

Collapse of aluminium foam in two different atmospheres

M. Mukherjee^{1,2,*}, F. Garcia-Moreno^{1,2}, J. Banhart^{1,2}

¹Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz, 14109 Berlin, Germany

²Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

The foaming behaviour of aluminium in air and argon was compared by means of in-situ X-ray radioscopy. A faster collapse was observed in argon suggesting a greater loss of the blowing gas through out-diffusion caused by a thinner oxide layer at the surface of the samples compared to the samples foamed in air. This interpretation is further supported by calculations that show a correlation between the gas loss and the thickness of the oxide layer.

* Corresponding author: M. Mukherjee. Address: Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz, 14109 Berlin, Germany. Phone: +49 30 8062 2820. Fax: +49 30 8062 3059.

E-mail: manas.mukherjee@gmail.com

Metal foams can be manufactured by various methods, among which the powder metallurgical (PM) route is one of the most important ones because it allows for processing of a wide range of materials and component geometries. In this route, ambient pressure and atmosphere influence foam evolution.^[1-3] The effect of ambient atmosphere (oxidizing or inert) on foam expansion has been attributed to the mechanical resistance of the outer surface oxide layer that is created during foaming.^[1,2,4]

In aqueous foams, coarsening is governed by intercellular diffusion of gas: large bubbles grow at the expense of small ones.^[5] In contrast, coarsening of aluminium foams occur solely through coalescence^[3,6] as intercellular diffusion is negligible due to the low pressure difference

between adjacent bubbles and thick cell wall.^[6] However, at the outer surface that is in contact with the surrounding atmosphere, the conditions for diffusion can be quite different when hydrogen is allowed to be removed continuously as it is the case in industrial foaming practice where open furnaces are used. Then, the driving force for diffusion is high and as hydrogen has a significant diffusivity in liquid aluminium at 660 °C it can diffuse up to 10^{-3} m in only 10 s.^[7] This should imply that when the usual metal hydrides are used for foaming, significant loss of gas (hydrogen) to the surrounding takes place, resulting in a low expansion of the foam. The associated fast collapse of foams has actually never been reported: foams appear very stable in most cases, suggesting that diffusion is hindered. In the context of a general study of foam collapse^[8] the question was formulated whether out-diffusion can contribute to instability.

In this article we show experimentally that the foaming atmosphere does play an important role for the evolution of foam by influencing the gas loss rate, provided that foaming is carried out under very pure argon atmosphere. Foam expansion was monitored in-situ using X-ray radiography to detect even small changes in volume and internal structure. A calculation is carried out to check the results obtained. The collapsed structure of foams was also studied by X-ray tomography.

Aluminium (Al) powders (Alpoco, purity 99.7%) and titanium hydride (TiH₂) powders (Chemetall grade N, purity 98.8%), heat-treated at 480 °C for 180 min in air, were used to prepare foamable precursors. 30 g Al powder was mixed with 0.5 wt.% TiH₂ powder in a tumbling mixer for 15 min. The powder blend was uni-axially compacted in air for 5 min at 400 °C by applying 300 MPa pressure. Samples of dimension $10 \times 10 \times 4$ mm³ were cut out of the pressed tablets (36 mm diameter). The compaction direction was along the shortest side (4 mm) of the sample.

Foaming was carried out in an X-ray-transparent, gas-tight resistive heater furnace that allows for foaming under controlled pressure and gas atmosphere. The ceramic heating plate on which the samples are foamed has a maximum heating power of 600 W. The sample temperature is measured by a thermocouple which is led through the heating plate and protrudes 0.5 mm into the foaming sample from below. The measured temperature does not provide the actual temperature of

the sample but is higher, because the thermocouple is close to the heating zone. Therefore, a suitable furnace temperature was determined beforehand by using two thermocouples – one at the bottom surface (0.5 mm inside the sample) and another deep inside the sample. The furnace temperature 750 °C was such that the temperature inside the sample is just above the melting point of Al (660 °C).

