

Improvement of aluminium foam technology by tailoring of blowing agent*

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Abstract

Aluminium foams produced by melting powder compacts containing a blowing agent are usually non-uniform which might lead to inferior mechanical properties. The reasons for this can be thermal gradients during foaming and a blowing agent which is not adapted to the melting range of the alloy to be foamed. We discuss various strategies to improve aluminium foams and then demonstrate that titanium hydride can be tailored by selective oxidation and partial discharge to yield more uniform foams. We find that the expansion potential of the foams and the uniformity of cell size distribution is improved and that the individual cell walls are smoother and less corrugated when the foam is blown with pre-treated TiH_2 .

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I. INTRODUCTION: FACTORS INFLUENCING ALUMINIUM FOAM QUALITY

Metal foams made by first compressing mixtures of aluminium alloy powders and titanium hydride (TiH_2) and then melting and foaming the resulting densified compact¹ are now being exploited commercially under trade names such as "Alulight" or "Foaminal"². Production volumes are still low owing to both the still relatively high costs and to the properties of foamed aluminium alloys which are not always sufficient for a given application. For this reason many research activities are directed towards improving the properties of such foams and to make manufacture more reliable, reproducible and, as a consequence, less expensive.

Intuitively one tends to assume that metal foam properties are improved when the individual cells of a foam all have a similar size and a spherical shape. This, however, has not really been verified experimentally. There is no doubt that both the density of a metal foam and the properties of the matrix alloy influence, e.g., modulus and strength of the foam³⁻⁵. A clear influence of cell size distribution and morphological parameters on foam properties, however, has not yet been established. The reason for this is that it has not yet been possible to control these parameter in foam making. Therefore studies of the interdependence of morphology and properties of foamed metals have in the past either been purely theoretical or have concentrated on more simple systems such as open cell structures or honeycombs which can be manufactured in a more controlled way. Still, there are various opinions on what the ideal morphology of a closed-cell foam yielding the highest stiffness or strength at a given weight should be. Some authors find an insensitivity of strength on cell size distribution^{6,7}, others claim that a bimodal distribution of cell sizes is especially favourable⁸. Irregular foams were found to have a higher tangent modulus at low strains, whereas regular foams with a more unique cell size were stronger at higher strains⁹. Size effects were found to be an important issue because a certain number of cells across a sample is necessary to ensure meaningful mechanical properties (see e.g. Ref. 10) which makes foams with small pores look more favourable. Importance has also been ascribed to the shape of cell walls. Especially corrugated cell walls seem to have a strong detrimental influence on foam properties¹¹. Foams with missing cell walls or cell walls containing holes or cracks were also studied and found to be mechanically weaker than perfect foams (see Ref. 12 for an overview). The variability of mechanical properties in a group of specimens of identical

nominal dimensions and densities has been analysed statistically and was found to be very large even for the most regular foams available at present¹³. It is likely that more regular foams, even if they do not show better mechanical properties, lead to a lower variability of these properties which would also be a very valuable feature.

Despite the unclear situation researchers are striving to make more uniform foams. If they think they can do so they use this fact as an argument for the superiority their production method (see e.g. Ref. 14). As the foaming process comprises various steps and each step can be influenced by many parameters the properties of the final foamed part can vary very much if production conditions are changed. Especially in the early days of metal foaming the search for appropriate foaming parameters was difficult because the mechanisms of metal foaming were unknown and the complex interdependence between parameters was not understood. Another problem is that there is no simple measure for the quality of a foam. Usually one assesses the uniformity of cells in a qualitative way by looking at sections through foamed specimens. Whenever a foam possesses many cells of a similar size it is often considered "good", if there are many obvious defects it is called "inferior". Fig. 1 shows four samples as taken from different batches of aluminium foam sandwich (AFS) panels made by the company *applied lightweight materials* (Saarbrücken, Germany) which clearly show a difference in foam quality. The problem with such qualitative measures is that important morphological features such as the asphericity of cells or crack alignments in three dimensions might not be detectable in this way. Therefore tomography and 3D image analysis were proposed and successfully applied. However, for the purpose of parameter optimisation this method is often too elaborate. Another problem encountered is the very restricted significance of individual foaming trials. Systematic variations in foam quality associated with the change of a processing parameter are not easy to detect and require a large number of experiments. Finally, there also seems to be a size effect in foaming. The smaller the samples are, the more uniform they usually appear which again makes comparison of different results difficult.

