mass spectroscopy instead of merely measuring the reaction enthalpy in DTA/DSC or the total mass loss in TGA.

2 Experimental

2.1 Sample preparation

Different hydride powders were purchased from commercial suppliers: TiH₂ (Chemetall GmbH, Frankfurt, purity 99%, < 63 μm, [7]), ZrH₂ (Chempur GmbH, Karlsruhe, purity 99.7%, < 44 μm) and MgH₂ (Th. Goldschmidt AG Essen, < 54 μm). The powders were characterised in the state "as received" without any further modification and were handled in air.

For making zinc foams, zinc powder (Eckart-Dorn, type AS, purity 99.9%, < 45 μm) was mixed with 0.3 wt.% of TiH₂, 0.56 wt.% of ZrH₂ or 0.16 wt.% of MgH₂. The weight fractions of the blowing agents were selected such that all samples contained the same amount of hydrogen. The mixtures were then hot pressed to virtually dense tablets (<0.3% porosity for TiH₂ and ZrH₂, up to 1.6% for MgH₂) for 15 minutes at 350°C (after 15 minutes of slow heating up from room temperature) for the mixtures containing TiH₂ and ZrH₂ and at both 250°C and 350°C for the powder blends containing MgH₂. The alternative lower compaction temperature for MgH₂ was chosen to be able to check whether hydrogen losses occur and affect foaming when compaction takes place at 350°C (the higher residual porosity in tablets containing MgH₂ indicates that there is some gas evolution during pressing). The pressure applied was 120 MPa and a cylindrical die of 32 mm diameter was used. These tablets can be foamed by heating the samples to temperatures above the melting point of zinc (419.5°C).

For making aluminium foams, aluminium powder (Eckart, purity 99.74%, < 150 μm) or a metal powder blend aluminium + 7 wt.% silicon (Oelschlaeger, purity 98.5%, < 100 μm) were mixed with 0.5 wt.% of TiH₂. The mixture was then hot pressed for 20 minutes at 450°C (after 20 minutes of slow heating up from room temperature) at 120 MPa to almost dense tablets (porosity <0.75% for pure aluminium, a bit higher for AlSi7, see also Ref. [8]). These can be foamed by heating the samples to temperatures above the solidification temperature of aluminium (660°C) or AlSi7 (577°C). In one case an AlSi7 powder mix was deliberately compacted applying parameters which produce a large residual porosity: pressing temperature was just 180°C, with the pressures and times as given for the full compaction. The resulting porosity was 10%.

For each of the alloys small pieces (3×3×3 mm) of the precursor material were cut out of the pressed tablet to be used for TDS.

Ball-milled metal hydrides were prepared in a high energy planetary ball mill (Fritsch Pulverisette 6), using a bowl and balls of stainless steel. The bowl was filled with the hydride powder, evacuated and re-filled with 1.1 MPa hydrogen. Then, the powder was milled at 440 rpm with 12 balls for 3 hours. After milling further powder handling took place in a protective argon atmosphere.

2.2 TDS measurements

TDS measurements are usually performed under high vacuum conditions since the mass spectrometer in use can only handle pressures up to 10^{-2} Pa. Nevertheless, in order to study the desorption kinetics of the tablets during the foaming process, TDS must also be carried out under normal pressure because in vacuum the desorption kinetics are expected to differ from those during the real foaming process.

Measurements under normal pressure were performed using differential pumping as seen in [Figure 1](#). With a valve the pressure at the forepump was set to 10^{-1} Pa. The pressure at the mass spectrometer behind the aperture then ranged from 10^{-3} to 10^{-2} Pa. With this set-up we could measure thermal desorption spectra in different atmospheres, i.e. He or air under atmospheric pressure. The helium gas was nominally 99.999% pure but no extra care could be taken to eliminate adsorbed oxygen or traces of moisture in the apparatus due to the given experimental conditions. Therefore, the actual purity was probably much lower. The air used was taken from the laboratory atmosphere without any further drying. The sample could be heated up from room temperature to 850°C with a heating rate of 5 K/min using a radiation furnace.

2.3 DSC/TGA measurements

In addition to TDS measurements, calorimetric and gravimetric measurements were carried out simultaneously in a Netzsch STA 409 C thermoanalyser. Measurements were made on loose TiH₂ powder only because the mass changes during foaming of precursors containing just 0.5 wt.% TiH₂ are not detectable. The heating range was from 20°C to 700°C with a heating rate of 10 K/min in an argon atmosphere.

2.4 Measurements of foam expansion

Precursor tablets of each powder mixture (Zn or Al alloy + blowing agent) with a diameter of 31 mm and a height of 5 mm were foamed in a specially designed foaming dilatometer ("expandometer") which allows us to monitor the volume of an evolving foam as a function of time or temperature [8]. For this a pre-heated folding furnace was slid around the cold foamable sample contained inside a thin-walled vertical steel tube limiting expansion to the upward direction. The height of the expanding foam was measured via the displacement of a small ceramic punch (weight = 9g) which was detected by an inductive sensor. During the entire foaming process the ceramic punch rested on the top of the foam. The temperature of the foam was measured with inconel-encased Ni-CrNi thermocouples inserted into the foam from the lower side of the foaming tube. The weight of the punch slightly influences foam expansion as was shown by carrying out contactless reference measurements using a laser sensor in a second device [8], but this effect is of little importance in the context of this work.

