

Anomalous Behaviour of Aluminium Foams During Solidification

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ABSTRACT

Solidification of metal foams was studied by in-situ X-ray radiography. Precursors were prepared by uni-axial hot compaction of metal/blowing agent powder blends, foamed in a X-ray transparent furnace and were then solidified. Foam evolution was continuously monitored. The cross-section of the foam at any instant was determined from the images by automated image analysis. During cooling of the sample an unexpected small transient expansion stage was observed. In order to explain this behaviour different possible effects are proposed and evaluated. Experiments were carried out for alloys with and without blowing agent, for different heating times and cooling rates to separate the various possible mechanisms. It was observed that the transient expansion strongly depends on heating time and cooling rate. Some transient expansion is also observed for alloys without blowing agent demonstrating that the effect can only be partially ascribed to the behaviour of the blowing agent.

1. INTRODUCTION

Metal foam has been identified as a potential material for light-weight construction and high absorption capacity for mechanical energy¹. Metal foam can be made by various methods among which the powder metallurgical route is one of the most important ones because it allows processing of a wide range of materials and component geometries. This method consists of consolidation of a metal powder mixed with a blowing agent, followed by heating into the mushy or liquid state in which the blowing agent releases gas and expands the material and finally by cooling to the solid state². While the foaming process^{3,4} as well as the morphologies and mechanical properties of foams^{5,6} were studied by many researchers, solidification of the foam has not yet been investigated in detail.

Solidification is an important process step to consider, not only because it is unavoidable in the manufacture of metal foams but also because solidification of metal foam can be expected to have an influence on mechanical properties both via the microstructure of the cell walls and via the mesostructure, e.g., by controlling crack formation or pore shape. The volume change of the foam upon cooling should be taken care of properly, especially when foaming is done inside a mould or large sandwich panels are manufactured.

During cooling of metal foams an unexpected small transient expansion stage was observed after the normal shrinkage. This transient expansion could be important for the manufacturing process of shaped metal foam components

and is therefore studied here. In the following the transient expansion is termed as *Extra Expansion (EE)* and the reasons for this phenomenon are investigated.

2. EXPERIMENTAL

2.1 Samples

An alloy AlSi6Cu4 was foamed using TiH₂ as a blowing agent and applying the powder metallurgical method. 90 wt% of aluminium, 6 wt% of silicon and 4 wt% of copper powder were mixed, after which 0.5 wt% TiH₂ powder (heat treated at 480°C for 180 minutes) was added. After mixing, the blend was hot-compacted uni-axially at 300 MPa pressure and 400°C for 5 minutes. The compacted precursor had 36 mm diameter and was approximately 10 mm thick. These compacts were cut to pieces of 10 mm square and 4 mm height. Samples not containing any blowing agent were also prepared in the same way.

2.2 Experimental set-up

The samples were foamed in X-ray transparent furnaces and were observed in-situ. A 150 kV microfocus X-ray source with 5 µm spot size and a 2240 × 2368 pixel² panel detector were used for imaging⁴. Two types of X-ray transparent furnaces were used. The first furnace had two IR-halogen lamps each of 150 W heating power⁴. Foaming was done inside a hollow steel tube. The open sides were aligned with the X-rays and were closed with thin aluminium foils to avoid heat losses due to air convection. The centre bottom of the steel cover had a hole through which a thermocouple was inserted to monitor the temperature at the sample's bottom surface. The second furnace was called pressure heater and allows for foaming under pressure⁷. This furnace was used to foam precursors without any blowing agent with the pressure induced foaming (PIF) method^{8,9}.

2.3 Experimental procedure

The precursor was heated to above the melting point of the alloy. After the end temperature (604°C) had been reached, temperature was kept constant for a certain time called *holding time* as shown in Fig. 1. After holding, the foam was allowed to cool down. Zero second holding time indicates that cooling started immediately after the temperature reached the end temperature. Ambient cooling (by simply turning off the power supply) and slow cooling (by decreasing the voltage to a lower value and then turning off the power supply when the temperature reached 520°C) were applied. The temperature was recorded once every second during the experiments while foam evolution was continuously monitored via X-ray imaging.

