

Influence of powder pre-treatments on metal foam pore structure

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Abstract

The present paper highlights results from the priority program "Cellular Metals" of the Deutsche Forschungsgemeinschaft (DFG SPP 1075). Aluminium foams were produced via the powder route in which blends of metal powders and blowing agent are first compacted and then melted. AlSi6Cu4 casting alloy was foamed using titanium hydride as blowing agent. The blowing agent was subjected to various oxidising pre-treatments in air prior to compaction. The decomposition behaviour of the pre-treated blowing agent was characterised by thermo-analysis. The effect of pre-treatment on foaming was described with tomographic imaging of foams in early stages of expansion, i.e. 60% porosity. We find a beneficial effect of pre-treatment on foam morphology and explain it with the effect of oxide films generated on the surface of the blowing agent particles.

Introduction

A very promising way for producing metal foams is the *powder compact melting process*: a powder mixture of one or more metals or alloys and a blowing agent is compacted and then melted [1]. The blowing agent releases gas and propels the foaming process. Aluminium alloys are mostly used and titanium hydride (TiH₂) proved to be the most suitable blowing agent for foaming these alloys [2].

The properties of metal foams depend on many morphological features such as pore size distribution, cell wall curvature, defects etc. [3]. Although the exact interrelationship between properties and structure is not yet sufficiently known, one assumes that a uniform distribution of convex pores free of defects is highly desirable. The task for the experimentalist is now to produce such structures. A short look at the existing foams shows that there is still much potential for development.

As there is a mismatch between the melting point of most commercial aluminium alloys and the temperature range of decomposition of titanium hydride, the often observed formation of irregular, crack-like pores is one of the deleterious side effect occurring if the hydrogen release take place far below the melting point of the alloy. In this paper the influence of different pre-treatments of TiH₂ on pore structure is investigated. To visualise pore structure we used synchrotron radiation tomography (SRT) which has been shown to be perfectly suited for investigating metallic foams [4]. High resolution studies can be performed on foams in early and late expansion stages. Using monochromatic radiation one can collect

information not only about the mass distribution within the sample, but also about the element distribution.

Experimental

Hydrogen release as a function of heating rate and temperature was studied using a Netzsch Simultaneous Thermal Analyser STA 409C with simultaneous differential thermal analysis (DTA), gravimetry (TGA) and mass spectrometry (MS). The analyser was equipped with a silicon carbide furnace and was connected to a quadrupole mass spectrometer via a skimmer coupling system. The method is explained more in detail in Ref. [5].

Foamable precursors were prepared by mixing aluminium powder (Eckart, purity 99.74%, <160 µm), silicon powder (Oelschlaeger, 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-% TiH₂ (Chemetall, purity 99%, <63 µm) in both the as received state and after various pre-treatments in air. Pre-treatments of the TiH₂ powder were carried out isothermally under air in a chamber furnace at various temperatures (440°C, 480°C, 520°C) for 90 or 180 minutes. The pre-treatment parameters were chosen to be suitable for technological approaches, therefore the pre-treatments at the lower temperatures decomposing hydrogen were not considered.

Powders were mixed for 90 min in a tumbling mixer to produce a uniform and homogeneous distribution of the TiH₂ in the aluminium alloy. The powder mix was then pre-pressed at room temperature in a cylindrical die of 36 mm diameter, after which the die containing the powder mixture was heated up to 450°C and held there for reaching desired pressing temperature. Subsequent

hot pressing for 30 min at about 200 MPa yielded tablets with more than 99% density. Samples of 4 mm thickness were cut off the pressed tablets by electric discharge machining (EDM).

The foamable precursor was converted into foam by heating it to above its melting temperature. For this a thin sample was placed on the sample holder (Figure 1) that is a steel block with a guide hole for a thermo-couple and which had been pre-heated to the foaming temperature (650°C). The 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. The temperature history inside one such sample is shown in Figure 2. We see the onset of eutectic melting at 525°C and the removal of the sample at 585°C.

Each foaming experiment was stopped as soon as a sample reached a certain porosity. We tried to foam all samples to the same final volume corresponding to about 60% porosity. As we had no visual control of the foaming experiment we prepared several samples of each composition by varying foaming times and selected the ones with the desired porosity for further examination. The preparation technique is explained in more detail in Refs.[6] and [7].

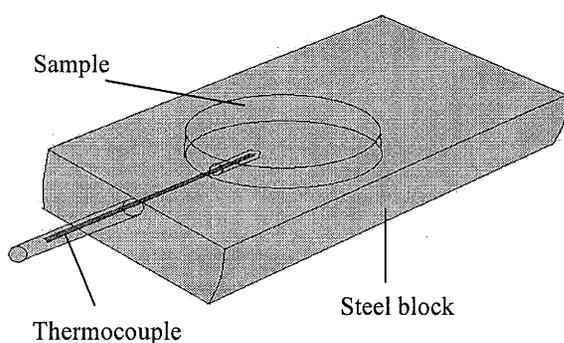


Figure 1: Sample holder used for foaming experiments.

