ZINC SPONGES SYNTHESIS EMPLOYING THE REPLICATION PROCESS

Sandro Báez Pimiento[1,], María E. Hernández Rojas[2], Juan B. Ramírez Rebollar[3], Heber I. Suarez Andrade[3], and Manuel E. Palomar Pardavé[4]*

1: Doctor en Ciencia e Ingeniería de Materiales, Departamento de Materiales, Universidad Autónoma Metropolitana Unidad Azcapotzalco, México D.F., México.
2: Doctora en Ingeniería de Procesos y del Ambiente, Departamento de Recursos de la Tierra, Universidad Autónoma Metropolitana Unidad Lerma, Estado de México, México.
3: Estudiante de Licenciatura en Ingeniería Metalúrgica, Universidad Autónoma Metropolitana Unidad Azcapotzalco, México D.F., México.
4: Doctor en Ciencias, Departamento de Materiales, Universidad Autónoma Metropolitana Unidad Azcapotzalco, México D.F., México.

*Contacto: sbpuamazc@gmail.com

ABSTRACT

This work reports the fabricating of zinc (Zn) sponges (open–pore Zn foams) which were manufactured through infiltration processes. The metal used for the present study was Zn ingots with 99.8 % purity. Sodium chloride (NaCl) granules in three ranges of particle sizes were choosen as space holder particles (SHP), range I from 4.75 to 3.98 mm, range II from 3.98 to 3.35 mm, and range III from 3.35 to 1.99 mm. The obtained sponges showed a highly porous structure with interconnected pores in all cases. The maximum porosity, and minimum density values resulted to be ~64 % and ~2.5 g/cm^3, respectively. This work demonstrates that it is possible to use NaCl with different particle sizes in the manufacturing of Zn sponges with high porosity and roughly 100 % interconnected pores. The results are interpreted in terms of NaCl particle sizes and its content in the sample.

Keywords: *Open–pore Zn foams, Cellular metals, Replication process*

RESUMEN

Este trabajo reporta la fabricación de esponjas de Zn (espumas de Zn con poro abierto), las cuales fueron fabricadas usando procesos de infiltración de rellenos removibles. Se usaron lingotes de Zn del 99.8 % de pureza y NaCl particulado como relleno removible, con tres rangos de tamaño de partícula diferente: rango I de 4.75 a 3.98 mm, rango II de 3.98 a 3.35 mm, y rango III de 3.35 a 1.99 mm. En todos los casos, las espumas obtenidas mostraron una estructura altamente porosa con poros interconectados. Los valores de porosidad máxima y densidad mínima fueron ~64 % and ~2.5 g/cm^3, respectivamente. Este trabajo demuestra que es posible fabricar esponjas de Zn con porosidad alta y aproximadamente 100% de poros interconectados usando NaCl como material removible. Los resultados son interpretados en términos del tamaño de partícula de NaCl y su contenido dentro de la muestra.

Palabras Clave: *Esponjas de zinc, Infiltración de rellenos removibles, Metales celulares*

Zinc sponges synthesis employing the replication process

Juan B. Ramírez Rebollar, María E. Hernández Rojas, Heber I. Suarez Andrade, Manuel E. Palomar Pardavé, Sandro Báez Pimiento