Simple heating of the samples not containing any blowing agent under these conditions does not produce any foam. For foaming they were first heated inside the pressure furnace at 5 bar over-pressure. After melting, the gas pressure was reduced to ambient pressure (1 bar) which produces a foam driven by the adsorbates present in the compacted samples^{8,9}. After foaming the experiment was analogous to that of the samples containing blowing agent.

The expansion of the foam was determined from the radiosopic images by automatised image analysis software package AXIM⁴. At any instant AXIM can determine the outer contour of the projected foam and calculate the projected area. This area *A* at any moment divided by the area at the beginning of heating (*A*₀) is referred to as area expansion (*A/A*₀). Volume expansion in a container-less foaming experiment will be always slightly higher than area expansion since the samples also expand in the beam direction but its determination would require additional effort without delivering much information for this work.

3. RESULTS AND DISCUSSION

3.1 Foaming process

Figure 1(a) shows a typical expansion curve of AlSi6Cu4+0.5 wt% TiH₂ alloy as a function of time including the temperature course during the foaming process. The temperature graph shows three distinct stages: the first is the heating stage, when temperature *T* rises from room temperature to above the melting point of the alloy (liquidus), i.e., 604°C. During this period the precursor starts foaming. In the second (holding) stage *T* is kept constant and the foam continues to expand. For sufficiently long holding times expansion reaches a nearly constant value if one ignores ever present fluctuations in the expansion graph due to the coalescence of bubbles. In the third stage heating is stopped by reducing heating or turning off the power supply and the foam starts shrinking and solidifying. In this communication only the cooling stage will be discussed.

It was mentioned before that the thermocouple is situated at the bottom of the sample. Therefore, only the temperature at the bottom of the surface can be measured. It is not possible to measure the temperature of the foam everywhere without disturbing the stability of the foam. Since the thermal conductivity of the foam is low it is expected that there is a reasonable temperature difference between the top and

bottom part of the foam¹⁰ but this can not be stated quantitatively. Although the end temperature in the temperature controller was fixed to 600°C, the temperature in the foam goes beyond the liquidus temperature of the AlSi6Cu4 alloy (604°C). This is shown later with the help of the derivative of the temperature curve.

3.2 Solidification

It can be seen in Fig. 1(a) that during cooling the foam starts shrinking and then at some point (*A*_{min}) it expands to a small extent (*A*_{max}) before shrinking again. This transient expansion is marked by a circle in the expansion curve. An enlarged view of the marked part is shown in Fig. 1(b). The effect is well visible and accounts for about 1.3% of the total foam expansion.

Figure 2 shows temperature and the first derivative of the cooling curve of the foam. The arrows marked on the cooling curve in Fig. 2 show three different events that represent the various phase formation temperatures in the AlSi6Cu4 alloy system. The first kink reflects nucleation of the primary α-aluminium phase, the second indicates formation of Al+Si eutectic and the third one shows the formation of the Al₂Cu phase¹¹. The occurrence of these three precipitation stages can be explained by the ternary Al-Si-Cu phase diagram. The temperatures of the three kinks (592°C, 530°C and 483°C respectively) read from Fig. 2 do not exactly agree with the temperature of formation of the mentioned phases as taken from the phase diagram. This can be explained by the temperature gradient explained above.

3.3 Possible reasons for the extra expansion effect

We shall briefly discuss possible explanations for the observed effect.