Foaming was performed in two different gas atmospheres – air and argon (Argon 5.0). When using argon, the furnace was first evacuated to 1 mbar and was then back-filled with argon at 1 bar. This sequence was carried out four times before performing the foaming at 1 bar argon. For foaming under air, the precursor was simply heated in an ambient atmosphere and pressure (1 bar) in the gas-tight furnace. For both air- and argon-foaming identical heating profile were employed. The samples were heated to a maximum temperature of 750 °C in about 50 s. During heating pressure increased to about 1.2 bars. Thereafter, the temperature was kept constant for 600 s, after which the foam was solidified by natural cooling. After the flushing sequence mentioned above, the oxygen content of the gas inside the furnace was measured under argon flow at 1.2 bars; the value obtained was 2.8 ppm.

Foaming was continuously monitored in-situ using an X-ray radiography set-up which consists of a micro-focus X-ray source and a panel detector, both from Hamamatsu (Japan).^[2] A quantitative analysis of sample expansion was performed on the radiographic images with the dedicated software AXIM.^[9] Expansion is measured in terms of the growth of the X-ray projected area of the sample. X-ray tomography of solidified foams was performed using the same X-ray source but rotating the samples through 360 ° in 1000 steps while acquiring images after each step of rotation. Three-dimensional (3D) reconstruction of the samples was performed using the commercial software ‘Octopus’.

Evolution in terms of area expansion and temperature profile of the samples is shown Figure 1, where each curve represents the average of two equivalent measurements. About 40 s after heating, rapid expansion can be observed. Up to maximum expansion, the behaviour of both

foams is similar. The argon-foamed sample shows a slightly higher expansion. After reaching maximum expansion, both foams show progressive collapse, i.e., a decrease in area and therefore volume. The collapse is higher for the argon-foamed sample than for the air-foamed one. For example, the time taken for 50% reduction in area after expansion to maximum is 218 and 514 s for argon- and air-foaming, respectively. The surface of the solidified foams showed wrinkled surfaces in all cases.

Tomographic reconstructions of a solidified sample from each group are shown in Figure 2. The higher amount of collapse in argon-foamed samples is obvious. In Figure 2(a) at the top, some individual cells can be seen that still exhibit fully convex cell walls as indicated by white solid arrows. At the bottom, a collapsed structure is seen. Some cells appear flat as indicated in Figure 2. While for the air-foamed sample, opposing faces of these flat cells are separated, opposing faces are almost in contact with each other in argon-foamed samples revealing a laminated structure. The outer contour of the foams is irregular in all cases, the strongest effect found in argon-foamed samples, see white dotted arrows.

As melting begins and the temperature rises, the foams expand rapidly because of the increasing gas production rate, expansion of pre-existing gas and less resistance by the matrix as the fraction of liquid phase increases. During isothermal holding and after complete melting, the expansion rate is influenced mainly by two phenomena: continuing hydrogen production from TiH_2 and losses, probably through a mechanism such as out-diffusion of hydrogen. In addition, if an outer surface bubble ruptures, a sudden drop in volume can occur. The smooth appearance of the expansion curve suggests that there is no such significant rupture at the outer surface. This was also verified from the radiosopic image sequence. Up to peak expansion, gas production dominates over gas loss. Beyond that, the rate of gas loss is always higher than gas production for the rest of the isothermal stage.

The rate of gas loss is estimated in the following way by representing the foam as a single spherical bubble. This is justified as gas can only be lost through the outer surface and foams in the

fully expanded condition appear nearly spherical. If a dynamic equilibrium condition of diffusion is assumed, the volume loss rate can be estimated by applying Fick's first law. After an initial transient, the volume loss rate of this bubble (foam) is easy to calculate, as the hydrogen concentration from a value C on the inner side of the bubble wall to the value 0 on the outer side where the escaping hydrogen is removed varies almost linearly. One obtains:

$$\frac{dV}{dt} = D_{H \rightarrow Al} \cdot \frac{C}{d_{Al,t}} \cdot A. \quad [1]$$

Here, V and A represents the volume and outer surface area of the bubble, respectively. $d_{Al,t}$ is the cell wall thickness at any instant t and $D_{H \rightarrow Al}$ is the diffusion coefficient of hydrogen in Al. C represents the concentration at the inner surface of the bubble wall. This is equal to the equilibrium solubility of hydrogen in Al, S_{Al} . The rate of change of radius of the bubble can be obtained from Eq. [1] by replacing V and A by their value in terms of the radius. Further simplification leads to the following equation

$$\frac{dr_t}{dt} = \frac{D_{H \rightarrow Al} \cdot C}{d_{Al,t}}. \quad [2]$$

Here, r_t is the inner bubble radius at any instant t .

