

# Effect of Relative Humidity on Pressure-Induced Foaming (PIF) of Aluminium-Based Precursors

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## ABSTRACT

Pressure induced foaming (PIF) is a novel technique which provides the possibility of foaming precursors prepared from powders without any addition of blowing agent. Along the manufacturing route the powders are exposed to relative ambient humidity (rH) during storage and compaction. Interaction during storage was studied using mass spectrometric (MS) analysis and heavy water ( $D_2O$ ) as a tracer on Al, Si, and  $Al_{12}Mg_{17}$  powders. It was found that after exposure to 75% rH for 21 days at room temperature the water and hydrogen content in the powders is increased. A mixture of as-received powders was prepared to yield an AlSiMg alloy. The mixture was then used to hot-press compacts under three different atmospheres: air, vacuum and 75% rH. MS analysis of the three kinds of compacts demonstrated that ambient humidity also interacts during compaction. The most relevant effect is that a humid atmosphere during compaction increases the hydrogen amount available for foaming. PIF experiments on the different compacts are consistent with the MS results. Compacts hot-pressed under vacuum yielded an area expansion factor of 1.6 and the most uniform pore structure. Compacts exposed to 75% rH during compaction produced an area expansion factor of 3.5 and the least uniform pore structure. For those compacts, big pores were formed as the result of cracking during early stages.

## INTRODUCTION

The powder metallurgical (PM) route to prepare aluminium-based foamable precursors consists of mixing metal powders and blowing agent, usually pre-oxidized  $TiH_2$ . After this, the mix is hot pressed in air, yielding a dense compacted precursor. Finally the foaming process is initiated by heating the precursors. PIF is a novel technique which provides the possibility of foaming compacted precursors without the need of an additional blowing agent, such as  $TiH_2$  [1]. PIF

consists of melting the precursor under gas overpressure to keep gas losses small. Then, foaming is induced by releasing the overpressure back to ambient pressure. To identify gas sources during PIF was one of the motivations for this study [2]. A second motivation is related to the effect that rH could have on the reproducibility of PM compacts foaming. However, in the PM route  $TiH_2$  has the dominant role during foaming and obscures the effect of additional humidity. This is the reason to carry out investigations in PIF experiments rather than foaming standard PM precursors.

It is well known that water in contact with the protective oxide layer of aluminium is adsorbed and forms hydroxides [3]. During thermal treatments,  $H_2O$  and  $OH^-$  ions are reduced by reaction with Al and Mg to form atomic hydrogen [4]. Hydrogenation of  $Al_{12}Mg_{17}$  results in  $MgH_2$  formation along grain boundaries [5]. The gas content in compacted precursors has to be taken into account for foaming, especially if the release takes place at temperatures below melting. In the manufacturing process of foamable precursors the powders are usually exposed to ambient humidity during storage and compact preparation. In this work the effect of relative humidity on the pressure induced foaming behaviour of Al-based precursors is presented.

## EXPERIMENTAL

Al (Alpoco Ltd., 99.7% purity,  $D_{90} = 75.50 \mu m$ ), Si (Alchem Ltd., 99.5% purity,  $D_{90} = 49.98 \mu m$ ) and  $Al_{12}Mg_{17}$  ( $D_{90} = 72.14 \mu m$ ) powders were used for this study. Loose powders were introduced in an exsiccator and exposed to 75% rH of  $D_2O$  (in saturated solution with NaCl) for 21 days at room temperature. rH was measured in the exsiccator by using a wire hygrometer. MS analysis was performed on powders exposed to  $D_2O$  and as-received ones. For MS analysis, 140 mg of each sample were heated up from 25 °C to 650 °C,

10 K/min under N<sub>2</sub> flow. D<sub>2</sub>O instead of H<sub>2</sub>O was used to distinguish between contributions from water being previously in the powders or in the furnace used for the MS analysis, and water absorbed by the powder during our treatments.

The three powders were mixed to yield a AlSiMg alloy. 30 g of mixed powders were pre-pressed to a 36 mm diameter compact at room temperature at 300 kN, and were then uni-axially hot-compacted at 400 °C, at the same load for 5 minutes. Heating from room temperature to 400 °C took 30 min. The compacts were prepared in three different atmospheres. The first kind of compact, designated as “A”, was prepared with the mixture of powders that were previously exposed to 75% rH of D<sub>2</sub>O for 21 days. This powder blend was pre-pressed and hot-pressed in air. The second and third kinds of compact were pressed in controlled atmospheres in a chamber specially designed to be mounted in the press. It was provided with connections to evacuate or to introduce gas. Other connections permitted to control in-situ, temperature, gas pressure and rH. A hole of 3.5 mm diameter was made through the die wall. The hole connected powder and atmosphere while the two open ends of the die were closed by the punches. The second kind of compact, designated as “V”, was prepared using as-received powders which were pre-pressed and hot pressed under mechanically pumped vacuum. The third kind of compacts, designated as “C”, was prepared by first evacuating the chamber and then introducing D<sub>2</sub>O vapour until 75% rH level was reached at room temperature. The vapour was introduced directly inside the die using a tube of 3 mm outer diameter. Eventually the vapour streamed out of the die into the chamber through the gap left between tube and die-hole. Pre-pressing and hot-pressing were therefore performed under D<sub>2</sub>O 75% rH. MS experiments were carried out