3.3.1 Recalescence effects

It is well known that precipitation of any phase from the liquid state requires nucleation sites. Pure systems contain a limited number of particles which act as nuclei. These particles have a poor nucleating potency and need a high degree of undercooling before they become active¹². Therefore, upon heat removal the temperature of any melt drops below its melting point before nucleation sets in and crystals start forming. As soon as the crystals have grown to a reasonable size, the latent heat liberated from the system

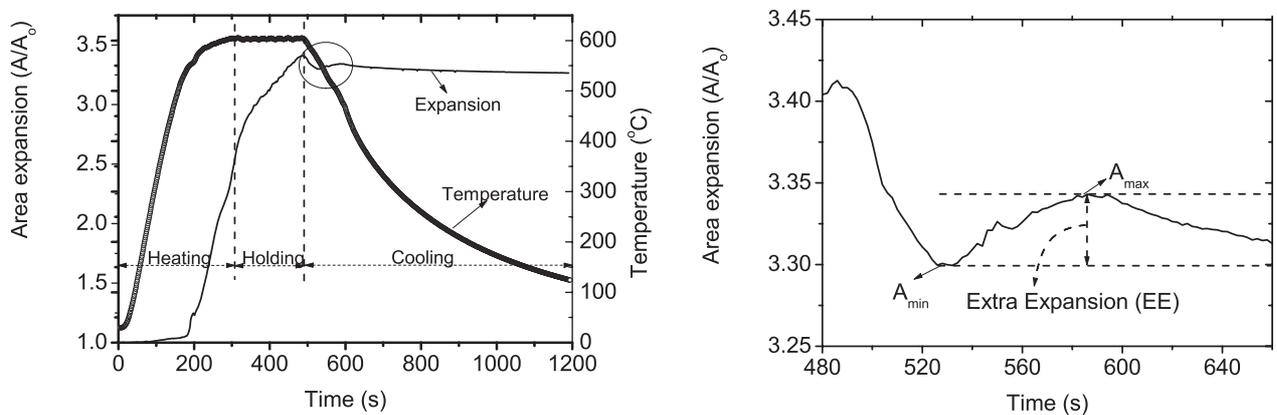


Fig. 1 : (a) Area expansion and temperature as a function of time for a AlSi6Cu4 alloy. (b) Enlarged view of the expansion graph's part marked by a circle in Fig. 1(a). Ambient cooling was applied and holding time is 200 s.

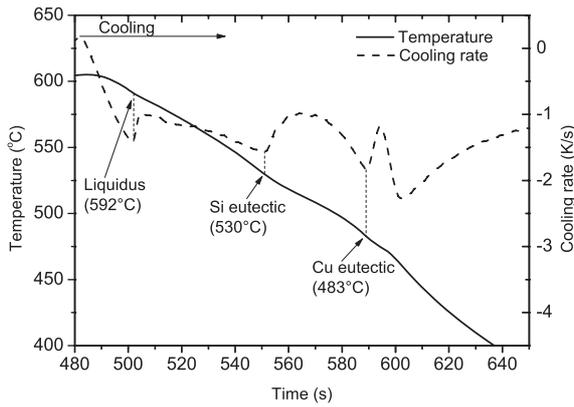


Fig. 2 : Cooling curve, first derivative and the representation of the precipitation of different phases during solidification of AlSi6Cu4+0.5wt%TiH₂ alloy. The temperature shown here corresponds to that in Fig. 1.

heats up the melt and brings the temperature of the whole system to the value corresponding to the actual state of crystallisation, an effect which is called *recalescence*. If such recalescence occurred in our foam the associated heating of the melt could both increase the volume of the gas present inside the bubbles or act on the remaining blowing agent in the alloy leading to a slightly increased production of gas. The alloy used in the present study cannot be considered as pure alloy because the powders used for making precursor sample always contain oxide layers around them¹³. Considering this it can be stated that heterogeneous nucleation is more likely to happen and as a result the amount of undercooling cannot be very high, typically less than 1K¹². This amount of undercooling would not be sufficient to explain the observed significant changes in foam volume.