The current state of knowledge suggests that the following rules have to be obeyed to obtain good aluminium alloy foams via the powder compact foaming technique:

The *melting behaviour* of the alloy system and the decomposition characteristics of the blowing agent have to be coordinated. Ideally, gas evolution is suppressed below the solidus temperature of the alloy to avoid formation of cracks before melting. After partial melting

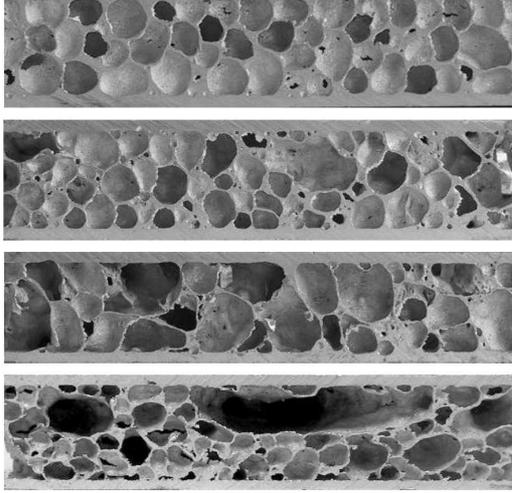


FIG. 1: Sections of aluminium foam sandwich materials as obtained in industrial production¹⁵; from bottom to top: improving quality (courtesy: H.-W. Seeliger).

the gas released by the blowing agent then leads to the formation of spherical pores provided that the liquid fraction is sufficiently high. As TiH_2 has a very low decomposition temperature – starting at about 400°C for untreated hydride – and commercial aluminium alloys have solidus temperatures above 525°C there is an obvious gap. The first foaming experiments¹⁶ were carried out with pure aluminium or AlCu4 and often yielded inferior results. A first improvement was the replacement of these wrought alloys by casting alloys such as AlSi7 and AlSi12 . Later the alloy AlSi6Cu4 was proposed and successfully foamed³. The solidus and liquidus temperatures of some of these alloys are given in Fig. 2 and are compared to the decomposition range – more precisely the range from the onset to the maximum of gas evolution – of TiH_2 . It is obvious that untreated TiH_2 does not fit to the melting range of none of the Al alloys shown, especially when taking into account that the decomposition of TiH_2 is shifted to even lower temperatures when it is embedded in the aluminium matrix by compaction (probably caused by the fracture of TiO_2 -layers covering each TiH_2 particle¹⁷). Further lowering of the melting point of aluminium alloys below the values given in Fig. 2 is restricted since the resulting alloys would have very unfavourable properties. Therefore, tailoring the blowing agent TiH_2 was considered next. Pre-treatment of TiH_2 under oxidising conditions was found to shift the decomposition range to higher temperatures^{18–20}. A detailed investigation of how these pre-treated TiH_2 powders influence

the foaming process is still lacking. However, Fig. 2 suggests that the pre-treated powder and the low melting AlSi6Cu4 alloy fit to each other rather well as indicated by the arrow.

Furthermore, *heating conditions* during foaming are important. When foaming parts – especially large and flat foam panels – differences in temperature over the extension of the part lead to non-uniform foaming. This not only makes it difficult to fully expand the entire component without any collapse taking place in the region of the highest temperature, but also leads to an inferior pore structure due to the formation of cracks in the foam²¹. The heating profile during foaming is also important. In pre-heated furnaces the temperature usually approaches the final temperature exponentially. In regulated furnaces almost arbitrary heating profiles can be realised. It was found that the temperature course around the melting point of the precursor significantly influences foam evolution²². Overheating can have a detrimental effect on foaming and should be avoided.

A further factor which influences foam uniformity is the *cleanliness* of powder processing. Use of impure powders or the presence of adsorbed water, dirt or gases entrapped in the precursor during compaction seem to have an adverse effect on foaming in the sense that these impurities can act as nuclei for big voids in early stages of gas evolution from the blowing agent. The voids are then thought to grow to large pores²³. These effects are rather spurious and have not been quantified but are based on the experience of a number of researchers including the present authors.

Other conditions during powder processing are also important. Overheating of the powder during extrusion was found to be detrimental to foam expansion²⁷. The compaction temperature during hot pressing has also to be selected carefully since even slightly elevated temperatures can lead to a reduced foam expansion²⁸.

