

Coloring of Pure Zinc Foams

Jaroslav KOVÁČIK*, Jaroslav JERZ, František SIMANČÍK, Natália MINÁRIKOVÁ

Institute of Materials and Machine Mechanics SAS, Dúbravská cesta 9, 845 13 Bratislava, Slovakia

*corresponding author, e-mail: ummsjk@savba.sk

Keywords: Foams, metallic foams, zinc foams, foaming agent, colouring

Abstract. The zinc foams were prepared by powder compaction method with various types (TiH_2 or MgH_2) and various amount (0.3, 0.6 and 1 wt.%) of foaming agent to investigate the effect of colouring of zinc foams during foaming process. It was observed that due to Archimedes' principle foaming agent particles with lower density as liquid zinc float over a liquid. As a result, on the foam outer skin they react with oxygen during cooling of the foam. Therefore, the significant colouring (purple, blue and dark blue) of pure zinc foams prepared using TiH_2 foaming agent was observed. On the contrary, MgH_2 decomposes almost completely during the foaming process of zinc. As a result Mg is either dissolved in zinc foam ($\text{Mg}_2\text{Zn}_{11}$) or MgO of white colour is created. Therefore no significant colouring of pure zinc foams was observed in this case.

1. Introduction

It is well known, that foam cannot be prepared from pure liquid because the bubbles within the liquid would rise to the surface and collapse almost immediately. Thus to generate any foam it is necessary to stabilize the melt-bubble solution. There are various ways how to do it: To reduce melt surface tension, to increase melt viscosity, and/or to create electrostatic forces within melt [1].

Everything, besides electrostatic forces (zinc is good conductor), applies also for zinc. The only parameter different from usual aqueous foams is temperature - pure zinc has melting temperature of 419.6 °C. Therefore, various types of the additives, that affect melt viscosity and surface tension, are required to operate as stabilizers to create metallic foam. The type and amount of additives depends predominantly on the preparation method of metallic foam. There are two basic types of foam preparation: Melt route and powder compaction method [2].

Melt route foam preparation uses typically 10 – 20 wt.% of ceramic particles such as Al_2O_3 or SiC to stabilise aluminium foam. They are usually admixed to molten metal prior foaming. Foaming gas is applied inside molten metal from ceramic nozzle under certain pressure. Nitrogen or air is usually used as a foaming gas. The created foam is conveyed from liquid surface and cooled to freeze foam structure.

On the contrary, foams prepared by powder compaction method (used in this study), are stabilised predominantly thanks to the oxides filaments [3, 4]. They originated from the surface oxide layer of metal powders used for the preparation of foamable precursor (mixing of powders, compacting, and hot extrusion). Further, alloying elements in metal can play also stabilising role

because they affect locally viscosity and surface tension of the melt. In this case foaming gas (usually hydrogen or calcium carbonate) is evolved subsequently directly inside of the foamable precursor. To create foam, precursor ought to be heated up to melting temperature of matrix metal/alloy.

Zinc foams are usually prepared by powder compaction method. To foam zinc MgH_2 , TiH_2 or ZrH_2 are often used as a foaming agent [5 - 9]. Very often colouring of zinc foams is observed after foaming process. Thus, the aim of this work is to investigate the effect of the type and amount of foaming agent on the colouring of pure zinc foams.

2. Experiment

The zinc foams were prepared by powder metallurgy [10]: Pure Zn powder (Chemetall GmbH, Germany, density 7.1 g.cm^{-3} , melting point 419.6°C) were mixed with a foaming agent (Chemetall GmbH, Germany, TiH_2 or MgH_2) powder of various amount (0.3, 0.6 and 1 w.%). Then the mixture was cold compacted into billets by cold isostatic pressing and then hot extruded at 230°C into a foamable precursor. The resulting porosity of foaming precursor was below 1%.

The foaming trials with foamable zinc precursors were performed in cylindrical mould of the diameter of 40 mm x 50 mm and at various foaming temperatures up to 500°C . The equipment enables independent control of the foaming temperature at constant heating rate of 5 K/minute. All foaming experiments were made in ambient atmosphere.

Scanning electron microscope JEOL 7600F, equipped with a Schottky thermal-emission cathode (thermal FEG - W-coated ZrO_2) as well as energy-and wavelength spectrometers from Oxford Instruments was used for the microstructure investigations.