3 Results and discussion

3.1 Decomposition of loose hydride powders

In a first step loose blowing agent powders were investigated. The powders were processed as received from the manufacturer and were handled in air. As it was known that the highest foam expansions could be achieved using TiH₂ as a blowing agent, this agent was selected for these measurements. The objective was to compare the characteristics of gas release under different conditions. Three situations were considered: air at 1 bar pressure, He at 1 bar and vacuum. The desorption spectra of TiH₂ obtained under these conditions are shown in [Figure 2](#).

Desorption in air produces a broad desorption range, starting slightly above 350°C and reaching a maximum at 655°C. At the maximum temperature reached in the experiment (850°C) hydrogen evolution still continues. In contrast to this, desorption in high vacuum also sets in slightly above 350°C but it already reaches its maximum at 516°C and all the hydrogen has been desorbed at 600°C.

The different desorption behaviour under vacuum and in a normal atmosphere can be explained by the oxidising influence of oxygen on the hydride. In order to obtain a qualitative measure of the oxidation sensitivity of the hydride a third case was considered: desorption under a helium atmosphere at 1 bar pressure. The gas used was very pure (99.999%) but the tubing used for the experiment could not be optimised to avoid any residual oxygen in the

recipient. Obviously, desorption under these conditions represents an intermediate case, however, closer to the measurement in air: when heated up, desorption again starts around 350°C but increases at a slower rate than measured under vacuum but at a higher rate compared to air. At 520°C we observe a shoulder which indicated that there might be a first desorption stage. Above about 550°C desorption in air and He take place in a similar way with a temperature difference of 35K between the two curves and a clear maximum above 600°C. This experiment shows that already a very small trace of residual oxygen can change the desorption behaviour significantly.

In order to check the TDS results, differential thermal analysis (DTA) and thermogravimetry (TGA) was carried out simultaneously under argon atmosphere (1 bar) for the same TiH₂ powder. Both the DTA curve and the derivative of the sample mass are shown in **Figure 3**. Both curves exhibit two peaks, the first of which is located around 530°C, the second around 625°C. This is in good agreement with the He-curve in **Figure 2** which shows a shoulder at 520°C and a peak at 620°C. This double peak structure has been explained by the two possible non-equivalent positions of hydrogen atoms in Ti, one with tetrahedral, one with octahedral symmetry [9], but alternative explanations have also been given such as the influence of different mixed phases of TiH₂ containing oxygen [10]. All these explanations still seem to be quite speculative. For giving a detailed microscopic model of the double peak structure the data available at the present is not sufficient.

Oxide layers on titanium hydride particles modify their hydrogen desorption behaviour because they form an efficient diffusion barrier [11][12]: hydrogen not only has to diffuse through the bulk titanium matrix from the inner region of each particle towards the surface but also has to overcome the oxide barrier which is an additional kinetic hindrance. This effect is already known and has been exploited to control hydrogen evolution from TiH₂ in metal foam manufacture [3].

Titanium hydride particles always have a slightly oxidised surface due to handling in air at room temperature which is almost inevitable in the preparation of metal foam precursors. Upon heating under vacuum, however, the oxide layers will be modified. Oxide films tend to disappear after which hydrogen can be desorbed from the hydride particles more easily. This effect starts at 300°C and ends at 450°C and is caused by oxygen diffusion from the surface of the particle into the bulk [13]. This explains the rather rapid hydrogen losses when powder is heated under vacuum. In addition to this effect one could speculate that differences in thermal

expansion coefficients between the hydride core and the oxide shell could create cracks in the oxide layer which would facilitate gas desorption, but there is no direct proof of this effect.

If the hydride is exposed to air during heating, the oxygen present will renew the thinning oxide layers on the surface, immediately close eventual gaps in the oxide shell created by thermal stresses and finally create an increasingly thick oxide layer which forms an effective barrier for hydrogen diffusion and further retards desorption.

3.2 Comparison of different hydrides embedded in bulk Zn

In a next step it was examined how blowing agents decompose when they are enclosed by the dense matrix of the metallic foamable precursor. Three different blowing agents were compared: MgH_2 , TiH_2 and ZrH_2 . The literature gives "decomposition temperatures" of 280°C [14], 450°C [15] and $>500^\circ\text{C}$ [14][16], resp., for these hydrides and we intended to check whether this order of decomposition "temperature" (which in reality is a range) can be obtained in the TDS measurements.

