Zirconium Hydride–a Possible Blowing Agent for Making Aluminium Alloy Foams

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Use of the hydrides of the titanium group (Ti, Zr, Hf) for making aluminium alloy foams was evaluated. Foams were produced by compacting mixtures of metal and blowing agent powders and melting the powder compact afterwards.

We subjected ZrH_2 hydride to an oxidizing pre-treatment prior to compaction in order to tailor decomposition characteristics. We found that zirconium hydride can be tailored in such a way that foams with an improved uniformity of pore size distribution are obtained. Therefore, ZrH_2 could be a serious competitor of titanium hydride which is currently mostly used in metal foaming.

Keywords: aluminium foam, metallic hydride, zirconium hydride

1. Introduction

Over the past 15 years metal foams have become one of the most challenging materials for scientific and industrial investigations. Almost every metal can be foamed but foams from aluminium proved to be a serious candidate for industrial applications especially in automotive industry [1,2]. Using the powder metallurgical route aluminium and zinc foams can be prepared in a cost effective manner [3]. It includes the mixing of a metal powder (pure metal or suitable alloy) with a foaming agent (TiH_2, ZrH_2, $CaCO_3$, etc.)[4], after which the mixed powders are compacted to a foamable precursor. The precursor is heated above the melting temperature of the metal or alloy. During this process gas evolves from the foaming agent blowing bubbles in the melting alloy. The product is a metal foam, a porous material with the combination of typical properties of cellular materials and those of metals [5].

The sometimes irregular structure of the foamed material can be of concern for some applications. One reason is the temperature difference between the decomposition temperature of the blowing agent and the melting point of most commercial aluminium alloys. This difference causes the formation of irregular, crack-like pores in early expansion stages which then can lead to irregularities in the final product[6]. To minimize this temperature mismatch the solidus temperature of the alloy can be lowered by further alloying, creating possibly unwanted side effects or the decomposition threshold of the blowing agent can be raised by thermal pre-treatment. If the blowing agent 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 ideally hydrogen is released during foaming only after the solidus temperature of the alloy has been reached [7].

The term "hydride" can be described as a binary combination of hydrogen and a metal or metalloid [8]. By the nature of the hydrogen bond, hydrides are classified into three principal categories: covalent or volatile, saline or ionic and metallic. Metallic hydrides have metallic properties in the accepted sense; these include high thermal conductivity and electrical resistivity, hardness and in some instances useful mechanical properties. The difference between metals and hydrides is that they are usually quite brittle. There is a wide range of possible applications. Metal hydrides possess properties that make them desirable for nuclear application, for the preparation of powders and very pure metals, for chemical reducing agents, for deoxidation and desulfurization of molten ferrous alloys and for use as high energy fuels. Some of the hydrides can be used as portable sources of hydrogen. It is interesting to mention that zirconium hydride contains about twice as much hydrogen atoms per unit volume then liquid hydrogen. Metal hydrides can be used as well for preparing a coating on metals. Titanium, thorium and zirconium hydrides are used effectively for metal-nonmetal bonds. Hydrides of transition elements were shown to be used as blowing agents for the foaming of metals. This paper we devote to the application of ZrH_2 powder for making aluminium foams.

2. Experimental Procedure

The release of hydrogen from ZrH_2 powder in the untreated state and after various pre-treatments in argon and air were studied using a Netzsch Simultaneous Thermal Analyser STA 409C with simultaneous differential thermal analysis (DTA), gravimetry (TGA) and mass spectrometry (MS). The method is explained in more detail in Refs. [9, 10].

ZrH_2 powder supplied by Chempur GmbH, Karlsruhe, (purity 99.7 %, <45 μm) was used in this study. The powder was characterised in the state "untreated" and after several pre-treatments. Pre-treatments of the ZrH_2 powder were carried out isothermally at various temperatures (400, 480, 520°C) and times (90 and 180 min) both in an argon atmosphere (purified by a zirconium getter to 10^{-12} ppm) inside a tube furnace and under air in a chamber furnace.

Foamable precursors were prepared by mixing aluminium powder (Eckart, purity 99.74%, <160 μm), silicon powder (Ölschläger, purity 98.5%, <100 μm) and copper powder (Chempur, purity 99.8%, <250 μm) in fractions that led to an alloy composition AlSi6Cu4 and admixing 0.5 wt.% ZrH_2 in either the untreated state or after one of the various pre-treatments in air. These powders were mixed for 90 minutes in a tumbling mixer to produce a homogeneous distribution of all components. The powder mixtures were first pre-pressed at room temperature in a cylindrical die of 36 mm diameter. Afterwards, the die containing the powder mixtures

was heated to 450°C and held there for 30 min. Subsequent hot pressing at about 200 MPa for 30 min yielded tablets with more than 99% density.