1 INTRODUCTION

The term "foam" has been defined as the uniform dispersions of a gaseous phase in a liquid or a solid phase [1]. In these two cases, each gas bubble is separated by a liquid or solid wall, thus the gas bubbles are entirely isolated and are not consistently interconnected to each other. Although, the term "foam" is utilized only for the dispersion of gas bubbles in a liquid, this foam morphology can be preserved for the solidified liquid metals in framework form, given that during the fabrication process of the material, a liquid metallic foam is generated, which finally is solidified and known as "metallic foam". In these cases, the expression "metallic foam" generally refers to a solid foam. Nevertheless, the solid foam is a special case that is more commonly designated as "cellular solid" [2]. The cellular solids (cellular metal in the case of the metals), can be classified as closed pore metals (metallic foams) and open pore metals or interconnected pore metals (metallic sponges) according to its topology. This kind of materials with high porosity have been developed to be used as new functional materials, since these materials present a unique combination of physical and chemical properties which can be derived from their cellular structure [3]. Cellular metals show increasing potential for applications in a wide range of structural and functional products, due to their exceptional mechanical, thermal, acoustic, electrical and chemical properties [4,5]. Metallic foams can be manufactured by a great variety of methods, including methods with the metal in the solid, liquid and gaseous state. The most commonly used method based on the liquid state is the infiltration process (replication process, RP), which involves the infiltration of a liquid metal within a space–holder–particles (SHP) bed. The fabrication route to produce cellular metals mainly consists of five steps: 1) Pre–form molding: a leachable SHP with specific form is put into a defined form mold, ii) Pre–form Sintering: the mold containing the SHP is put into the furnace to sinter the SHP and to produce a leachable stiff pre–form of interconnected particles, iii) Metal melting: after the SHP pre–form is cooled, the metal is put on the SHP pre–form and introduced into the furnace again to melt the metal, iv) Metal infiltration: the liquid metal is infiltrated in the stiff SHP pre–form to fill its empty voids, and v) Pre–form leaching: after the SHP/Liquid metal system is taken out of the furnace to solidify the metal, and the SHP is leached with an adequate solvent to obtain a metallic sponge with interconnected pores. In the present work, the RP is employed to obtain Zn–sponges (porous Zn with interconnected pores) with high porosity, low density and using NaCl particles as SHP in three ranges of particle sizes. The range I from 4.75 to 3.98 mm, the range II from 3.98 to 3.35 mm, and the range III from 3.35 to 1.99 mm.

2 EXPERIMENTAL TECHNIQUES

The Zn sponges topology was characterized through digital photographs to visually determine the obtained pore size, pore form, and the pores interconnection (Sony 3D). For each specimen, after the melting and solidification processes of metal, the weights and dimensions of the Zn/NaCl compact were measured. Similarly, the weights of NaCl content in the Zn/NaCl compact after the NaCl leaching were quantified, and the final weight and dimensions of the resultant Zn sponges were also measured to determine their volume and density. The weights were registered using a balance Ohaus with a maximum capacity of 310 g and readability of 0.001 g. Using these data, the Zn/NaCl compact density ρ_c, Zn sponge density ρ_s, compact porosity P_c, and sponge porosity P_s, were determined through the equations 1 to 4 [6,7]. Where, M=mass, V=volume, ρ_{th} is the

theoretical compact density, ρ_{Zn} is the zinc density, W_{Zn} is the zinc weight fraction in the compact and ρ_{NaCl} is the NaCl density.

$$\rho = \frac{M}{V} \tag{1}$$

$$P_c = 1 - \frac{\rho_c}{\rho_{th}} \tag{2}$$

$$\rho_{th} = \left(\rho_{Zn} * W_{Zn} \right) + \left(\rho_{NaCl} * \left(1 - W_{Zn} \right) \right) \tag{3}$$