To allow for an assessment of foamability of the various compacted mixtures of Zn and hydride powders, foam expansion curves were recorded. **Figure 4** shows expansion and temperature curves for Zn foamed with 0.3 wt.% TiH_2 . It is easy to notice that foam expansion sets in after the Zn compact has melted (horizontal part of temperature curve) and reaches a maximum value after all the material has become liquid and the temperature has risen to about 500°C . Note that the initial heating rates before melting are almost 200 K/min which is nearly 40 times higher than the rates in the TDS experiments which has to be kept in mind when comparing foam expansion curves and TDS data. Instead of plotting volume expansion and sample temperature as functions of time, one can plot expansion as a function of temperature with time as an implicit parameter. This is done in **Figure 5a-c** (solid lines). We observe a sudden onset of foam expansion at about the melting point of Zn (419.5°C) and a maximum expansion at 500°C for all three blowing agents. Note that the temperature slightly decreases after the metal has melted. This is clearly an artefact: as soon as the expanding foam encloses the tip of the thermocouple completely, the temperature reading slightly drops. Such effects depend on the local geometry around the thermocouple and are therefore insignificant.

Figure 5a shows the hydrogen desorption of the Zn + 0.16 wt.% MgH_2 precursor tablet compacted at 350°C as measured in a helium atmosphere. The desorption rate has a maximum at 384°C and a large fraction (78 %) of the hydrogen is desorbed well below the melting point

of zinc and the onset of foaming. Foam expansion is only about 400 % near the maximum and therefore the lowest of the 3 blowing agents. Tablets which had been compacted at 250°C and 350°C exhibited the same expansion behaviour thus proving that there is no significant impact of hydrogen losses on foaming when compacting powder mixtures containing MgH₂ at 350°C.

In the case of Zn + 0.56 wt. % ZrH₂ (see **Figure 5b**) the hydrogen desorption rate reaches its maximum at 392°C, which is 9 K higher than in the case of MgH₂. Here, only 53% of the hydrogen is desorbed below the melting point of zinc, which is less than for MgH₂. Consequently, a higher maximum expansion of 680 % is reached because more hydrogen gas contributes to bubble formation and inflation compared to MgH₂.

Finally, the desorption spectrum of the Zn + 0.3 wt. % TiH₂ tablet and its expansion are plotted in **Figure 5c**. The desorption has a sharp maximum at 404°C which is the closest to the melting point of zinc of all three examined samples. Accordingly, the maximum expansion is the highest of the three samples (980 %) although slightly more hydrogen is lost below the melting point as for ZrH₂ (61%).

It can be concluded that TiH₂ yields the best foam expansion results because it shows the highest gas release rate at and above the melting point of the metal. Of course the precise desorption characteristics are influenced by the heating rate applied: higher heating rates would shift the peaks to higher temperatures, but the relative order of the three hydrides can be expected not to change. Therefore, if we could carry out TDS at the high heating rates occurring in foaming, the TDS peak would move closer to the expansion peak. TiH₂ in comparison to the other hydrides would still show the highest gas evolution rate in the temperature region of interest, i.e. between melting point and maximum expansion.

Comparison of the desorption peak for TiH₂ as shown in **Figure 5c** with the peaks in **Figure 2** demonstrates that titanium hydride particles decompose at much lower temperatures if they are enclosed by metal as they do as free powders. The same applies to zirconium hydride which was found to have a decomposition maximum above 650°C when measured on loose powder. At first sight this result seems counterintuitive since one might expect that hydrogen losses would be delayed in metallic precursors because evolving hydrogen can be thought to accumulate in shells around hydride particles building up a hydrogen counter-pressure around each particle. SEM micrographs of expanding foams in which the foaming process was interrupted indeed show such surrounding shells (**Figure 6**). There are at least two explanations for this behaviour. Firstly, as the heating rates are quite low (5K/min)

hydrogen can escape from the powder compacts via the residual porosity before melting and the counter-pressure is relieved. Second and even more important, the hydride powders are modified during compaction owing to severe mechanical deformation. Compaction of powder to a dense billet (>99%) implies heavy deformation of all the individual particles. The metallic Zn particles will deform plastically while the brittle TiH₂ particles are likely to break up into smaller sharp-edged fragments. The newly formed fragments possess fresh and non-oxidised surfaces which are easy to be passed by hydrogen when the compact is heated. This explains why hydrogen evolves from powder compacts at much lower temperatures than from loose powders.

A similar effect was recently observed by Frei et al. [18]: foamable precursor material prepared by admixing TiH₂ to an aluminium alloy melt and subsequently solidifying showed a higher foam expansion rate if the precursor was subjected to an extrusion step prior to foaming. The explanation given by Frei et al. postulates the same mechanism proposed for the powder compaction effect here: extrusion creates heavy shearing in the material thus fragmenting the hydride particles, creating fresh non-oxidised surfaces and facilitating hydrogen desorption.

This idea can be verified by TDS measurements on TiH₂ powder which has been ball-milled for 3 hours under a hydrogen atmosphere after which the powder is transferred to the TDS without any further contact to air. The milling treatment creates fresh non-oxidised surfaces on the TiH₂ powder particles due to mechanical fragmentation while the protective hydrogen atmosphere prevents the new surfaces from oxidising. Some of these particles can be seen in **Figure 7** which demonstrates that milling creates a wide dispersion of irregularly shaped particles. As shown in **Figure 8** the desorption rate for loose milled powder reaches its maximum at the same temperature as it was found for the hydride embedded in the powder compact. However, the desorption range is much broader and the onset of desorption occurs at very low temperatures. This higher desorption rate from the ball milled TiH₂ at low temperatures can be explained by a large quantity of very small particles which are formed during ball milling and release gas easily. Desorption of hydrogen from untreated TiH₂ is shifted to higher temperatures by more than 100K.