on 180 mg of shavings prepared from the three kinds of compacts. Heating of 10 K/min from 25 °C up to 650 °C under N<sub>2</sub> flow was applied. Shavings were used instead of compacts since they release gas more easily.

8×8×4 mm<sup>3</sup> large samples were cut from each compact for PIF experiments. They were melted under 10 bar of Ar while heating up to 640 °C within 30 s. After 90 s, the overpressure was released to ambient pressure and PIF took place. The heating element was turned off simultaneously. The temperature was measured with a thermocouple in contact with the compact at the bottom part. PIF experiments were performed in an X-ray transparent chamber so that foaming could be monitored in-situ by radioscscopy. A micro focus X-ray source (spot size 5 μm, 100 kV, 100 μA) and a flat panel detector (120×120 mm<sup>2</sup>) were used. Cross-sectional foam expansion was determined using the self-developed image analysis software AXIM [6].

## RESULTS AND DISCUSSION

### Effect of ambient humidity during storage

Fig. 1 presents the MS analysis on powders for the atomic masses of interest. Ion currents are detected by the quadrupole mass spectrometer. Ion current as a function of temperature is proportional to the thermal desorption rate for each mass. Fig's 1(a), 1(b) and 1(c) correspond to the as-received condition, whereas Fig's 1(d), 1(e) and 1(f) correspond to 21 days of exposure to 75% rH D<sub>2</sub>O. Mass 2 corresponds to H<sub>2</sub><sup>+</sup> or D<sup>+</sup> ions. In the as-received condition, mass 2 corresponds mainly to H<sub>2</sub><sup>+</sup> ions. After exposure to D<sub>2</sub>O, H<sub>2</sub><sup>+</sup> and D<sup>+</sup> ions contribute to mass 2. Mass 3 corresponds to DH<sup>+</sup> ions and mass 19 to DHO<sup>+</sup> ions. There is no significant background superimposed on

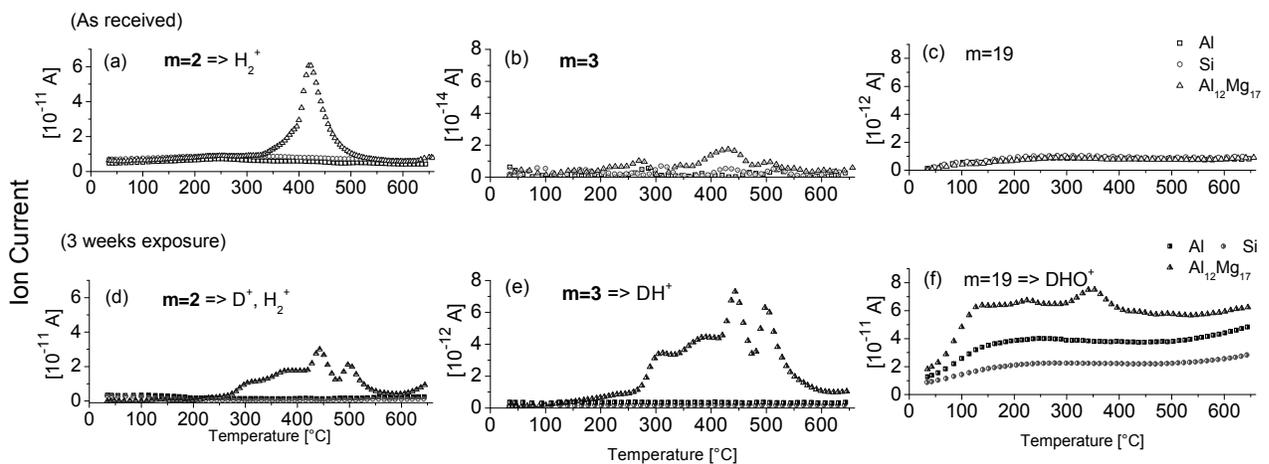


Figure 1. Mass spectrometry results of masses 2, 3, and 19 as a function of temperature for Al, Si and Al<sub>12</sub>Mg<sub>17</sub> powders, comparing as-received and 21 days exposure conditions. (a), (b) and (c) correspond to the as-received condition whereas (d), (e) and (f) correspond to 21 days of exposure to 75% rH (D<sub>2</sub>O) condition.