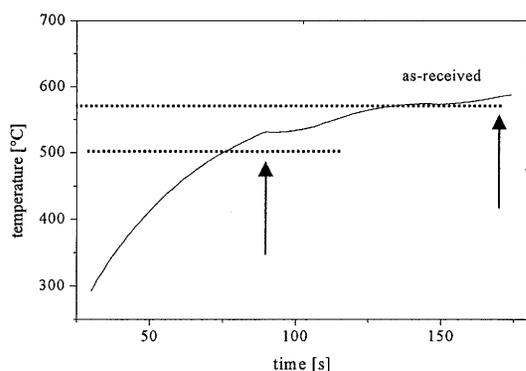


Figure 2: Heating curve of a AlSi₆Cu₄ sample containing as-received blowing agent powder. It was placed into a pre-heated furnace on a pre-heated steel block. The dotted lines represent the ternary eutectic and the final sample temperature in the moment of sample removal, the arrows the corresponding times.

The foamed samples were cut into appropriate sizes (20×7×7 mm³) by EDM and examined with SRT. The tomographic set-up used was that available at the BAM line (BAM - Federal Institute of Materials Research and Testing, Germany) located at BESSY II (Berlin electron storage ring, Germany). The achievable resolution was 3.5 μm in our case using an energy of 30 keV. 900 projections are needed to fully reconstruct a 3D volume and these were obtained by rotating the object through 180° and collecting a radiograph every 0.2°.

Results

Figure 3 shows the decomposition behaviour of various titanium hydride powders under constant heating conditions. Gas release is monitored by mass spectrometry. The gravimetric and thermal signal could also have been used as it was done in other studies [8][9] but MS yields the most undisturbed and direct measure for gas evolution.

As-received titanium hydride powder shows two decomposition peaks. Gas release starts already at 400°C and reaches a maximum at 524°C and 626°C.

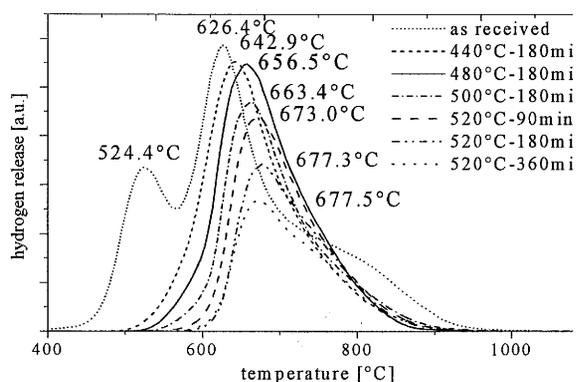


Figure 3: Mass spectrometry on as-received and heat treated under air TiH₂ powders at a heating rate of 10 K/min in argon atmosphere.

Heat treatment at 440°C for 180 minutes eliminates completely the first decomposition stage and increases the temperature at which maximum gas expansion occurs. Treatments up to 360 min or treatments at higher temperatures up to 520°C shift both the onset temperature of gas evolution and the peak position to even higher temperatures. Figure 4 shows this dependence for the peak of gas evolution.

The total amount of hydrogen released – given by the area under the curves in Figure 3 also decreases both with prolonged times and higher temperatures.

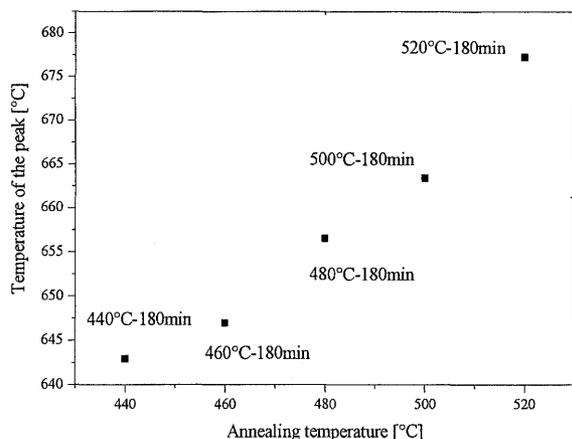


Figure 4: Temperature of maximum gas release as a function of annealing temperature

Figure 5 shows the dependence between foaming time and the final temperature at which experiments are stopped in order to reach the desired expansion. The final temperature increases steadily with time. Therefore, the observation is that precursors which contain a blowing agent that has been more heavily pre-treated (at a higher temperature) needs a longer time (and correspondingly a higher final foaming temperature) to expand to a given volume.

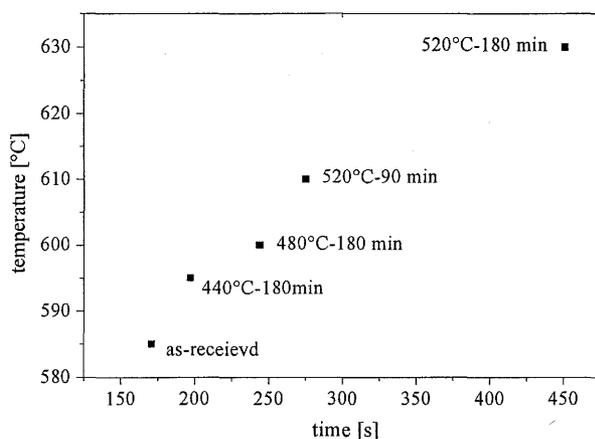


Figure 5: Final foaming temperature reached when foaming up to 60% porosity as a function of foaming time.