Although the volume of the bubble decreases, the volume of the metal in the cell wall remains constant. If the initial cell wall thickness and inner radius of the bubble are $d_{Al,0}$ and r_0 , respectively, then at any instant t , the cell wall thickness and inner radius is given by the following equation

$$\frac{4}{3}\pi[(r_0 + d_{Al,0})^3 - r_0^3] = \frac{4}{3}\pi[(r_t + d_{Al,t})^3 - r_t^3]. \quad [3]$$

As $d_{Al,t} \ll r_t$, we can write

$$d_{Al,t} = \frac{r_0^2}{r_t^2} \cdot d_{Al,0}. \quad [4]$$

Combining Eqs. [2] and [4], we obtain

$$\frac{dr}{r_t^2} = \frac{D_{H \rightarrow Al} \cdot C}{r_0^2 \cdot d_{Al,0}} \cdot dt. \quad [5]$$

If from time $t=0$ to time $t=t'$, the radius r_t changes from r_0 to r' , then integration of Eq. [5]

yields

$$t' = \frac{(r_0 - r') \cdot r_0 \cdot d_{Al,0}}{r' \cdot D_{H \rightarrow Al} \cdot C} \quad [6]$$

$D_{H \rightarrow Al}$ at 660 °C is $3.2 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$ [10], a typical value of d_{Al} is 100 μm . A spherical foam with 320% area expansion (the maximum expansion of the argon-foamed sample in Figure 1), has a radius of 7.3 mm considering the present precursor dimensions. It has already been mentioned that $C = S_{Al}$. At 660 °C and 1 bar pressure, S_{Al} is 0.63 $\text{cm}^3/100 \text{ g Al}$ [11], with the gas volume referring to 300 K. As foaming takes place near the melting point of Al (933 K), the actual gas volume is $(933 \text{ K}/300 \text{ K}) = 3.11$ times higher. The density of liquid Al at 660 °C is $2.368 \text{ g} \cdot \text{cm}^{-3}$ [7]. So, the effective S_{Al} is about $0.05 \text{ cm}^3/\text{cm}^3$ of Al.

At first we study a case of 50% reduction in maximum area expansion value (equivalent to \approx 65% reduction in volume). The radius scales with $\sqrt{A_p}$, where A_p is the projected area of a sphere. Therefore, the initial radius $r_0 = 7.3 \text{ mm}$ is reduced to $r' = r_0/\sqrt{2} = 5.2 \text{ mm}$. The required time, t' , to reach this state is 19 s according to Eq. [6], but about 218 and 514 s for argon- and air-foamed samples according to Figure 1. The observed times are one order of magnitude higher than the calculated one.

The much lower observed collapse rate is because of the presence of oxide (alumina) layers on the surface of the foams. This oxide layer acts as an additional barrier against out-diffusion of hydrogen. The situation inside the foam is the same both for argon- and air-foamed samples as the cells are filled with hydrogen in both cases. But when foaming in air, the outer surface of the foam is oxidized. However, even for foaming under technically pure argon, oxidation of the outer surface cannot be prevented.^[4] According to the Ellingham-Richardson diagram, the partial pressure of

oxygen must be below 10^{-50} bar to stop oxidation of Al.^[12] The argon gas used in this study contains 2.8 ppm oxygen, which is sufficient for oxidation. Nevertheless, the oxide layer is thinner (e.g. 12 nm in the absence of air compared to 36 nm in the presence of air^[13]) in the case of argon-foaming. This leads to a slightly higher expansion (7% in Figure 1) in argon-foamed samples than in air-foamed ones as shown in Figure 1 as the foams experience less resistance from the thinner oxide layer.^[4]

For pure Al, the oxide film is initially amorphous alumina which eventually transforms into crystalline phase.^[7] The diffusion coefficient ($D_{H \rightarrow Al_2O_3}$) of hydrogen in alumina at 660 °C is about $3.2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ ^[14], which is five orders of magnitude lower than that in liquid Al. This suggests that the main determining factor is the diffusion through the outer surface oxide layer.