$$P_s = 1 - \frac{\rho_s}{\rho_{Zn}} \tag{4}$$

3 EXPERIMENTAL PROCEDURE

Zn sponges were prepared through RP from initial Zn ingots with 99.9 % purity provided by "*Metales Águila S. A. de C. V.*" and using NaCl particles as SHP in three ranges of particle sizes provided by "*Droguería cosmopolita S. A. de C. V.*". The range I from 4.75 to 3.98 mm (Figure 1a), the range II from 3.98 to 3.35 mm (Figure 1b) and the range III from 3.35 to 1.99 mm (Figure 1c). The metal was employed to produce the main framework of the Zn sponge, and the NaCl particles with an equiaxed shape were used to generate the internal pores.
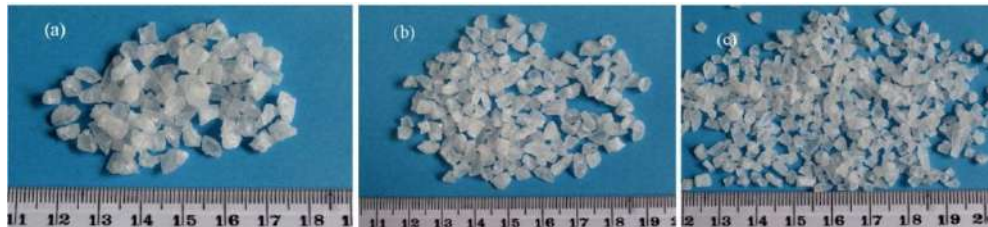

Figure 1. Sizes of NaCl particles used in the manufacturing of Zn sponges: a) size from 4.75 to3.98 mm, b) size from 3.98 to 3.35 mm and c) size from 3.35 to 1.99 mm.

Each range of NaCl particle size was put into a mold until it was totally filled. The Zn mass was placed inside of a container provided of a hole in the central part of the bottom. The container was placed on the mold containing the NaCl to guarantee the permanent contact of NaCl particles. The mold/container system was introduced in a vertical electrical furnace to melt the Zn at 500 ºC for 30 min. When the Zn was melted, the NaCl particles bed was infiltrated with the liquid Zn by gravity. After the infiltration process, the mold/container system was cooled to obtain a Zn/NaCl compact. The amount of NaCl in the compact was leached by immersion in a water bath at 25 ºC for two hours, to generate the Zn sponges with interconnected pores. Finally, to determine the NaCl volume in each sponge, the water leaching was evaporated on a warming plate, later, the salt was dried in a stove at 105 ºC until a constant weight was reached. The NaCl content for each obtained Zn sponge resulted to be 48.62 %vol for the size particle range I, 53.76 %vol for the size particle range II and 48.62 %vol for the size particle range III.

Zinc sponges synthesis employing the replication process

Juan B. Ramírez Rebollar, María E. Hernández Rojas, Heber I. Suarez Andrade, Manuel E. Palomar Pardavé, Sandro Báez Pimiento

4 RESULTS AND DISCUSSION

Figure 2 (top line) shows the obtained Zn sponges through RP and manufactured using equiaxed NaCl particles with particle sizes in the range I (Figure 2a), range II (Figure 2b) and range III (Figure 2c) after the machining and NaCl leached processes. The figure 2 (middle line) shows the sponge's upper view. In the samples, a relatively uniform distribution of pores is observed. This homogeneous pore distribution results in a Zn sponge with a highly homogeneous framework as it is required for reliable measurements of mechanical properties in this kind of materials.
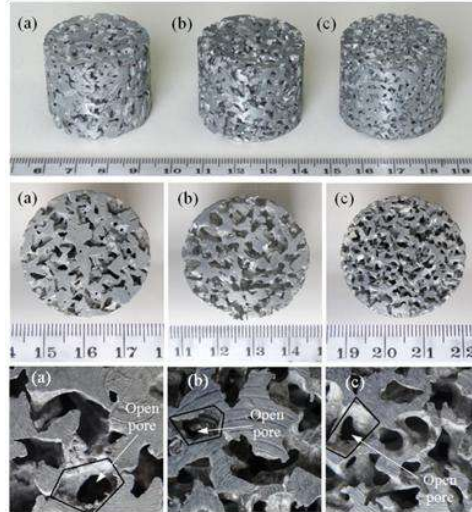
Figure 2. Images of obtained Zn sponges after the NaCl leached process: a) pore size in the particles range I, b) pore size in the particle range II, and c) pore size in the particle range III.