It can be instructive looking at the decomposition pressures of the different hydrides: TiH₂ has a decomposition pressure of about 10 Pa at 380°C, while the decomposition pressure of MgH₂ is as high as 1.4 MPa [19]. It is conceivable that due to the high pressure of MgH₂ a substantial part of the hydrogen is lost by permeation at temperatures lower than the melting

point of zinc. In the case of TiH_2 , the lower decomposition pressure leads only to low permeation losses due to diffusion through the zinc matrix below the melting point.

ZrH_2 is the hydride with by far the highest “decomposition temperature” of the three hydrides considered. Even so ZrH_2 releases gas already at quite low temperatures making this agent the one with the broadest decomposition range of all the three. This can be seen in **Figure 2** where the decomposition of untreated ZrH_2 under vacuum is compared to the analogous decomposition curve of TiH_2 . This shows that one has to be careful with arguing with the “decomposition temperatures” taken from the literature mentioned at the beginning of this section. Such data is usually obtained under varying conditions and does not reflect the complex desorption kinetics as revealed by our TDS measurements.

3.3 Desorption of TiH_2 embedded in bulk Al alloys

In **Figure 9** the hydrogen desorption spectra of Al + 0.5 wt. % TiH_2 and AlSi7 + 0.5 wt. % TiH_2 are shown along with their expansions.

In both alloys hydrogen starts to permeate through the metallic matrix at temperatures around 400°C , which is ~ 50 K higher than in Zn. The onset of hydrogen desorption is difficult to locate and the increase of desorption is much slower than for Zn. Maximum desorption is reached at much higher temperatures around 520°C for AlSi7 and $530\text{-}560^\circ\text{C}$ for Al compared to Zn (404°C) which, however, is still far below the melting points of AlSi7 (577°C) and Al (660°C). Desorption from pure Al shows a double peak structure. Therefore, 75% (90%) of the hydrogen are desorbed below the melting points of AlSi7 (Al), which leads to the poor maximum expansions of 471% (400%) for the two aluminium alloys.

The expansion curves for the two alloys show considerable expansion already in the solid state, a phenomenon which cannot be seen for zinc. The reason for this difference is the higher gas pressure which builds up in solid aluminium-based compacts due to their higher melting temperatures. Solid-state expansion is highest in pure aluminium where it reaches about 150% followed by about 100% for AlSi7. Hydrogen desorption in Al alloy powder compacts starts at lower temperatures than from loose TiH_2 heated in air due to the same mechanism already postulated for Zn: powder compaction creates fresh surfaces and facilitates hydrogen desorption. This can be seen in **Figure 10** where the two corresponding curves are compared. A third TDS measurement showing hydrogen desorption from an insufficiently compacted sample is also displayed. This curve lies between the curve for the loose powder and the fully compacted sample. Insufficient compaction therefore does not

created so many fractured fresh surfaces on the TiH_2 particles and hydrogen desorption is shifted to higher temperatures compared to full compaction.

One obvious reason for the difference in hydrogen desorption between aluminium alloys and zinc could clearly be the compaction temperature: aluminium alloys were compacted at 450°C , zinc at 350°C . During the 20 minutes of compaction some hydrogen might already be desorbed and escape from the Al compact. Due to this thermal pre-treatment the onset of hydrogen desorption in a subsequent heating cycle (i.e. the TDS) is shifted to higher temperatures. We cannot quantify the hydrogen loss during compaction and it has to be expected that it depends on the size of the compacted sample and the compaction conditions (pressure-time-profile). Hydrogen losses are probably smaller when large samples are compacted and reaching the maximum compaction pressure in a short time can be assumed to reduce hydrogen losses. As the pressed samples are 300 times larger in size than the samples cut out for TDS, hydrogen losses in both cases cannot be compared directly.

In any case these hydrogen losses at comparatively low temperatures do not affect foaming in a negative way. In contrary, the effect is beneficial for foaming as hydrogen evolution in the solid phase bears the danger of premature crack formation and the formation of large irregular pores [4]. A current strategy of foam manufacturers is therefore to further tailor blowing agents by pre-treatments at even higher temperatures than 450°C including pre-oxidation in air [3]. In order to maximise hydrogen release the blowing agent powders are heat-treated before compaction.

In order to further increase the foamability of aluminium alloys, i.e. their maximum expansion, their melting point has to be lowered by alloying to match the maximum desorption peak of TiH_2 . The use of higher fractions of magnesium or copper would allow for such low melting ranges, but their impact on mechanical properties (ductility) or corrosion behaviour could be negative. More investigations are therefore necessary.