The foamable precursor was converted into a foam by heating above its solidus temperature. A sample was placed on a steel block, pre-heated to the foaming temperature of 650°C inside a furnace and held at the same temperature. A thermocouple was in contact with the samples at all times so that we were able to monitor the temperature inside the foam during the entire process. Each foaming experiment was stopped as soon as a sample reached a given porosity and the foaming time t_f and final foaming temperature T_f was recorded. We tried to foam all samples to the same final volume corresponding to about 60% porosity. The preparation technique is explained in more detail in Refs. [9-11].

3. Results

The following experiments are based on powders pre-treated in air or argon prior to characterisation. At this stage no further oxidation occurs since thermal analysis is carried out under argon. ZrH_2 powder solely releases hydrogen which is also the case when metals are foamed. The decomposition peak is defined as the location of the maximum value of the mass spectrometric curves, while the onset is defined as the point where the curve has risen from the baseline to 1% of the peak value.

Fig. 1a shows the decomposition behaviour of untreated ZrH_2 powders, as well as ZrH_2 previously pre-treated under argon. Argon flow and a heating rate of 5 K/min were applied. Three peaks can be observed in the mass spectroscopic (MS) curve of untreated powder. The first step of hydrogen release as identified by mass spectrometry applying the 1% criterion starts at 205°C, a relative maximum is located at 436°C. A second dehydrogenation step starts at about 480°C and reaches a maximum at 552°C. The third dehydrogenation step starts at about 580°C with a small shoulder and reaches the maximum at 752°C.

We see that heat treatment at 400°C for 180 min eliminates the first decomposition stage and leaves two peaks only. The double peak structure remains the same even for treatments at higher temperatures or for longer durations. The position of the remaining two peaks is shifted to lower temperatures compared to that of untreated ZrH_2. The maximum peak shift is -120 K. Another observation is that the onset of gas evolution at 205°C is not changed significantly by pre-treatments under argon, with all onset temperatures being between 205°C and 211°C. Gas release levels off for temperatures beyond the peak and ends between ≈950°C for untreated powder or powders pre-treated at 400°C, and ≈900°C for powders pre-treated at 480 and 520°C.

The powders pre-treated in air prior to thermal analysis show a different decomposition behaviour as demonstrated in Fig. 1b. As it was already observed for pre-treatment under argon, heat treatment for 180 min at 400°C in air eliminates the first decomposition stage. Unlike treatment under argon, however, treatment in air significantly changes the temperature of the onset of gas evolution. Treatments up to 180 min or treatments at higher temperatures up to 520°C shift the onset up to +258 K, while peak positions decrease by up to -103 K. For all treatments gas release is smaller than that for untreated

powders and ceases earlier, namely at ≈850°C for treatment at 400°C, and ≈800°C for treatment at 480 and 520°C, 90 min, and ≈750°C for treatment at 520°C, 180 min as compared to ≈950°C for untreated powder.

(a)

(b)
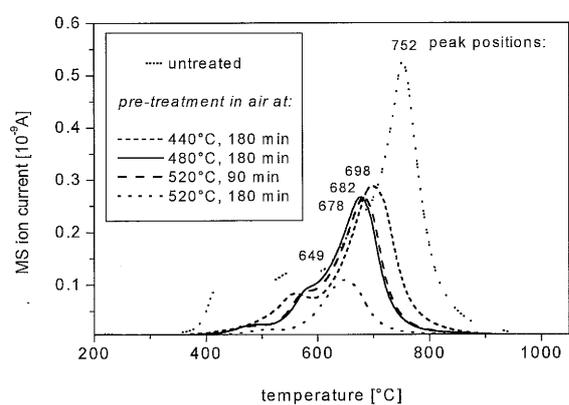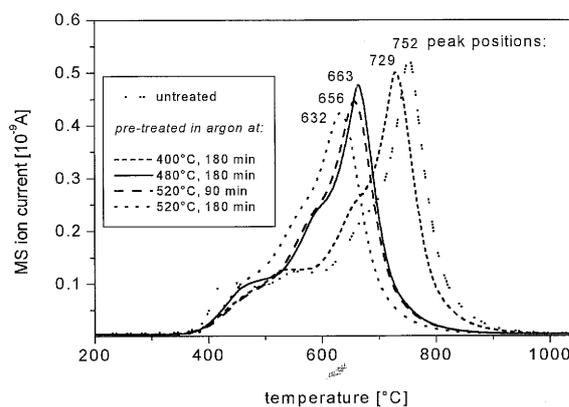
Fig. 1 Mass spectrometric analysis of untreated and pre-treated ZrH_2 powders during heating from 30°C to 1050°C at 5 K/min in an argon atmosphere (low temperature range omitted). The curve for untreated powder is shown in both cases for comparison. Peak positions are specified in the diagrammes (in °C); a) powders pre-treated under Ar, b) pre-treatment in air.