In conclusion, the best recipe for a good foam, i.e. a foam with a high expansion factor developing a uniform cell size distribution and fairly smooth convex cells seems to be:

- use a low-melting aluminium alloy,
- use TiH₂ as blowing agent which has been adapted to the alloy by pre-treatment,
- process powders under clean and reproducible conditions,
- take care to avoid overheating during powder compaction,

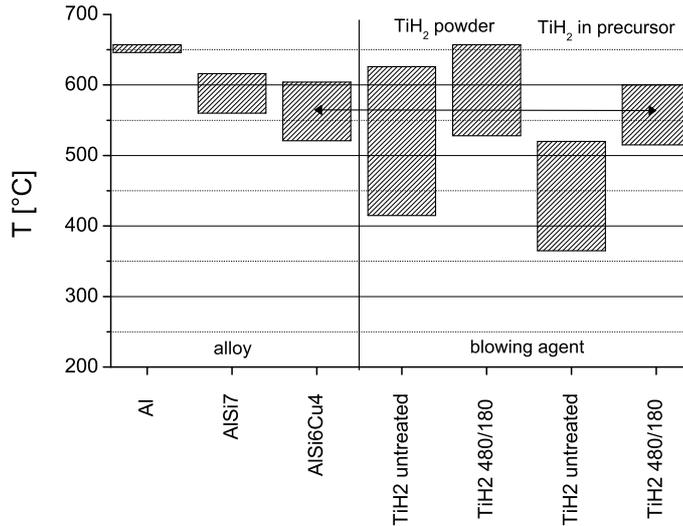


FIG. 2: Temperatures governing the foaming process of metals. Left part: range between solidus and liquidus for 3 commercial Al alloys^{24,25} ("Al"=AW-1050, "AlSi7"=A356.0, "AlSi6Cu4"=A319.0.) Right: range between the onset and maximum of hydrogen release from TiH₂-powder and pure Al precursor containing this TiH₂. Values for untreated TiH₂ and TiH₂ pre-treated at 480°C for 180 min. are given. Data is derived from mass spectrometry experiments²⁶ at a constant heating rate of 10 K/min.

- carefully select the temperature profile during foaming: high heating rates without overheating and uniform temperature distributions are preferable.

We shall devote the remaining paper to the investigation of the effect of pre-treatment of TiH₂ on the expansion of aluminium alloy foams and their cell morphology after solidification.

II. EXPERIMENTAL

Al (Eckart), Cu (Chempur), Si (Oelschlaeger) and TiH₂ (Chemetall) powders were mixed in proportions corresponding to the alloy AlSi6Cu4 containing 0.5 wt.% TiH₂²⁶. Various modifications of TiH₂ were used: untreated powder as received from the manufacturer and powder annealed in air at 440, 460, 480 and 520°C for 180 min. In addition, an annealing treatment for 90 min at 520°C for was carried out. 12 g of each of the powder mixtures were

hot-pressed to tablets of 36 mm diameter at 450°C for 30 min at a pressure of 200 MPa. These tablets were foamed in a so-called "expandometer". This dilatometer was specially constructed for metal foam characterisation and allows us to heat up and foam a piece of precursor in a quartz glass tube at given heating profile while recording sample temperature and vertical expansion. Expansion can be interrupted by turning off the heating lamps and by starting cooling with pressurised air²⁹. The cooling rates achieved are about 2 K/s.

Two types of experiments were carried out: i) experiments in which the precursor sample was foamed following a given temperature profile, and ii) experiments in which the foaming process was interrupted to reach a given volume expansion. In the former case the temperature profile chosen included a constant heating rate of 1 K/s up to 650°C and a constant temperature after. In the latter case the final temperature was kept slightly lower — at 630°C — to slow down the foaming process. Samples were retrieved after cooling, sectioned (using a microtome or EDM), photographed with a digital Camera and further investigated in the SEM.

In order to check the reproducibility of the expandometer measurements five experiments were carried out for each set of parameters. As the resulting curves showed pronounced variations a measurement was accepted whenever three curves were identical within an error limit given by the precision required for the analysis.

III. RESULTS

Fig. 3 shows results of non-interrupted expansion experiments for the six different modifications of TiH₂ considered. For all the samples we observe an onset of expansion after about 600 s followed by continuous foaming up to expansion factors above 4.5. The foaming process can be divided into three stages for all the experiments: i) a small initial expansion after which there is a short pause, followed by ii) a stage with a high expansion rate which turns into iii) an almost linear expansion regime with a lower expansion rate. Expansion comes to an end rather abruptly, after which the volume is constant.