4 Summary

The hydrogen desorption from titanium hydride powder is influenced by the atmosphere in which the powder is heated up. Heating in vacuum leads to a sharp desorption peak at relatively low temperatures (516°C) while heating in air delays decomposition to much higher temperatures (peak at 655°C). Even helium containing only traces of residual oxygen leads to such delays. The key point is the oxide layer on each hydride particle which acts as a very effective diffusion barrier. It was shown that in discussing the desorption of hydride from metal foam precursors, which are compacted metal/hydride mixtures, thermal analysis of

loose hydride powders can be misleading because the hydrogen desorption behaviour is largely modified by the powder compaction step necessary for making foamable precursor. Due to the creation of fresh and non-oxidised surfaces during compaction desorption already sets in at quite low temperatures and reaches a peak value around 400°C for TiH₂. A favourable condition for obtaining high expansion factors is a high hydrogen desorption at and above the melting point of the metal to be foamed as was demonstrated for zinc using three different hydrides. Best foaming was obtained with TiH₂, followed by ZrH₂ and MgH₂. Desorption far below the melting point (or solidification temperature) leads to comparatively low foam expansions, e.g. for Al and AlSi7 alloys using TiH₂.

Acknowledgements

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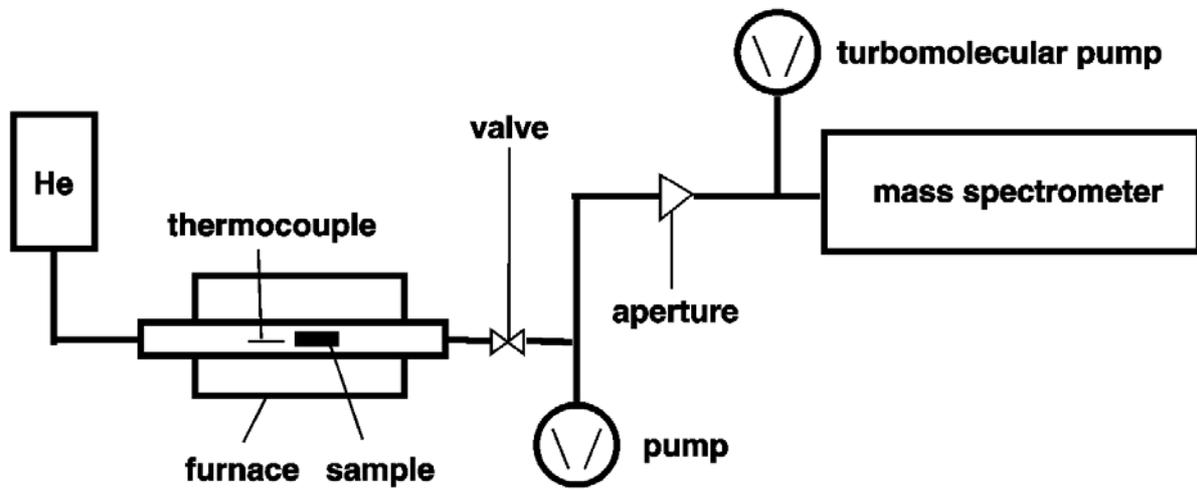


Figure 1. Principle set-up of thermal desorption (TDS) measurements.

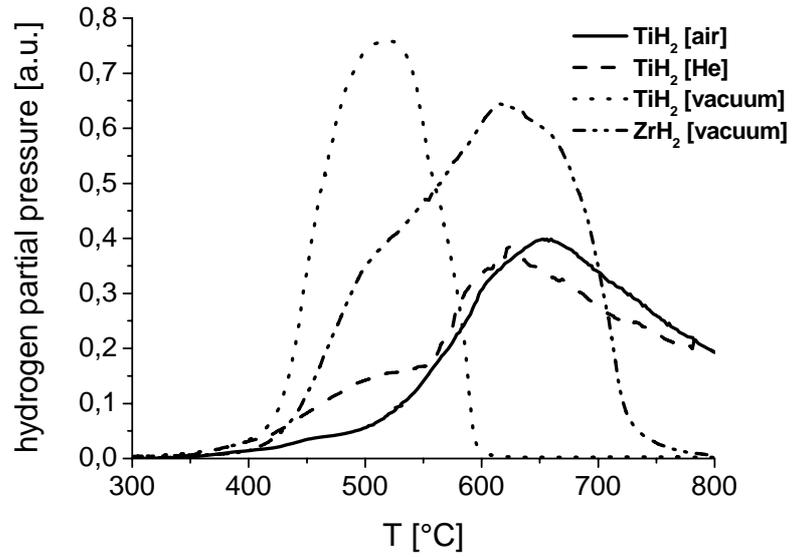


Figure 2. TDS measurements on loose TiH₂ powder (as acquired, handling in air) under three different atmospheres: air@1 bar, He@1 bar, vacuum. For matters of comparison TDS on ZrH₂ powder under vacuum is also shown. The heating rate was 5 K/min in all cases.