At steady state, the flux per unit area through the cell wall (Al) is equal to that through the oxide layer, see Figure 3. This can be written as

$$D_{H \rightarrow Al} \cdot \frac{C - C_{\text{int}}}{d_{Al}} = D_{H \rightarrow Al_2O_3} \cdot \frac{C_{\text{int}}}{d_{Al_2O_3}}. \quad [7]$$

Here d_{Al} and $d_{Al_2O_3}$ are the thickness of the Al and alumina layer in the cell wall, respectively. C_{int} is the hydrogen concentration at the interface of Al and alumina. Boundary conditions are $C = S_{Al}$, $C_{\text{int}} < S_{Al}$ and $C_{\text{int}} \leq S_{Al_2O_3}$, where $S_{Al_2O_3}$ is the equilibrium solubility of hydrogen in Al_2O_3 . The concentration at the outer surface of alumina layer is assumed to be zero in Eq. [7]. In terms of effective volume, as explained earlier, the solubility of hydrogen in alumina at 660 °C is $\approx 0.05 \text{ cm}^3$ of H/cm³ of Al_2O_3 ^[15]; accidentally this is same as in molten Al. Leitmeier et al. measured the thickness of the oxide formed on Al alloy foams produced by gas injection: 12 and 36 nm for nitrogen- and air-blown, respectively.^[13] Accordingly, we assume that the oxide thickness in the present foams is 12 and 36 nm for the argon (inert like nitrogen) and air-foaming. Using these values in Eq. [7], C_{int} is 0.0462 and 0.0486 for argon- and air-foamed samples, respectively. The modified gas loss can be calculated by considering the hydrogen flux through either of the layers, i.e., either through Al or through Al_2O_3 . To estimate the flux through the Al, the concentration C in

Eq. [6] should be replaced by $(C - C_{int})$. Accordingly, the collapse in both atmospheres was calculated from Eq. [6] and plotted in Figure 1. The calculation was performed for an isothermal condition at temperature 660 °C. In the initial stages of collapse, the calculated curve follows the measured one quite closely for both foaming. At later stages, while in the case of air-foaming the calculated collapse gradually deviates from the measured one, in the case of argon-foaming the deviation is rapid after 50–60% reduction in the area. Going back to the case of 50% reduction in area, in the presence of oxide layer the times required are about 249 and 674 s for the argon- and air-foamed samples, respectively. This is quite close to the observed times.

In the calculation, a spherical geometry is assumed during collapse of the foam. This is valid only if the outer surface contains pure metallic melt. In the presence of an oxide layer, the outer surface becomes more rigid, and therefore does not shrink in proportion.^[1] As a result, the stretched shape of the outer surface transforms into a wrinkled one as becomes obvious from Figure 2. Thus, the surface area is larger than that of an equivalent sphere. This results in higher rate of out-diffusion than the calculated rate, and could be one reason for the discrepancy between measurement and calculation. A reliable estimate of the corrugated surface area is impossible. Since the collapse is faster in argon, at a given time during collapse the surface of the argon-foamed sample is more wrinkled than the surface of the air-foamed sample. That is why for the same foaming period the surface of the argon-foamed samples shows more wrinkles, see Figure 2. Consequently, the deviation between measurement and calculation also grows faster for argon-foaming than for air-foaming.

There are other factors that could also give rise to the observed discrepancy. (i) Obviously, the oxide thickness assumed does not correspond to the actual samples measured (different oxide thicknesses have been reported^[4]) and (ii) in the calculation, a constant thickness of the oxide layer is considered although in reality it should increase with time.^[7] Hence, at the beginning, out-diffusion is likely to be faster due to a relatively thinner oxide layer. (iii) During growth of foam, the outer surface oxide layer continuously breaks and new oxide layer forms.^[16] The newly formed

layers are thinner and therefore a higher out-diffusion is possible through them. (iv) The diffusivity of hydrogen in alumina could be higher in reality, and so the out-diffusion. Extrapolation of high temperature data (obtained above 1273 K ^[14]) to 660 °C is a rather crude estimate. (v) Some foam collapse can also be caused by mechanical forces, e.g. hydrostatic pressure. The internal gas pressure of the foam has to overcome the hydrostatic pressure resulting from the weight of the metal. Hydrostatic pressure increases towards the bottom of the foam. Consequently, the bottom part of the foam collapses more than the upper part as can be seen in Figure 2. While (ii) to (v) should increase the collapse rate, the ongoing (but at decreasing rate) production of hydrogen by the blowing agent tries to counteract the collapse to some extent.