Defining the onset of expansion as $\eta = 1.01$, i.e. 1% expansion, one can read the time and temperature from Fig. 3 and display it as shown in Fig. 4. The points determined in this way must all lie on the global temperature course imposed on the sample by the furnace (broken lines). That this is indeed the case shows the good control of temperature in the

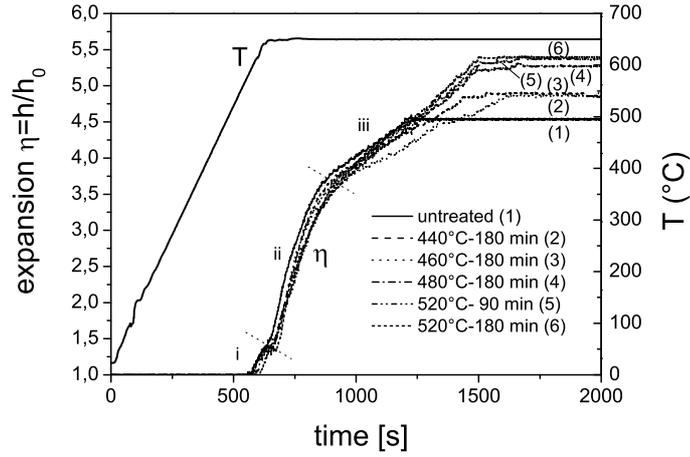


FIG. 3: Expansion curves of precursors based on six different modifications of TiH_2 . Volume expansion $\eta = V/V_0 = h/h_0$ is given for all samples, the temperature curve is shown for one sample only. The various expansion stages discussed are marked by i, ii, and iii.

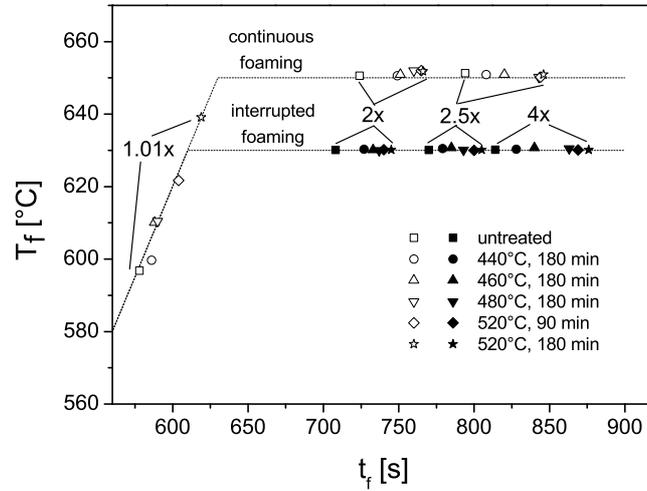


FIG. 4: Sample temperatures T_f measured in foaming experiments in the moment t_f when a given volume expansion η was reached (specified as $\eta \times$). Open symbols: values for continuous foaming experiments as read from Fig. 3, full symbols: values for interrupted foaming experiments in the moment the lamps were turned off and air cooling was started. Broken lines are the overall temperature profiles applied.

experiment. In an analogous way we determine points corresponding to volume expansions of $\eta=2$ and 2.5 (open symbols).

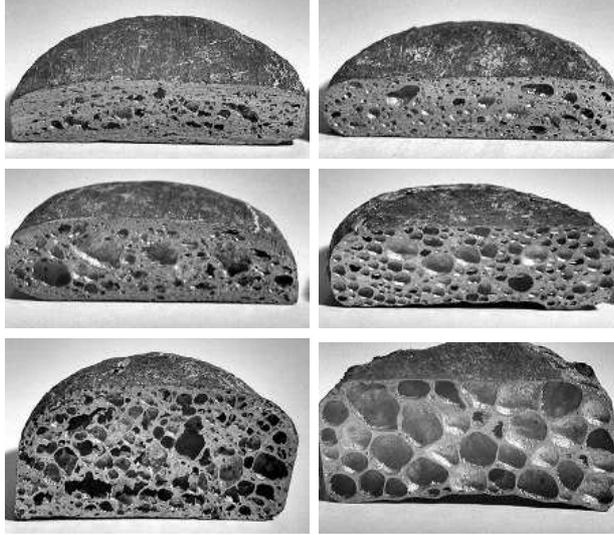


FIG. 5: Aluminium foams after expansion to a height of approx. 2, 2.5 and 4 times the height of the original precursor (from top to bottom). Foamed with, left column: untreated TiH_2 , right: TiH_2 treated at 520°C for 180 minutes. Sample width is 36 mm.