3. Results and discussion

At first experimental investigation was focused on the effect of the amount and type of the foaming agent on the foaming of zinc. As the matrix melts at the melting temperature of metal the volumetric expansion takes place. Its maximum depends predominantly on the inner pressure of hydrogen, which ought to overcome external pressure and pressure due to gravity force within melt and surface tension on liquid metal - hydrogen interface. Further both types of used hydrides were compared. It was observed that TiH_2 is significantly better for the foaming of zinc as MgH_2 (see Fig. 1). This is in agreement with observation by Von Zeppelin et al. [11]. They performed a particular study concerning hydrogen desorption from pure zinc precursor for various foaming agents and found that the expansion of zinc was the highest for TiH_2 , followed by ZrH_2 and MgH_2 .

It was confirmed, that zinc foams could be successfully prepared using TiH_2 as a foaming agent (Fig. 1). The obtained structures are of reasonable quality and homogeneity. Maximal obtained porosity for pure zinc was 90.6% at 450°C . It is also due to the fact that for pure zinc, besides changes of surface tension and viscosity of melt, the solubility of Ti in Zn increases significantly above melting temperature of zinc. At approximately 420°C eutectic reaction of Zn with Ti gives $Zn_{15}Ti$ phase. At 445°C peritectic reaction $L + Zn_{10}Ti \leftrightarrow Zn_{15}Ti$ takes place [12].

Visual observation of obtained structures indicates that there are often very dense regions within cross sections of pure zinc foam structure. This is probably due to the low thermal conductivity of zinc ($110 \text{ W.m}^{-1}.\text{K}^{-1}$) that leads to the thermal gradient within precursor and thus to the heterogeneous heating/foaming of various pieces of precursor.

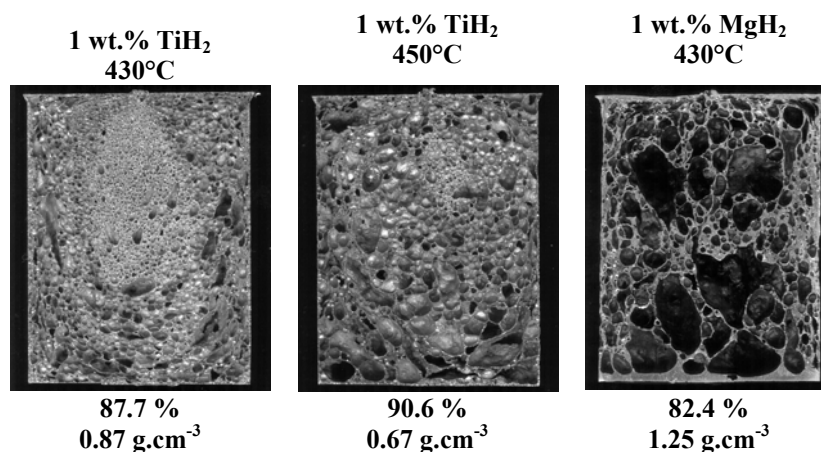


Fig. 1. The foaming agent, furnace temperature, corresponding structure, porosity and apparent density of pure zinc foams

MgH₂ foaming agent is less suitable for the foaming of pure zinc. Not only maximal experimental porosity at 430°C was just 82%, but also resulting structure is very heterogeneous. For pure zinc foams, the resulting structures created using MgH₂ possess pore coarsening as indicated by large pores within structure; drainage as shown by pore-free metal on the bottom of samples; and a lot of collapsed/deformed pores in the vicinity of foam surface.

There are probably following sources: One is high inner pressure within bubbles at molten metal with no additional hydrogen evolved at higher temperatures. This means coalescence only of the existing bubbles and not with new ones, thus creating very early large bubbles and decreasing pressure inside of large bubble. The probability of breaking of liquid walls between bubbles increases significantly when large bubbles with low inner pressure occur within the foam. Finally, rapid foam collapse can take place.

Another reason for full hydrogen development is probably a solubility of Mg in zinc: Mg has significantly higher solubility (0.165 wt.% at 364°C) in zinc as Ti or Zr (0.02 wt.% at 400°C for both) [12]. Moreover, creation of Mg₂Zn₁₁ phase occurs around 381°C. Therefore higher solubility of Mg in zinc can enhance rapid decomposition of MgH₂ to Mg + H₂ in solid precursor. Besides this, different surface tension and viscosity due to presence of Mg-Zn compounds can influence resulting foam stability also.