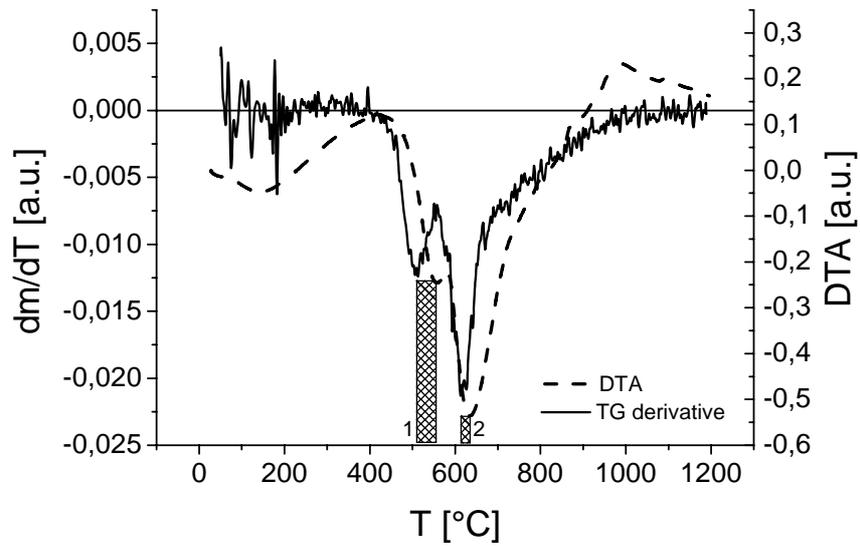


Figure 3. Simultaneous DTA and thermogravimetry on TiH₂ powder carried out in an argon atmosphere. The heating rate was 10 K/min. The derivative of the gravimetric (mass) signal is shown. The range of the suspected decomposition peaks is marked by vertical bars and numbered (peak 1 at 510-550°C, peak 2 at 610-640°C).

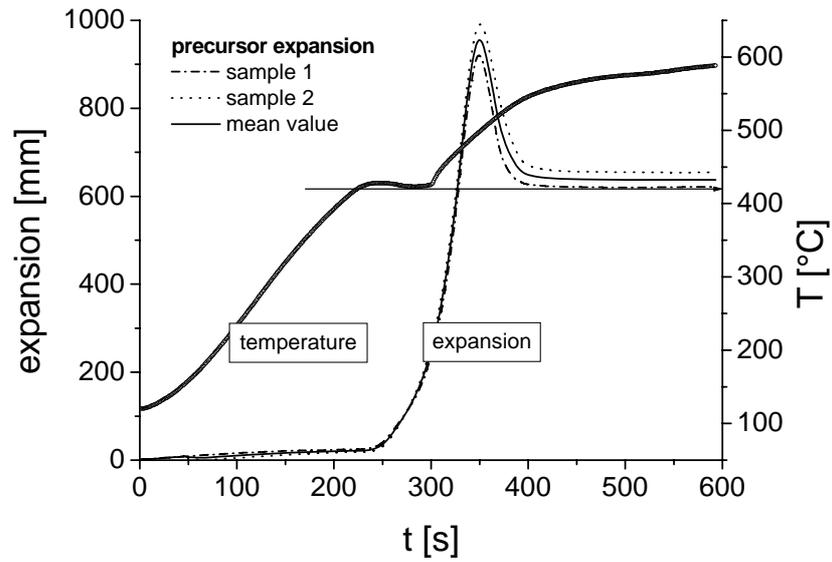
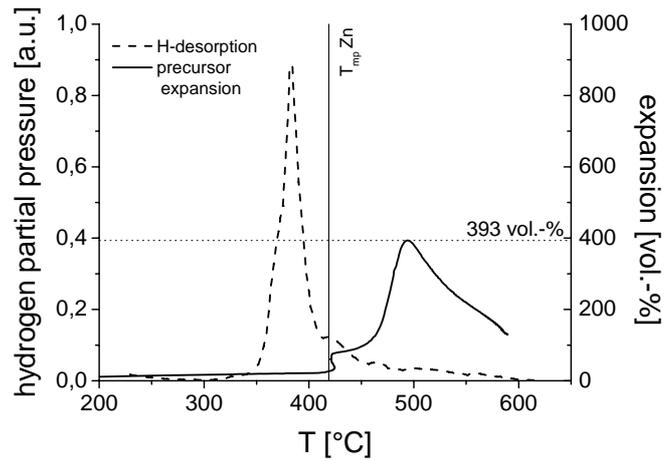
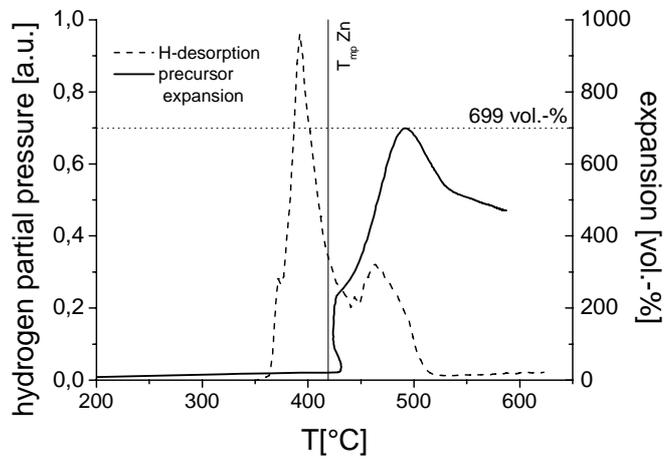


Figure 4. Expansion curve of zinc foam containing 0.3 wt.% TiH_2 as blowing agent. Two individual measurements (broken lines) are shown which were averaged to the third curve (full line). The sample temperature corresponding to the averaged curve is also shown.