Figure 2 (bottom line) shows the pores interconnection and form obtained. The regions enclosed by the black lines display the approximated form of the equiaxed NaCl particles employed to produce the Zn sponges. It is seen that the pore size in the samples and the NaCl particles size match quite closely. Moreover, in the bottom line all images clearly show the pores interconnectivity (indicated by an arrow and corresponding to a black zone in the image of all specimens), generating an open pore structure with practically all pores communicating with each other. Figure 3 shows, as a function of the NaCl content in the compact, the changes in the ρ_{th}, ρ_c and ρ_s. In this plots, the ρ_{th} (Figure 3a), ρ_c (Fig. 3b) and ρ_s (Figure 3c) decreased with the increasing NaCl content. In the figure 3a, the diminishing in the ρ_{th} is explained by the lower value of the NaCl density (2.165 g/cm^3) compared to Zn density (7.14 g/cm^3). Given that the proportion of SHP in the compact increases, the ρ_{th} decreases. On the other hand, the diminishing in the ρ_c in the figure 3b results to be lower than the ρ_{th}, this reduction is caused by two reasons: i) the lower density value of the NaCl compared to Zn, and ii) the empty spaces found inside the compact and located around the contact points among NaCl particles. These empty spaces are generated because the liquid metal does not wet completely the NaCl particles caused by its superficial tension and consequently the liquid metal can not infiltrate these small empty spaces inside the NaCl bed. In the figure 3b a slight increase in the ρ_c for a NaCl content of 52.32 %vol (particle sizes in the range III) is observed. In this case, the slight increase could be associated with a packing low efficiency of NaCl particles. This packing low efficiency lets the NaCl

particles bed be infiltrated with a higher quantity of liquid metal and consequently the ρ_c increase, regardless of the used particle size. Figure 3c shows the fast decreasing in the ρ_s, which is attributed to two empty spaces contributions: i) the empty spaces found inside the Zn/NaCl compact, and ii) the empty spaces left by the NaCl particles after their leaching. The minimum obtained ρ_s value was 2.54 g/cm^3, which corresponds only to 34.55 % of the Zn density (7.14 g/cm^3).
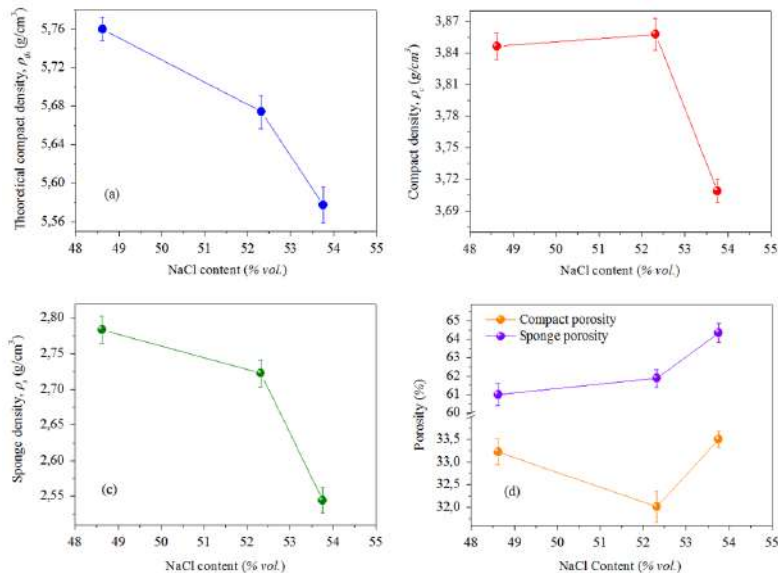
Figure 3. Variations in the densities and porosities as a function of NaCl content: a) theoretical compact density, b) compact density, c) sponge density, and d) compact and sponges porosity.