4. Foaming atmosphere

In air, under heating up to the melting point of metal, the metal oxides on the precursor surface are created or grow instantly. These oxides have to be broken prior any expansion can occur. Therefore, certain gas energy is used for oxides rupture instead of the expansion of pores. The rupture of very thick oxide layer may even lead to a rupture of cell wall, which results in the loss of foaming gas. Both effects reduce maximal foam expansion [13]. Further, the brittle solid oxides on the foam surface play positive and also negative role on solidification and cooling: They stabilise the foam and prevent it from collapsing, but the arising pressure difference and dissimilar material shrinkage with decreasing temperature lead to corrugations of pore walls (for ductile alloys) or to their fracture (for brittle alloys).

For these reasons, the resulting surface of foam incorporates the rests of initial precursor surface, which is often observed as darker regions on the foam surface (see Figs. 2-3).

In the case of TiH_2 purple blue colour was observed on the zinc foam surface (Figs. 2 and 3). It was showed that the colour has the origin in the used hydride: By diminishing of the amount of TiH_2 the intensity of blue colour reduces significantly (Fig. 3). Kennedy [14] showed that heat treatment of TiH_2 powder at different temperatures in air results in colouration of the powder: At the lowest temperature, 400 °C, the initially black powder turned olive green, at 450 °C, purple and at 500, blue. This is probably the reason of the colour changes of pure zinc foam that have been observed in this work (see Fig. 4). The change in colour of the powder is an indication of a different surface oxides being formed on the TiH_2 powder particles at different thickness [15].

On the contrary, various amount of MgH_2 (0.3, 0.6, 1 wt. %) has no effect on the colour of zinc foam surface. It is probably either due to Mg oxidation (MgO has white colour) or that Mg reacts preferably with Zn to create alloy compounds.

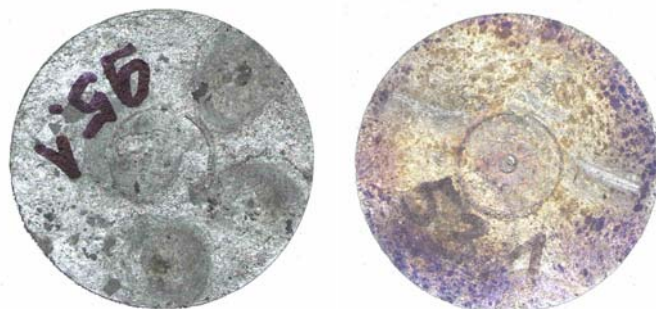


Fig.2. Oxidation of pure zinc foam surface for various hydrides: foaming temperature 430°C, left 1 wt.% MgH_2 , right 1 wt.% TiH_2 .

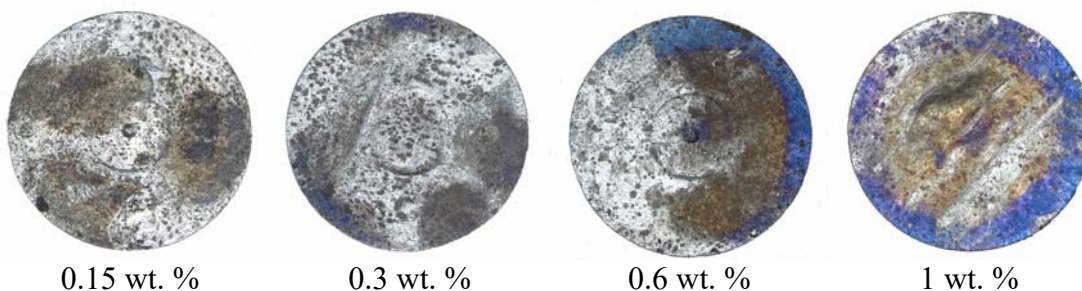


Fig.3. The effect of TiH_2 amount on the oxidation of pure zinc foam surface: foaming temperature 450°C.