3.3.2 Kinetic effects

Foam evolution during cooling can be considered a result of various processes, (i) shrinkage of the gas inside the foam due to the decrease of temperature and, (ii) gas losses due to diffusion or effusion out of the foam and, (iii) a decreasing rate of H₂ production by the blowing agent due to dropping temperatures and progressing discharge of the hydride¹⁴. Mechanism (i) depends on temperature only, while (ii) is almost purely a function of time and (iii) depends both on temperature and time. The volume of gas bubbles will therefore be given by:

$$V_k(t') = V^{(i)}(T) + \int_0^{t'} \left(\frac{\partial V^{(ii)}}{\partial t} + \frac{\partial V^{(iii)}}{\partial t}(T) \right) dt \quad (1)$$

where $T(t)$ is implicitly a function of time. Here, $V^{(i)}(T) \propto T$ if the gas is treated as ideal. The second term contains all gas losses and is always negative, while the third term is positive and tends to compensate such losses via generation of new gas. Whenever a foam is cooled steadily, $V^{(i)}(T)$ will slowly decrease assisted by $\partial V^{(ii)}/\partial t < 0$. $\partial V^{(iii)}/\partial t > 0$ will counteract but below a certain temperature cannot longer dominate. If however, the slope of cooling changes due to solidification processes gas production could gain importance against gas losses and lead to an intermediate expansion stage.

3.3.3 Anomalous solidification behaviour of silicon

Pure silicon expands as much as 10% during solidification¹⁵ and an analogous effect might be visible in Al-Si alloys. The volume fraction of silicon in AlSi6Cu4 alloy is approximately 7.1%. For an expansion factor of 3.5, the volume fraction of silicon in AlSi6Cu4 foam is approximately 2%. Therefore, on solidification of AlSi6Cu4 foam, the expansion contribution from silicon solidification can not be more than 0.2%. So, the presence of silicon in the foaming precursor sample can cause some volume expansion during foam solidification. Expansion of foam due to silicon solidification is based on hypothesis and without any detailed measurement it is not possible to state the exact value.

3.3.4 Hydrogen precipitation from the melt

There is a significant difference of hydrogen solubility in liquid and in solid metal or alloy. During solidification, the hydrogen is rejected from the liquid metal at the solid/liquid interface¹⁶. Therefore, solidification of any phase can result in an expansion of the foam. The contribution of the volume increment due to the precipitation of dissolved gas (V_{prec}) should be included in Eq. (1) to calculate the total volume of foam. So, the total volume of foam (V_{tot}) at any instant can be given by

$$V_{tot}(t') = V_k(t') + V_{prec}(T) \quad (2)$$

Using values for hydrogen solubility in AlSi6 one can calculate that the maximum EE which can be expected is of the order of 0.2%, but it might be higher considering the presence of 4 wt.%Cu.

Considering these four possible reasons of EE, reason (2) and (4) can be assumed the most likely reasons for EE. There is no direct evidence for reasons (1) and (3).

3.4 Discussion and further experiments

It has already been shown in Fig. 2 that there are three peaks in the first derivative of temperature. Therefore, considering reason (2) as the main factor of EE, three EEs are expected. Figure 1, however, only shows one EE. A possible reason could be that additional EEs are small or are superimposed on each other during comparatively fast ambient cooling.

Figure 3 shows the cooling part of the expansion graph of an experiment with 200 s holding time measured with a slower cooling rate than applied for the experiment shown in Fig. 1. The corresponding temperature is shown in Fig. 3. By cooling the foam with a slower cooling rate than the ambient cooling rate two EEs can be observed. In case of ambient cooling, the rate of foam shrinkage at the beginning of cooling is higher than the expansion of the foam due to the H₂ production. But when the shrinkage is reduced by decreasing the cooling rate then the production of H₂ shows an EE at the early stage of cooling. However, three EEs were not observed as it was expected. Possible overlapping of shrinkage and EE could be the reason. A *relative EE* (rEE) is calculated to compare the EEs of different experiments, defined by $rEE = 100 \times (A_{max} - A_{min}) / A_{min}$ (%). These quantities in Fig. 3 are $rEE_1 = 10.7\%$ and $rEE_2 = 0.95\%$. This can be explained by the production of more H₂ at the higher temperature (of EE 1) than the lower temperature (of EE 2).