The influence of the pre-treatment parameters on the oxide layer around the core of TiH_2 particle on the shape of pores is shown in Figure 6 using tomographic images. As-received TiH_2 produced pores with sharp edges and a non-uniform size distribution. Associated with the oxidation level of the hydride are notable changes in pore shape. Pores are becoming more spherical and have smooth surfaces even for the shorter pre-treatments. Uniformity of cell size seems to improve gradually with longer pre-treatment times but a quantitative measure for this effect is still lacking.

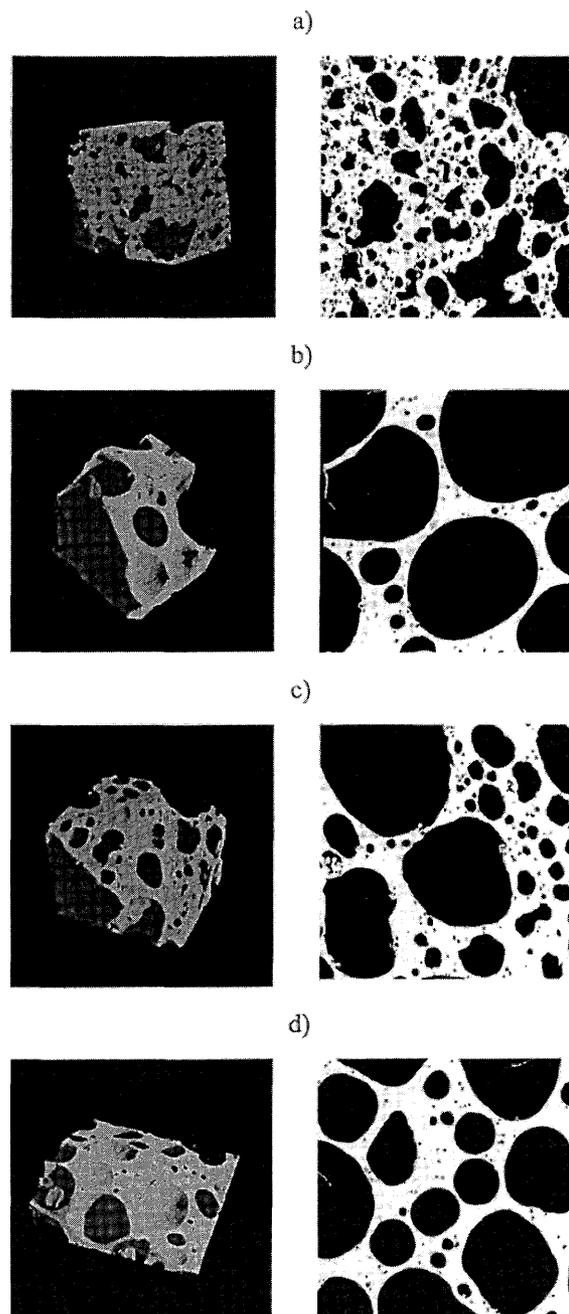


Figure 6: SRT images of AlSi6Cu4 foams foamed using a) as-received TiH_2 b) pre-treated $440^\circ\text{C}-180\text{min}$ c) pre-treated $480^\circ\text{C}-180\text{min}$ d) pre-treated $520^\circ\text{C}-180\text{min}$. Left column: 3D rendering, right column: 2D slice through sample

Discussion

The shift of blowing agent decomposition to higher temperatures with increasing pre-treatment temperature can be measured precisely. All three methods – DSC, TG and MS – yield comparable results [10]. The interpretation of the results is that decomposition of TiH_2 is impeded due to the slow diffusion of hydrogen through the oxide layers built up during pre-treatment [8][9][11]. Hydrogen not only has to diffuse through the bulk

titanium matrix from the inner region of each particle towards its surface but also has to overcome the oxide barrier which is an additional kinetic hindrance. This effect is well known and has been exploited to control hydrogen evolution from TiH_2 in metal foam manufacture [5].

The measurements also show that coupling of DSC, thermo-gravimetry and mass spectrometry permits a detailed insight into the course of decomposition associated with the desorption of gaseous products from TiH_2 .

Foaming the selected aluminium alloy $AlSi6Cu4$ with pre-treated powder delays foaming and increases temperatures at which the foam evolves by up to 35 K as seen in Figure 5. 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. The tomographic images obtained therefore confirm this picture of a beneficial effect of the pre-treatment of blowing agent.

Summary

It was shown that artificially produced oxide layers around individual TiH_2 particles not only influence hydrogen release in the foaming process but also have a beneficial effect on pore shape and perhaps even size distribution of aluminium foams. Foams made using as-received, i.e. unoxidised TiH_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, one can positively influence the pore structure of metallic foams.

Acknowledgements

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