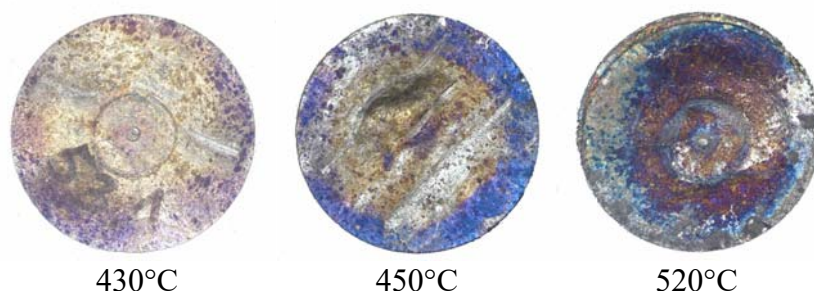


Fig.4. The effect of foaming temperature on the oxidation of pure zinc foam surface with 1 w. % TiH_2 .

To change the colour of foam surface, TiH_2 particles ought to be present on the foam surface in a reasonable concentration and ought to react with atmospheric oxygen. According to Archimedes' principle hydride particle will float over liquid zinc because it displaces liquid whose weight is greater than the weight of particle. It takes place more or less for both considered hydrides, because each of them has the density below the density of liquid zinc (6.55 g.cm^{-3}). As confirmed Fig. 5 the

foaming agent particles are actually present on the outer surface of zinc foam after foaming. There, exposed to atmosphere they react with oxygen and create oxides. Bright TiH_2 particles in Fig. 5 are simple confirmation of the oxidation. The brightness is the result of presence of non-conducting phase (titanium oxide), which causes the charging of the particle under electron beam in SEM microscope. The observed rests of MgH_2 particles are of average size $6\ \mu\text{m}$ and less, while the rests of TiH_2 particles are of size about $10\ \mu\text{m}$ and more.

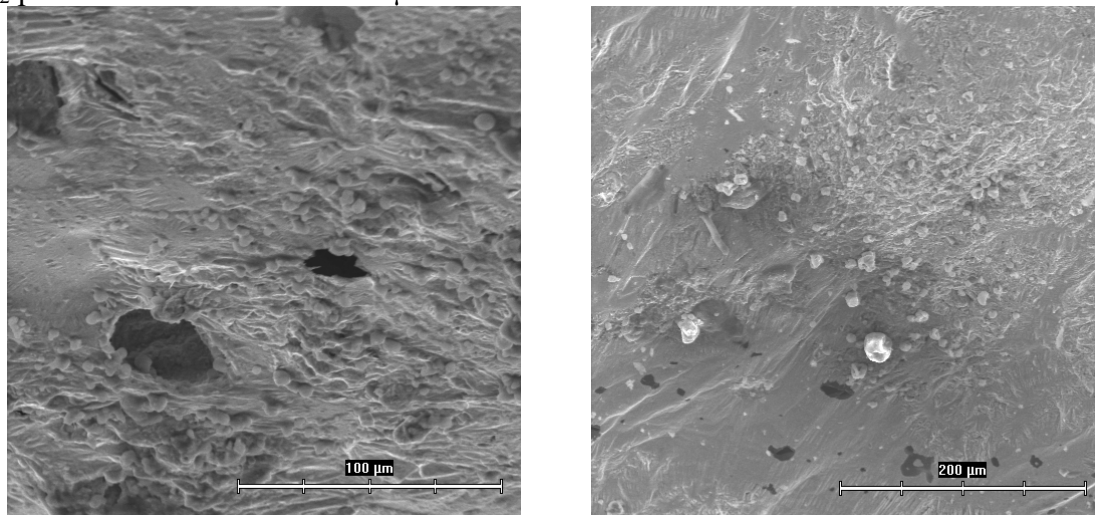


Fig.5. SEM microphotographs at various magnification of foaming agent particles on the surfaces of zinc foams: left pure Zn foam prepared with MgH_2 with MgH_2 particles on the surface, right Zn foam prepared with TiH_2 with TiH_2 particles on the surface.

5. Conclusions

The pure zinc foams were prepared by powder metallurgy. TiH_2 and MgH_2 of various quantities were used as a foaming agent. It can be concluded, that MgH_2 is less appropriate for the foaming of zinc. The structure of such zinc foams is usually very heterogeneous: Large pores, drainage and collapsed pores are regularly present.