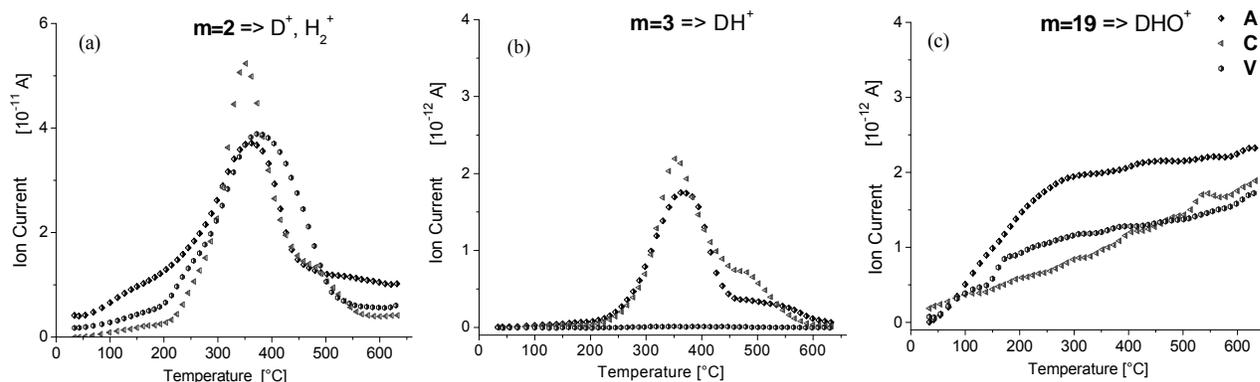


Figure 2. Mass spectrometry results of masses 2, 3, and 19 as a function of temperature for shavings prepared from compacts hot-pressed under three different atmospheres. Symbols are labelled A, C and V according to the three atmospheres used which were previously described in the experimental paragraph of this work.

these mass signal – as shown in Fig’s 1(b) and 1(c) – which validates the use of  $D_2O$  as a tracer. Hence, masses 3 and 19 become the appropriate ones to represent the interaction between  $D_2O$  and powders. In the as-received condition,  $H_2$  released from  $Al_{12}Mg_{17}$  powder is the primary gas source, Fig. 1(a).  $H_2$  release has an onset at  $330\text{ }^\circ\text{C}$  and a peak at  $423\text{ }^\circ\text{C}$ . After 21 days of exposure to 75% rH, masses 3 and 19 increase by 2 and 1 order of magnitude, respectively. Gas released from  $Al_{12}Mg_{17}$  corresponding to mass 3 starts slightly above  $100\text{ }^\circ\text{C}$ . The first important onset for masses 2 and 3 is at  $275\text{ }^\circ\text{C}$ . The temperature desorption range broadens and gas evolution is divided into more peaks. This change in the gas evolution behaviour is not yet fully understood in the frame of these experiments. However it is reported that  $MgH_2$  is formed along grain boundaries of  $Al_{12}Mg_{17}$  after hydrogenation [5]. Exposure to water vapour seems to hydrogenate  $Al_{12}Mg_{17}$  powder. Mass 19, representing water adsorbed and chemisorbed, indicates that all the three powders react with ambient humidity during storage.  $Al_{12}Mg_{17}$  interacts more strongly than Al and Si. Water is released at lower temperature than hydrogen from powders exposed to humid atmosphere.

### Effect of ambient humidity during compaction

The mass spectrometric analysis performed on shavings corresponding to compacts A, C and V is presented in Fig. 2. For compact V, mass 2 corresponds in Fig. 2(a) basically to  $H_2$  since the powders used have not been exposed to heavy water. This is the reason for compact V to show no peak for mass 3 in Fig. 2(b), at least compared to the other two compacts. In the case of compacts A and C, mass 3 corresponds to  $DH^+$  ions. This signal for compact A indicates that gas uptake during previous exposure to humidity is not eliminated during hot compaction. Correspondingly,  $DH^+$  ion signal for compact C indicates that ambient humidity during compaction results in gas uptake as well. Mass

19, in Fig. 2(c), corresponds to  $DHO^+$  ions. For the three compacts, the desorption behaviour is rather similar, which is particularly unexpected for compact V.

### Effect of ambient humidity during PIF

PIF behaviour of the three compacts is represented in Fig. 3(b) in terms of area expansion as a function of time. Several experiments were performed using the same temperature profile for each kind of compact. The foaming behaviour and resulting structures are similar for each kind of compact. Therefore, only one representative expansion curve was plotted for each compact, to keep the graph simple. In Fig. 3(a), three sets of radioscopic images, representing 34 s, 90 s and 190 s, reveal cracking events, the formation of big bubbles and the resulting pore structure. The highest area expansion factor of 3.5 after 90 s was obtained for compact C, followed by 2.8 for compact A, and finally 1.6 for compact V. Pore structure in terms of uniformity ranked in the opposite way. Pore structure resulted to be the most uniform with smallest pores for compact V, followed by compact A with bigger pores than in V and bigger pores at the bottom within itself. The least uniform pore structure was obtained for compact C.