Fig. 2 shows the interdependence between foaming time and the final temperature at which the experiments were stopped in order to reach a desired expansion of about 60%. The data were measured on samples containing differently pre-treated ZrH_2 in air. The heating conditions were identical in all cases. The final temperature T_f increases steadily with foaming time t_f. The main observation is that a precursor which contains a blowing agent which was intensively pre-treated (at a higher temperature or for a longer time) needs more time (and correspondingly a higher final foaming temperature) to expand to a given volume.

The influence of the oxidation level of the blowing agent on the shape of the pores created during foaming is demonstrated in Fig. 3. Untreated ZrH_2 produced pores with jagged boundaries and a non-uniform size distribution. Associated with an increasing oxidation level of the hydride are notable changes in pore shape. Pores become more spherical and have smooth surfaces even for the shorter pre-treatments. Moreover,
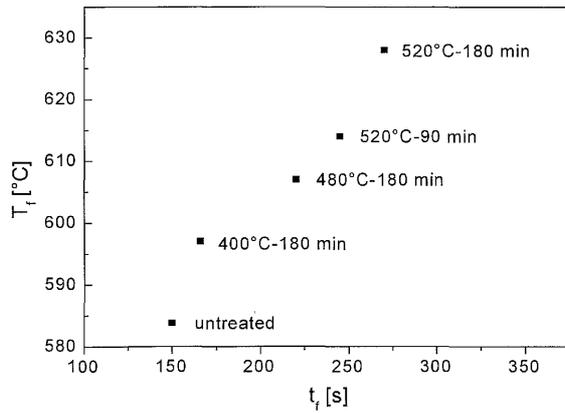
Fig. 2 Final sample temperature T_f vs. foaming time t_f for aluminium samples AlSi6Cu4 foamed up to a given porosity level of ≈60% with ZrH_2 pre-treated in air on different ways as specified. Furnace temperature was 650°C.
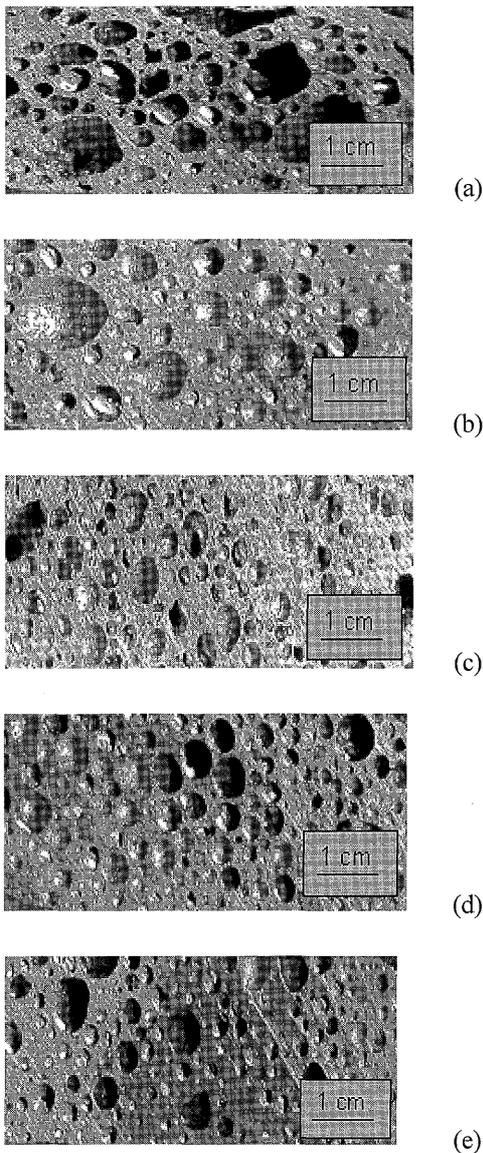
Fig. 3 AlSi6Cu4 foamed using a) untreated ZrH_2 (porosity P=58%), b) pre-treated ZrH_2 in air, 400°C, 180 min (P=50%), c) 480°C, 180 min (P=50%), d) 520°C, 90 min (P=53%), e) 520°C, 180 min (P=52%). The direction of expansion was from the bottom to the top.

there is a positive influence on pore size distribution. Powders pre-treated at 520°C produce more uniform foams than powders pre-treated at lower temperatures. An extended pre-treatment in air leads to more spherical and homogeneous pore distribution.