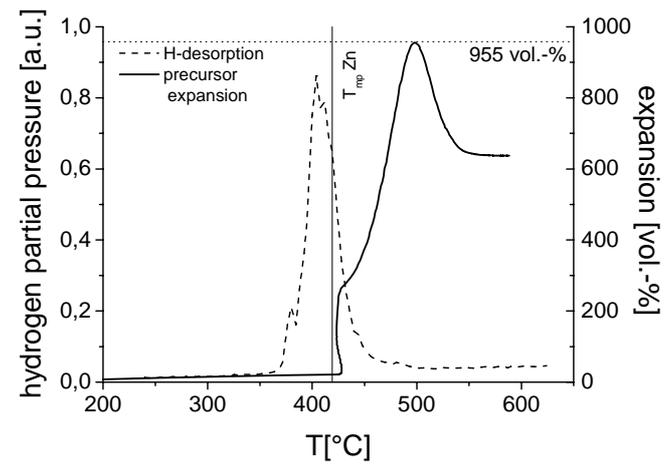
Furnace temperature was 600°C . Horizontal line: m.p. of Zn.



a)



b)



c)

Figure 5. Broken lines: TDS measurement in He atmosphere on zinc precursor containing a) MgH_2 , b) ZrH_2 , c) TiH_2 . Heating rate 5 K/min.

Full lines: corresponding expansion curves of foams measured as described for **Figure 4**.

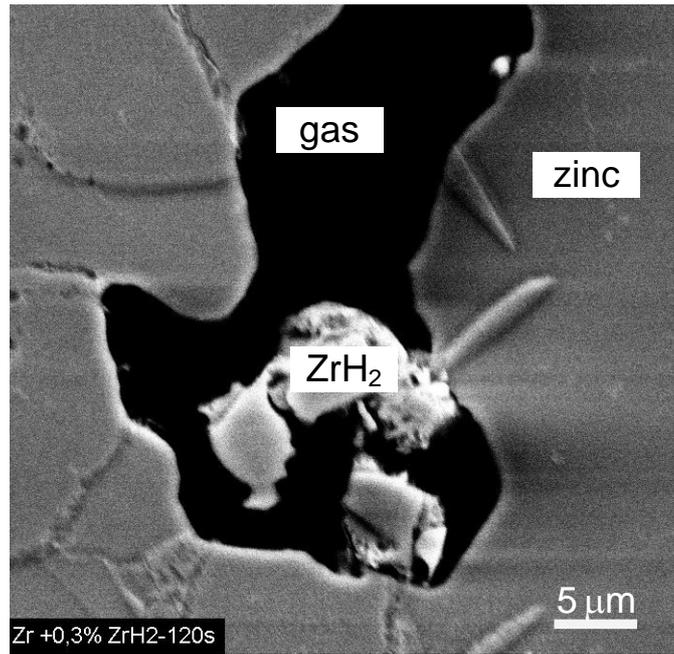


Figure 6. Zinc foam in a very early expansion stage showing the characteristic gas shell around the blowing agent particle (ZrH_2). See Ref. [17] for a description of sample preparation.

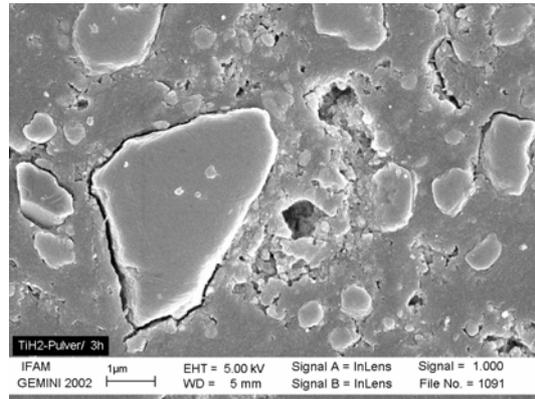


Figure 7. Titanium hydride particles after 3 hours of milling in a hydrogen atmosphere. Particles were embedded in resin and covered with a 4nm layer of PdPt.