Altogether, the very good agreement, at least in the initial stages of collapse, between calculation and experiment appears partially accidental but indicates the correct order of magnitude.

Gas loss due to diffusion does contribute to foam collapse and depends a lot on the surrounding atmosphere. Whenever calculating the expansion or collapse behaviour of metal foams both the mechanical influence and the influence on gas diffusion of the outer oxide layer has to be taken into account.

We thank Andreas Benz for his help with X-ray tomography. The discussions with Carolin Körner, Catalina Jiménez and Hans Martin Helwig are gratefully acknowledged.

1. F. Simancik, K. Behulova, and L. Bors: in *Cellular Metals and Metal Foaming Technology*, J. Banhart, M.F. Ashby, and N.A. Fleck, eds., MIT - Verlag, Bremen, Germany, 2001, pp. 89–92.
2. F. Garcia-Moreno, N. Babcsan, and J. Banhart: *Coll. Surf. A*, 2005, vol. 263, pp. 290–94.
3. C. Körner, M. Arnold, and R.F. Singer: *Mater. Sci. Eng. A*, 2005, vol. 396, pp. 28–40.
4. A. Dudka, F. Garcia-Moreno, N. Wanderka, and J. Banhart: *Acta Mater.*, 2008, vol. 56, pp. 3990–4001.
5. D. Weaire, and S. Hutzler: *The Physics of Foams*, 1 st ed., Oxford University Press, Oxford, United Kingdom 1999, pp. 88–101.

6. J. Banhart, H. Stanzick, L. Helfen, and T. Baumbach: *Appl. Phys. Lett.*, 2001, vol. 78, pp. 1152–54.
7. J. Campbell: *Castings: The New Metallurgy of Cast Metals*, 2 nd ed., Butterworth-Heinemann, Oxford, United Kingdom, 2003, pp. 188, 206, 147–148.
8. M. Mukherjee: PhD Thesis, Technische Universität Berlin, Berlin, 2009, pp. 54–56.
9. F. Garcia-Moreno, M. Fromme, and J. Banhart: *Adv. Eng. Mater.*, 2004, vol. 6, pp. 416–20.
10. W. Eichenauer, and J. Markopoulos: *Z. Metallkunde*, 1974, vol. 65, pp. 649–52.
11. P. Lutze, and J. Ruge: *Metall*, 1990, vol. 8, pp. 741–48.
12. D.R. Gaskell: *Introduction to the Thermodynamics of Materials*, 4 th ed., Taylor and Francis, New York, USA, 2003, pp. 359.
13. D. Leitmeier, H.P. Degischer, and H.J. Flankl: *Adv. Eng. Mater.*, 2002, vol. 4, pp. 735–40.
14. E. Serra, A.C. Bini, G. Cosoli, and L. Pilloni: *J. Am. Ceram. Soc.*, 2005, vol. 88, pp. 15–18.
15. S.K. Roy, and R.L. Coble: *J. Am. Ceram. Soc.*, 1967, vol. 50, pp. 435–36.
16. E. Solorzano, M.A. Rodriguez-Perez, F. Garcia-Moreno, N. Babcsan, and J. Banhart: in *Porous metals and metallic foams*, L.P. Lefebvre, J. Banhart, and D. Dunand, eds., DEStech Pub., Pennsylvania, USA, 2008, pp. 79–82.

Figure captions

Fig. 1–Expansion and collapse behaviour of aluminium foams in air and argon atmosphere. Each curve (*measured*) is the average of two experiments. The temperature profile, shown for only one experiment, is almost identical in all the experiments. For each atmosphere, theoretical collapse (*calculated*) from the maximum expansion was estimated based on gas loss due to out-diffusion from the foams. Arrows in the measured curves point to a value of 50% of the maximum expansion.

Fig. 2–X-ray tomographic reconstruction of the (a) air- and (b) argon-foamed samples solidified after the end of foaming. Images show 2D sections along the foaming direction. Hollow arrows indicate almost flat cells, white dotted arrows indicate wrinkles in cell walls. White solid arrows show cell walls that are stretched.

Fig. 3–Illustration of the hydrogen flux through the metallic and oxide part of a cell wall and the concentration at different places.