For compact C cracks were formed during heating. They can be observed for the first time in the radioscopic images after 30 s, although they probably had developed before due to early gas overpressure in the compacts (see Fig. 3(a), sample C). Despite the overpressure the metal matrix relaxes internal pressure by cracking, rendering later a non-uniform structure in form of big pores. As temperature increases, too much gas is eventually released and the material has no longer enough strength to hold the expanding gas. On the one hand, hot-pressing under vacuum enhances consolidation compared to a humid atmosphere. And on the other hand, humidity increases the gas content in

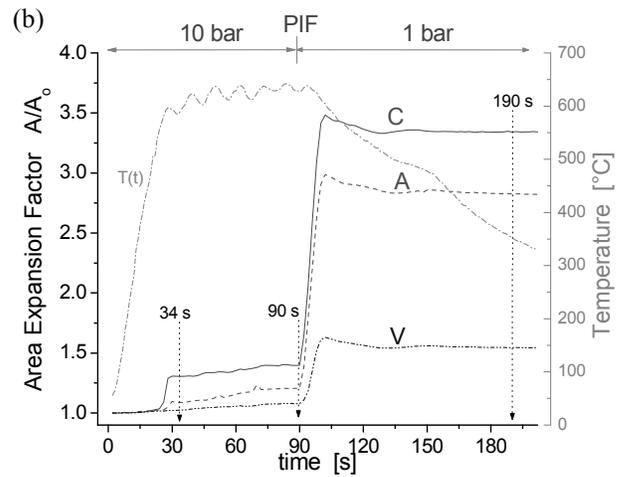
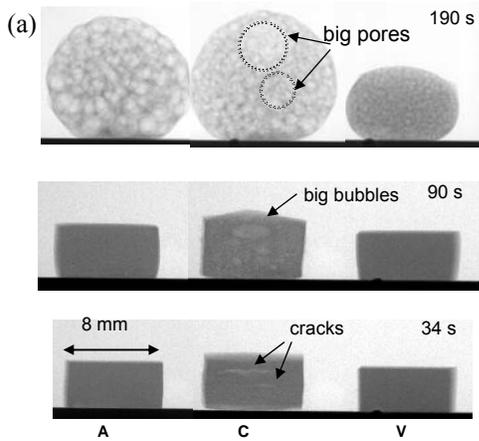


Figure 3. Pressure induced foaming of compacts A, V and C. Area expansion is presented as a function of time. At 90 s, the pressure is released from 10 to 1 bar. The three picture sets show particular events occurring during PIF namely, cracks at 34 s, big bubbles at 90 s just before releasing over pressure, and the resulting pore structure after 190.

the compacts, leading e.g. to higher expansion. A higher expansion is equivalent to a lower density, which is a desirable property. However a uniform pore size distribution is needed as well.

For MS experiments performed at ambient pressure on shavings, the peak corresponding to masses 2 and 3 is slightly above 350 °C and gas evolution is observed up to melting. For PIF, a much higher heating rate (~1200 K/min), overpressure and compacts instead of shavings were used, which of course delay gas evolution. Hence, MS and PIF experiments are consistent.

After melting, the cracks turned into big bubbles which are shown at 90 s just before the overpressure was released resulting in the least uniform pore structure. The results indicate that H<sub>2</sub> drives pressure-induced foaming of these three kinds of compacts. Relative ambient humidity, especially during compaction seems to increase the H<sub>2</sub> amount in the compacts available for foaming. Further investigation has to be carried out varying the rH level in the chamber during hot pressing. Particularly interesting would be to simplify the system preparing pure aluminium compacts.

## SUMMARY

The results demonstrated that relative ambient humidity interacts with the powders during storage and compaction. The relevant consequence of such interaction for foaming is an increase in the amount of hydrogen in the compacts which is released below melting. Pressure induced foaming of these compacts is driven by H<sub>2</sub> release. Compacts hot pressed under vacuum resulted in the most uniform pore structure and the lowest area expansion factor around 1.5. Compacts exposed to humidity during hot compaction reached the maximum expansion factor around 3.5, but the less

uniform pore structure. For this compact, cracking events occurred below melting. Above melting those cracks became big bubbles and pores subsequently.

## ACKNOWLEDGEMENTS

Support by DFG is gratefully acknowledged. Eusebio Solórzano, Holger Kropf and Christian Abromeit helped to overcome experimental difficulties, preparing countless samples, and giving generous scientific advice.

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