3. Discussion

The changes of the decomposition characteristics of ZrH_2 powders by prior thermal and oxidising pre-treatments are the main concern of the current work. Whereas pre-treatments under air and Ar both remove the first decomposition peak, only annealing under air shifts the onset of gas evolution to higher temperatures. Fig. 1b explicitly proves the importance of oxidation since the annealing treatments were identical in the two cases with the exception of the type of ambient atmosphere. A pre-treatment in air of the blowing agent ZrH_2 (by variation of dwell time and temperature) is leading to an oxide layer on each powder particle. This effect is already known and has been exploited to control hydrogen evolution from TiH_2 and ZrH_2 in metal foaming [7,13].

Three steps of hydrogen release from untreated powder were observed by other authors, as well [14]. They reported that the decomposition of ZrH_2 is accompanied by phase conversions $\varepsilon \rightarrow \delta + \beta \rightarrow \alpha$. Both ZrH_2 and TiH_2 are crystallized in the CaF_2-structure, in which the protons are occupying the tetrahedron vacancies. There is no structural evidence for larger differences with respect to the physical properties. Thus, the differences in outgassing are attributed to the oxide layer. TEM images have shown, that TiH_2 is primarily covered with Ti_3O followed by a TiO_2 coating [10]. The layer is crystallized in the Rutile structure. Rutile is known to be a n-type semiconductor. The structure is tetragonal with an oxygen pair on the basal plane. It might be stated that the crystallographic structure has no close similarity to the TiH_2 structure. In contrast zirconia is known to crystallize also in the cubic CaF_2-structure. The Zr- ion site again occurs in the fcc arrangement with the oxygen being located on the tetrahedron sites, i.e. the same location as the protons in the hydride structure. Hence, zirconia is an oxygen ionic conductor. The conductivity needs anion vacancies for fast transport. For tetragonal zirconia which is a slightly modified derivative of the fluoride structure proton conduction was observed using ERDA [15]. Summarizing one can state that the Ti-oxides show a quite different crystalline structure compared to the hydride structure, whereas the similarity between the zirconia and the hydride lattice would indicate a faster penetration of hydrogen through the layer. This would be the most plausible explanation for different hydrogen release rates.

The onset temperatures are shifted to higher values by pre-treatment in air, compared with the pre-treatment under argon where the onset temperatures are almost unchanged. Onset and peak positions found in Fig. 1b are displayed and compared in Fig. 4. The onset of hydrogen evolution is shifted to higher temperatures (and longer times) with more intense pre-treatment reflecting the fact that oxidation is increasingly more effective at higher temperatures and longer times. The peak positions (upper curve) move to lower temperatures. As the variation of the onset temperature is larger, the difference between peak and onset temperature drops with increasing pre-treatment temperature (see data derived from Fig. 1b

shown in inset of Fig. 4). This is important as this means that the range of strong hydrogen evolution narrows from 547 K to 186 K when replacing untreated by pre-treated powder.

In a technological sense the result shown in Fig. 1b is the most important one since it allows us to tailor the decomposition characteristics of the blowing agent. Higher annealing temperatures reduce the total amount of hydrogen available but shift the decomposition range to higher temperatures. It is worth to mention that the hydrogen release is in the temperature range between 500 and 700°C which is the temperature range significant for foaming aluminium alloys.
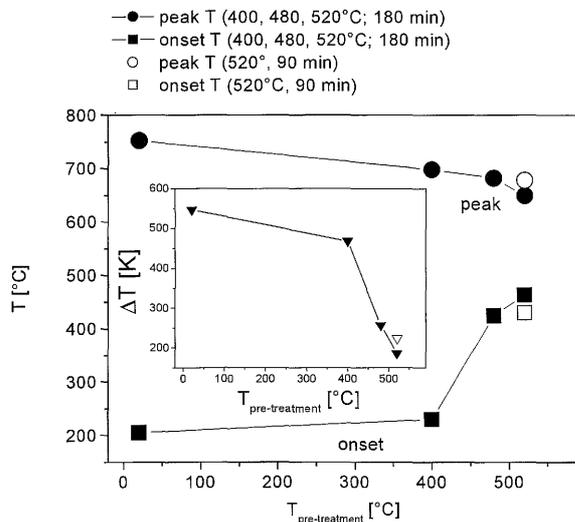
Fig. 4 Position of onset (lower) and peak (upper) of gas evolution derived from the results shown in Fig. 1b. Open symbols correspond to 520°C. Inset: difference between onset and peak temperature ΔT is shown for the measurement shown in Fig. 1b.