Interrupted foaming leads to samples in different expansion stages which can be analysed after cooling. Expansion factors of $\eta=2$, 2.5, and 4 were chosen. Foaming was interrupted a short time before the desired volume was reached to take account of the thermal inertia of the expandometer which leads to a certain after-foaming. As a rule, the volume still increased for 45 s after interrupting and the corresponding volume expansion was about 0.5 on the η -scale in Fig. 3. The corresponding foaming times and temperatures in the moment of initiation of cooling are given in Fig. 4 as solid symbols. They lie on the horizontal line at 630°C .

Some of the corresponding foams are shown in Fig. 5. The morphology of foams in different expansion stages blown with untreated (left) and pre-treated (right column) TiH_2 can be compared. Images corresponding to other modifications of TiH_2 were also obtained and evaluated but are not shown here.

SEM images provided further insight into the samples. Fig. 6 and Fig. 7 show low-magnification images of foams blown with both untreated and pre-treated TiH_2 .

An interesting observation was that the evacuation of the SEM chamber took 4 times

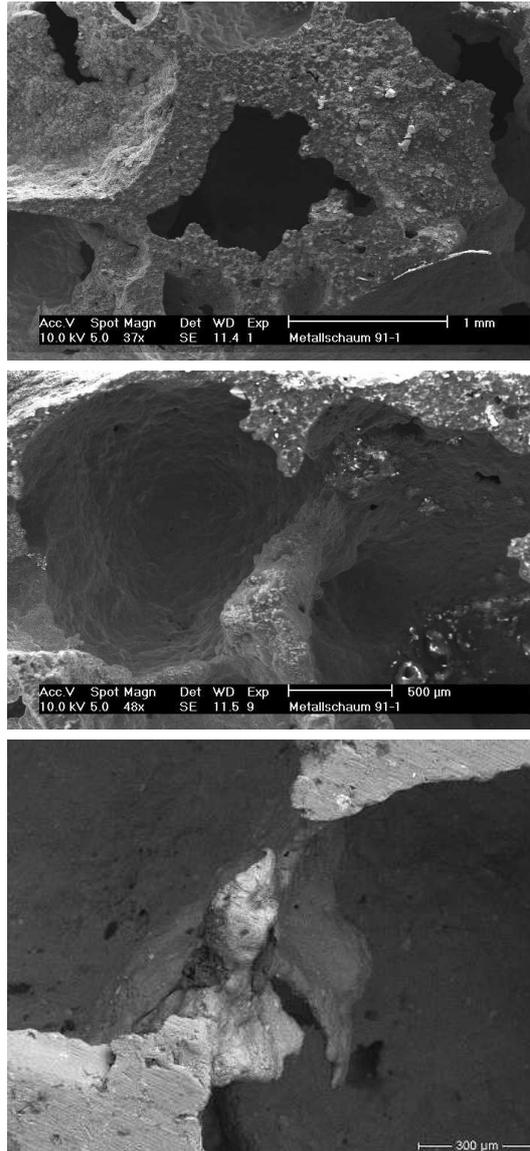


FIG. 6: SEM images of selected features of a foam expanded with untreated TiH_2 to 4 times the height of the original precursor (sample on the lower left in Fig. 5).

longer for the foams blown with untreated TiH_2 (as shown in Fig. 6) than for the foams blown with pre-treated TiH_2 such as the one in Fig. 7, indicating a different gas permeability of the two foam types.

IV. DISCUSSION

Foam expansion starts at about 590 to 640°C depending on the pre-treatment of TiH_2 as seen in Fig. 3 and even more clearly in Fig. 4. These temperatures should not be taken too

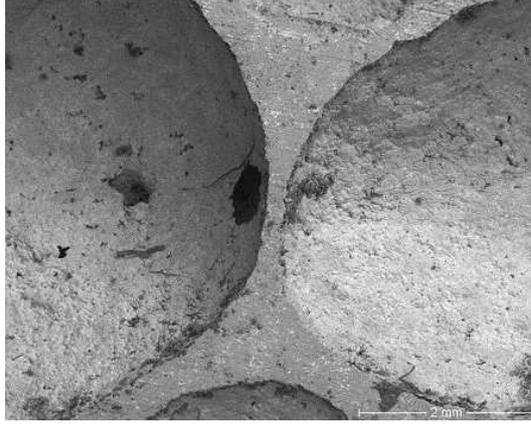


FIG. 7: SEM image of a foam expanded with TiH_2 pre-treated at 520°C for 180 minutes to 4 times the initial precursor height (sample on the lower right in Fig. 5).

literally because there might be a delay between the measured temperature and the true sample temperature due to the limited heat flow within the expandometer as the thermocouple is fixed in the middle of the 3 mm thick substrate supporting the sample. It is obvious that pre-treatments of the blowing agent delay the expansion process. Not only the onset of expansion is observed at higher temperatures but also a given volume expansion is reached at a later time as shown for three expansion factors in Fig. 4.