Figure 3d shows, as a function of the NaCl content, the variations in the P_s and P_c. The decreasing observed in the P_c for a NaCl content of 52.32 %vol (particle sizes in the range III) could be associated with a packing low efficiency of NaCl particles as it was mentioned before. As the packing low efficiency permits the infiltration of a higher quantity of liquid metal into the NaCl particles bed, the space filled by the metal into the bed is increased and consequently the empty space in the bed is decreased. As a result of this, the compact porosity is reduced, regardless of the used particle size. On the other hand, the changes in the P_s of the Zn sponges, after the dissolution processes, indicated a continuous enhance with the increase in the NaCl content. In this case, a higher NaCl content produces a higher empty space in the sponge when the NaCl is leached and consequently the porosity is enhanced, as it would logically be expected. The Zn sponges with densities between 2.54 and 2.78 g/cm^3 presented porosity from 61.01 to 64.36 %. These results are very similar to Zn based foams reported in the literature. In particular, S. R. Casolso et. al. [8] obtained Zn–Al–Cu foams and reported porosities of 58.49, 52.83 and 67.50 %, using NaCl particle sizes of 6.5, 3.5 and 1.5 mm, respectively. The obtained porosity values in our work employing NaCl with similar particles size like the used by Casolso et. al. (6.5 and 3.5 mm) resulted to be higher. This higher value in the Zn sponges porosity processed in our laboratory can be attributed to the interconnection among pores caused by the NaCl particles immobility when the metal container is placed on the crucible containing the NaCl and consequently a sponge is obtained. A higher interconnection among pores involves a higher porosity. The high interconnection among pores (approximately 100 %) was quantified through

Zinc sponges synthesis employing the replication process

Juan B. Ramírez Rebollar, María E. Hernández Rojas, Heber I. Suarez Andrade, Manuel E. Palomar Pardavé, Sandro Báez Pimiento

NaCl volume variation, before and after its leaching process. The difference between these volumes results to be ~0.08 % in all cases (~0.031 g). This small value implies a great and almost total NaCl leaching into the sample, which indicates that approximately 100 % of NaCl was removed; hence the ~100 % of interconnected pores in the sample are present. On the other hand, the high interconnection among pores is possible since the NaCl particles in the crucible were not budged due to the contact between the metal container and the NaCl filled crucible guarantees the permanent touching among NaCl particles.

5 CONCLUSION

Zn sponges containing porosities between ~61 to ~64 % and minimum densities of 2.54 g/cm^3 were successfully produced through infiltration of liquid Zn into a NaCl bed. A highly interconnected porous structure was obtained for all samples. This high interconnectivity among pores was caused by the contact among NaCl particles in the bed, which was promoted by the placement of the metal container on the mold containing the NaCl particles in the configuration used in the present study. This configuration avoided the NaCl particles movement due to densities effects. The reached open–pore structure is important for applications where the matter or energy transportation and the superficial area of the metal is essential. The results presented indicate that the use of RP is an excellent method to obtain Zn sponges with homogenous pores distribution.

6 ACKNOWLEDGEMENTS

7 REFERENCES

1. Banhart J., "Foam metal: the recipe", Europhysics News, 30, 17–20, 1999.

2. Banhart J., "Manufacture, characterization and application of cellular metals and metal foams", Progress in Materials Science, 46, 559–632, 2001.

3. Davies G. J. and Zhen S., "Metallic foams: their production, properties and applications", Journal of Materials Science, 18, 1899–1911, 1983.

4. Gibson L. J. and Ashby M. F., "Cellular Solids: Structure and Properties" Cambridge UK, Cambridge University Press, p. 6–7, 1997.

5. Banhart J. and Eifert H., "Metal Foams", Bremen, Verlag MIT Publishing, 1997.

6. Bafti H. and Habibolahzadeh A., "Production of aluminum foam by spherical carbamide space holder technique–processing parameters", Materials and Design 31, 4122–4129, 2010.

7. Jee C. S. Y., et. al., "Preparation of high porosity metal foams", Metallurgical and Materials Transactions B, 31(6), 1345–1352, 2000.

8.Casolco S. R., et. al., "Processing and mechanical behavior of Zn–Al–Cu porous alloys", Materials Science and Engineering A, 471, 28–33, 2007.