Foaming aluminium alloy AlSi6Cu4 with pre-treated powder is delayed and start at up to 30 K higher temperatures as seen in Fig. 2. This is exactly the effect sought, since gas evolution at higher temperatures was expected to produce round pores instead of cracks because the metal is already partially liquid when gas is generated. This helps avoiding problems associated with expansion already in the solid state, namely cracks and large pores.

4. Conclusion

It was shown that artificially produced oxide layers around individual ZrH$_2$ particles not only influence hydrogen release in the foaming process but also have a beneficial effect on pore shape and perhaps even pore size distribution of aluminium foams. Foams made by using untreated, i.e. unoxidised ZrH$_2$ have sharp edges and are irregular. Pre-treated powders delay pore formation to higher temperatures and produce more spherical and smoother pores. Therefore, by selecting the heat treatment parameters of the blowing agent in co-ordination with the melting point of the alloy appropriately, the pore structure of metallic foams can be influenced positively.

REFERENCES
1) J. Banhart: Int. J. Vehicle Design **37**(2005)114-125.
2) H.-W. Seeliger: *Cellular Metals and Metal Foaming Technology*, ed. by J. Banhart, M. F. Ashby and N. A. Fleck, (MIT-Verlag, Berlin, 2001) pp. 5-16.
3) F. Baumgärtner, I. Duarte and J. Banhart: Adv. Eng. Mater. **2**(2000)168-174.
4) V. Gergely, D.C. Curran and T.W. Clyne: Compos. Sci. Technol. **63**(2003)2301–2310.
5) M. F. Ashby, A. Evans, N. A. Fleck, L. J. Gibson, J. W. Hutchinson and H. N. G. Wadley: *Metal foams – a design guide*. (Butterworth – Heinemann, London, 2000).
6) L. Helfen, T. Baumbach, H. Stanzick, J. Banhart, A. Elmoutaoaukkil and P. Cloetens: Adv. Eng. Mater. **4**(2002)808–813.
7) S.E. Speed: Foaming pf metal by catalysed and controlled decomposition of zirconium hydride and titanium hydride. US Patent 3,981,720, 1976.
8) J. P. Blackledge: *An Introduction to the Nature and Technology of Hydrides, Metal Hydrides*, ed. by W. M. Müller, J. P. Blackledge and G. G. Libowitz (Academic Press, New York, 1968), pp.1-20.
9) B. Matijasevic, S. Fiechter, I. Zizak, O. Görke, N. Wanderka, P. Schubert-Bischoff and J. Banhart: *PM Lightweight and Porous Materials, Powder Injection Moulding, PM Functional Materials*, ed. by H. Danninger, R. Ratzi (European Powder Metallurgy Association, 2004) pp. 149-155.
10) B. Matijasevic-Lux, J. Banhart, S. Fiechter, O. Görke, N. Wanderka: Acta Mater. submitted.
11) A. Bütow: *Strukturuntersuchungen an Metallschäumen in verschiedenen Entwicklungsstufen*, Diploma Thesis, Technical University Berlin (2004).
12) J. Banhart, D. Bellmann and H. Clemens: Acta Mater. **49**(2001)3409-3420.
13) V. Gergely and T.W. Clyne: Adv. Eng. Mater. **2**(2000)168-176.
14) V. Zh. Shemet, A. P. Pomytkin, V. A. Lavrenko and V. Zh. Ratushnaya: Int. J. Hydrogen Energy **18**(1993) 511-516.
15) O. Kruse, H.D. Carstanjen, P.W. Kountouros, H. Schubert and G. Petzow: *Science and Technology of Zirconia V*, ed. by S.P.S. Badwal, M.J.Bannister and R.H.J.Hannink (Technomic Publishing Company, Inc., Lancaster, Pennsylvania, 1993)pp.163-170.