The results showed that universal foaming agent for the foaming of pure zinc alloys is TiH_2 . The obtained foam structure is relatively homogeneous and foam with significantly higher porosity can be prepared. Certain dense regions observed within structure of foam are due to heterogeneous heating/foaming of precursor because of low thermal conductivity of zinc.

It was confirmed that during foaming not only certain amount of hydrogen is lost prior precursor melting, but foaming agent particles also move within melt. The thermal movement is influenced by wetting of particle with liquid metal and by Archimedes' principle. Due to large density difference, hydride particles float over zinc melt in high concentration. In the contact with atmosphere they react with oxygen, create oxides and change the colour of zinc foam surface. Presence of particles on foam surface was confirmed via SEM observation and by colour changes of pure zinc foam foamed with TiH_2 . On the contrary, MgH_2 decomposes almost completely during the foaming process of pure zinc. Therefore Mg is either dissolved in zinc foam or MgO of white colour is created. For this reason no significant colouring of pure zinc foams was observed in this case.

Acknowledgements

The financial support from the Slovak R&D Agency (project: Heating/cooling panel based on aluminium foam filled by PCM, APVV-0692-12) and VEGA agency projects 2/0044/17, 2/0065/16, 2/0152/17 are gratefully acknowledged.

References

- [1] P. Walstra, Principles of Foam Formation and Stability, In. Foams: Physics, Chemistry and Structure, ed. by A.J. Wilson, Springer-Verlag, London, 1989, p.10
- [2] Handbook of Cellular Metals: Production, Processing, Applications, Editor(s): Hans-Peter Degischer, Brigitte Kriszt, Weinheim, Wiley-VCH, 2002
- [3] Baumgärtner, F., Duarte, I. and Banhart, Industrialization of Powder Compact Foaming Process, J., Adv. Engng. Mater., 2000, 2, 168 – 174
- [4] A.E. Markaki and T.W. Clyne, The Effect of Cell Wall Microstructure on the Deformation and Fracture of Aluminium-Based Foams, Acta Materialia, 49(9), 2001, pp. 1677-1686.
- [5] Thornton, P.H. - Magee, C.L.: Deformation characteristics of zinc foams. In: Met. Trans. 6A, 1975, p. 1801.
- [6] Banhart, J. – Baumeister, J.: Deformation characteristics of metal foams. J Mat Sci., 33, 1998, p. 1431.
- [7] Kováčik, J. – Simančík, F.: Comparison of zinc and aluminium foams in deformation and fracture, In: Deformation and Fracture in Structural PM Materials DF PM '99. Ed. by L. Parilák, H. Danninger. Vol. I. Košice: IMR SAS, Slovakia, 1999, p. 106
- [8] Kováčik, J. – Simančík, F.: Comparison Of Zinc And Aluminium Foam Behaviour. In: Kovove Mater., 42, 2, 2004, p. 79.
- [9] Kováčik, J. – Simančík, F.: Use of zinc foam for filling of hollow steel profiles. In: Metal Foams and Porous Metal Structures. Ed. by J. Banhart, M.F. Ashby, N.A. Fleck. Bremen: MIT-Verlag Publishing, 2001, p. 355.
- [10] Allen, B.C.: US Patent 3087 807, 1963.
- [11] von Zeppelin, F. - Hirscher, M.- Stanzick, H. - Banhart, J.: Desorption of hydrogen from blowing agents used for foaming metals. Composites Science and Technology, 63, 2003, p. 2293.
- [12] Hansen, M. - Anderko, K.: Constitution of Binary Alloys. New York: McGraw-Hill, 1958.
- [13] Simančík, F. – Behulová, K. – Borš, L.: Effect of ambient atmosphere on metal foam expansion. In: Cellular Metals and Metal Foaming Technology. Bremen: MIT Verlag, 2001, p. 89.
- [14] Kennedy, A.R.: The effect of TiH₂ heat treatment on gas release and foaming in Al–TiH₂ preforms. In: Scripta Mater., 47, 11, 2002, p. 763-767.
- [15] Kennedy A.R., Lopez V.H., 2003. The decomposition behavior of as-received and oxidized TiH₂ foaming-agent powder, Mat Sci and Eng., A357, 1-2, 2003, 258-263.