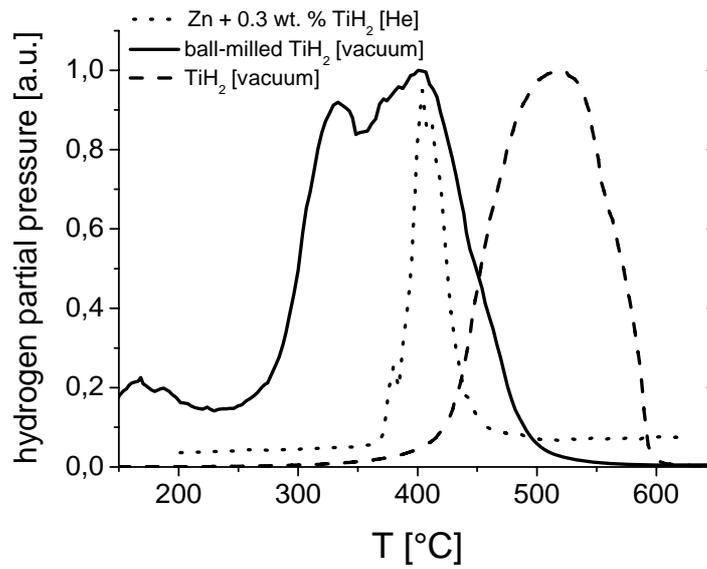


Figure 8. TDS measurement on loose ball-milled TiH₂ powder (full line) compared to TDS on Zn+0.3wt.% TiH₂ precursor (dotted, as shown in [Figure 5c](#)) and TDS on untreated powder (dashed line, as given in [Figure 2](#)). Powders were both measured under vacuum, precursor in a helium atmosphere. Heating rate 5 K/min.

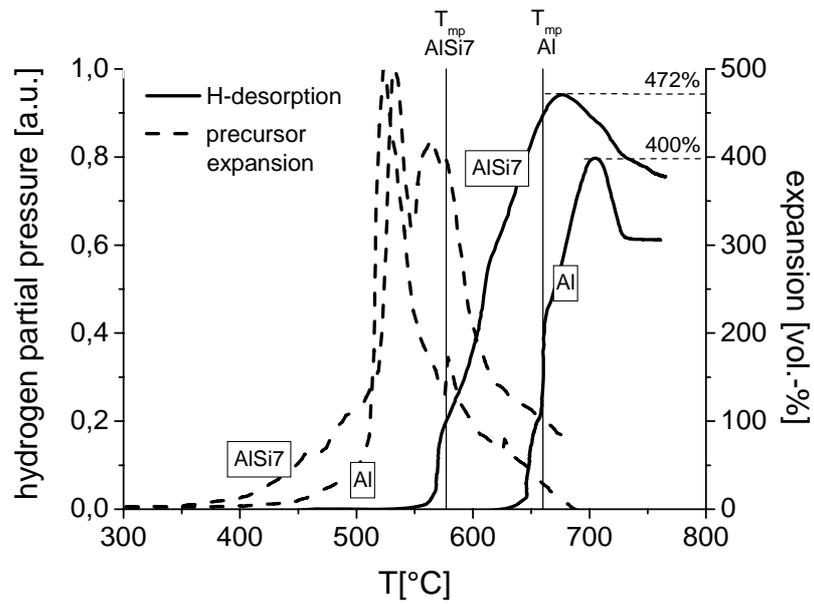


Figure 9. Broken lines: TDS on Al and AlSi7 precursors containing 0.5 wt.% TiH₂. Measurements were carried out in air at a heating rate of 5 K/min. Full lines: corresponding foam expansion curves.

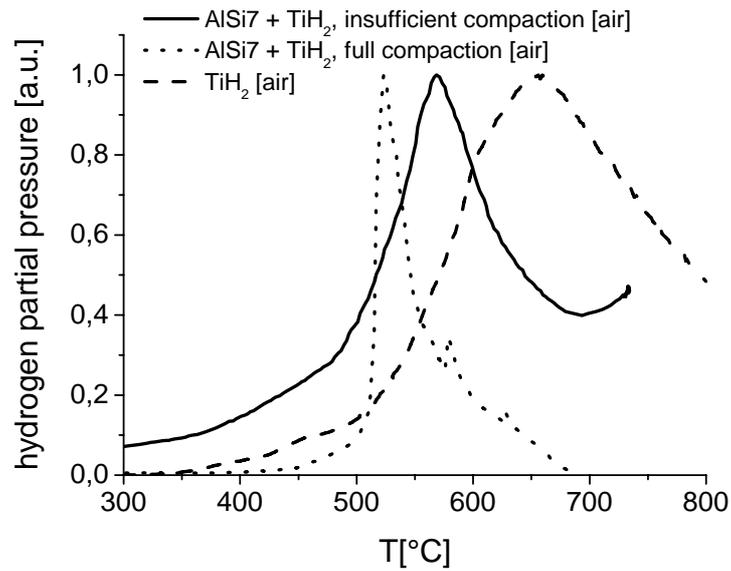


Figure 10. TDS measurement on AlSi7 precursor containing 0.5 wt.% TiH₂ which was insufficiently compacted (full line). For matters of comparison the curves corresponding to full compaction (dotted line) as shown in **Figure 9** and the curve of loose TiH₂ heated in air (dashed line) from **Figure 2** are shown. All TDS measurements were carried out in air at a heating rate of 5 K/s.