The times required for reaching a given foam expansion slightly vary between the two foaming experiments which is understandable since there are two differences: first, the foaming temperature is 20 K higher in the continuous foaming experiment which leads to faster foaming. Second, however, foaming was interrupted prior to reaching the desired volume in the interrupted foaming experiments to account for after-expansion. Therefore the true foaming time corresponding to the expansion value given would be about 45 s higher. The result is a near compensation of the two effects, leading to the slight difference observed.

In general the time delay during foaming is larger for blowing agents subjected to a higher pre-treatment temperature or pre-treated for a longer time. The shift of the onset of foaming to higher temperatures is beneficial for pore formation since the fraction of liquid present when gas starts to evolve is higher and correspondingly the partially molten metallic matrix can accommodate the emerging gas in bubbles. As a consequence, we observe a difference in morphology between the various foams as demonstrated in Fig. 5 for

two different TiH_2 powders. As untreated powder leads to early gas evolution already in the solid state and an earlier onset of expansion the corresponding foam structure (see left column) is less uniform and the individual pores are jagged and more irregular than for the foam blown with a pre-treated TiH_2 -powder (right column). During foaming the alloy melts in both cases and some of the imperfections created in early stages disappear, but some of the non-uniformities survive even in the fully expanded foam.

The SEM images confirm this picture. Fig. 6 shows irregular pores (top) and cell walls which are partially punctured or ruptured in the foams made using untreated TiH_2 (second and third image). In contrast, foams made using pre-treated TiH_2 exhibit round cells and smooth, non-ruptured and regular cell walls (Fig. 7). The observed longer evacuation time in SEM investigations of foam blown with untreated TiH_2 is an indication that many cells are interconnected by microscopic cracks or holes and that gas continues to flow for a long time when the sample is placed into a vacuum.

Another effect of TiH_2 pre-treatment is that it increases the value of maximum expansion as seen in Fig. 3. Untreated TiH_2 leads to expansions around 4.5, while pre-treated powders lead to values up to 5.5. The increase is correlated with the temperature and time of pre-treatment in a sense that higher pre-treatment temperatures and longer times improve foam expansion within the parameter range investigated. This result is surprising since the total amount of hydrogen available in the blowing agent is reduced by a pre-treatment. Isothermal measurements at 600°C revealed that the amount available for foaming drops to about 50% when TiH_2 is pre-treated at 520°C for 180 minutes²⁶. The explanation for this apparent contradiction is that hydrogen is released from pre-treated blowing agents at higher temperatures and in a narrower temperature range than from untreated powder. Therefore, non-treated blowing agent releases gas in early stages where it can escape through residual pores and the gas supply runs out in later stages. Pre-treated blowing agent, in contrast, still provides blowing gas in late stages and therefore leads to a higher final expansion.

A related study was carried out by Kennedy³⁰. He subjected TiH_2 to heat treatments in air at 400 to 550°C for 15 minutes and produced pure aluminium foams in free foaming experiments. There was a slight increase of 13% in maximum foaming height when untreated powder was replaced by powder pre-treated at 500°C . The time to maximum foaming was also slightly delayed in accordance with our findings.

V. CONCLUSIONS

There are many factors influencing aluminium foam evolution. A key point is the use of an appropriate blowing agent which releases gas at the right temperature to ensure high expansion and the formation of a uniform porosity.

By pre-treating TiH_2 in air at a certain temperature and for a given time we found:

- the onset of foaming is delayed by pre-treatment. In the current configuration the delay can be up to 45 s, corresponding to a temperature difference of 45 K,
- reaching a given foam volume takes a longer time, up to 60 s in the present case,
- final expansion of the foam is increased. We observe a gain from $\eta=4.5$ to 5.5,
- uniformity of the emerging foam is improved and the pores are rounder, the cell walls smoother.

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