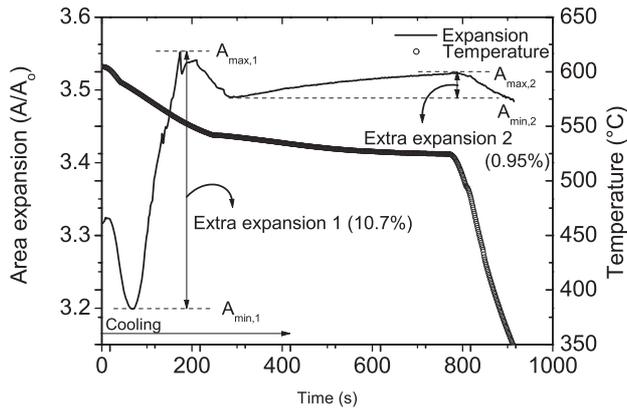


Fig. 3 : Area expansion against time for 200 seconds holding time and slower cooling rate than ambient cooling. It shows two extra expansions.

Production of gas from TiH₂ should decrease with increasing holding time because the amount of hydrogen available decreases¹⁴. A series of experiments were performed for different holding times to study its effect on EE. Figure 4 shows the rEE in such experiments. In the range of 0 to 200 s holding time, rEE increases. This could be explained by the time required for the activation of the whole TiH₂ present in the sample¹⁴. It can be seen that rEE is strongly dependent on holding time in the range of holding of 0 to 600 seconds. After that rEE becomes almost constant at the level of about 0.4%. This should not be the case if the production of H₂ decreases continuously with increasing holding time. Therefore some other factor can be thought to cause this constant effect in the range of 600 to 3000 seconds. Hydrogen precipitation from the liquid could be this effect.

Experiments were carried out with samples not containing any blowing agent to find out whether the blowing agent is the only controlling factor of EE. Precursors of AlSi6Cu4 alloy without blowing agent were foamed inside a pressure furnace as described in Sec. 2.3. Ambient cooling of these

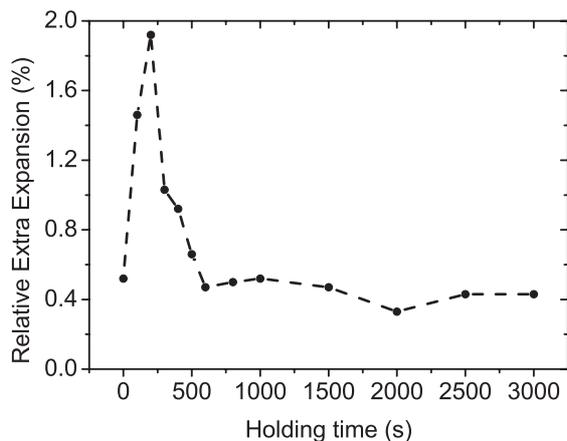


Fig. 4 : Relative extra expansion (rEE) for different holding times. All the experiments were done with ambient cooling. Solid circles show the measured value, the dashed line is drawn to show the trend.

foams did not reveal any EE. However, when they were cooled with a slower cooling rate than ambient cooling some EE could be observed. Experiments with 0, 50, 150 and 200 seconds holding time showed a rEE of 0.7, 0.7, 0.7 and 0.6%, respectively. Since there is no blowing agent present these expansions can only be associated with either the precipitation of dissolved gas during solidification or with an expansion due to silicon solidification (see 3.3.2) or with gas expansion in the pores.

Some experiments were also performed using samples of AlSi11+0.5wt%TiH₂. These samples showed no EE with ambient cooling but a small rEE of 0.2% with slower cooling. A sample of Al+0.5wt%TiH₂ did not show any EE for both ambient and slow cooling.

4. CONCLUSIONS

A small transient extra expansion (EE) was observed in the cooling stage of AlSi6Cu4 metal foams. A balance between production of H₂ associated with the decrease in the cooling rate due to precipitation of solid phases during solidification and gas losses was identified as probably the main influential factor of EE for foams containing blowing agents. Precipitation of dissolved hydrogen could be another factor. EE was also observed for samples foamed without any blowing agent. It was observed that the EE strongly depends on the holding time and cooling rate. EE was also observed to vary for different alloy systems. The complete picture is not clear and further investigations are required.

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